

**Evaluation of Organic and Inorganic Draw solutions using  
Submerged Osmotic Membrane Bioreactor (OMBR) for Municipal  
Wastewater Treatment**



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It is certified that the contents and form of thesis entitled

**“Evaluation of Organic and Inorganic Draw solutions using Submerged  
Osmotic Membrane Bioreactor (OMBR) for Municipal Wastewater  
Treatment”**

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## List of Abbreviations

<b>Abbreviation</b>	<b>Description</b>
CASP	Conventional activated sludge process
CER	Cat-ion exchange resin
C-MBR	Conventional membrane bioreactor
COD	Chemical oxygen demand
CST	Capillary suction time
DCMD	Direct contact membrane distillation
DI	De-ionized water
DO	Dissolved oxygen
DS	Draw solution
EPS	Extra polymeric substance
F/M	Food to microorganism ratio
HF	Hollow-fiber
HRT	Hydraulic retention time
J	Operational flux
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids

OLR	Organic loading rate
OMBR	Osmotic membrane bioreactor
PAOs	Phosphorus accumulating organisms
SEM	Scanning electron microscopy
SMBR	Submerged membrane bioreactor
SMP	Soluble microbial products
SOUR	Specific oxygen uptake rate
SRT	Sludge retention time
TN	Total nitrogen
TOC	Total organic carbon

**Abstract:**

In this study, chloride and acetate based salts were investigated as draw solutions to evaluate their viability in osmotic membrane bioreactor (OMBR). Two inorganic divalent chloride based ( $\text{CaCl}_2$ , and  $\text{MgCl}_2$ ) and two acetate based ( $\text{NaOAc}$  and  $\text{MgOAc}$ ) organic salts were compared with commonly used  $\text{NaCl}$ . For the production of clean water and draw solute recovery, direct contact membrane distillation (DCMD) unit was coupled with OMBR setup to develop hybrid OMBR-MD system. Results demonstrate that organic draw solutions (DS) were able to mitigate the issue of salinity buildup in bioreactor as compared to inorganic DS. Prolonged filtration runs were observed with  $\text{MgCl}_2$  and  $\text{MgOAc}$  in contrast with other DS at same molar concentration. Rapid decline and high initial water flux was witnessed with  $\text{NaCl}$  and  $\text{CaCl}_2$ . Significant membrane fouling was observed with  $\text{NaOAc}$  as compared to other salts. In comparison with inorganic DS, organic salts were found to reveal the improved characteristics of mix liquor in terms of sludge filterability, particle size, and biomass growth. Moreover, the degradation of soluble microbial products (SMP) and less accumulation of carbon content in bioreactor was observed with acetate based salts. More than 98% removal of  $\text{NH}_4^+\text{-N}$ , COD, and  $\text{PO}_4^{3-}\text{-P}$  was achieved in permeate for each salt because of dual barriers of high retention membranes (FO and MD).

## **Introduction**

### **1.1 Background**

Trend towards more stringent regulations for effluent quality, reduced areal foot prints and effective biodegradation of organic matter increasingly raised the use of membrane bioreactors (MBRs) as a wastewater reclamation solution worldwide (Zhang et al., 2014). MBR technology, combination of biological treatment with membrane separation, exhibits complete removal of suspended solids and less production of sludge over conventional activated sludge (CAS) process (Wang et al., 2016; Judd, 2011). Nevertheless the pore size of currently used micro and ultrafiltration membranes in MBR technology put forward a bottleneck that these type of membranes are not sufficient to cling all undegradable organics that further threatens the use of reclaimed wastewater (Ramesh et al., 2006). Other drawbacks include intensive membrane fouling resulting in performance decline, rapidly increased pressure (TMP) and severe drop in flux requires frequent O&M cost because of repeated cleaning of membrane (Wang et al., 2014; Wang et al., 2016).

To address these flaws Cornelissen et al., (2008) and Achilli et al., (2009) introduce a novel submerged osmotic membrane bioreactor (OMBR) at the end of last decade, an alternate solution that requires less energy and works on a natural osmotic process (Aftab et al., 2015). Forward osmosis (FO) technique in MBR setup gives a new option as OMBR. In this configuration of MBR the water permeates across the FO membrane due to the osmotic pressure gradient of both feed solution (FS) and draw solution (DS). In contrast with conventional MBR having ultra and microfiltration membranes under high pressurized suction force which results in rapid membrane fouling, the OMBR configuration that extract water from low saline sludge into highly

concentrated DS mitigating the problem of intensive biofouling and increase the removal of small particles, trace organic compounds (TrOCs) and dissolved species with less consumption of energy (Wang et al., 2016; Achilli et al., 2009; Holloway et al., 2014). Therefore, a conventional MBR running with either ultra or microfiltration membranes can be replaced with an appropriate DS-aiding osmotic MBR. In spite of these rejection properties of OMBR, FO membrane also offer limitations in parallel like lower membrane flux, internal concentration polarization (ICP), reverse transport of salute into the bioreactor from DS side which couples with rejected solutes of feed wastewater by membrane results in building-up of salinity with in the bioreactor (Qiu and Ting, 2013; Aftab et al., 2015; Wang et al., 2016).

Internal concentration polarization (ICP) states the accumulation of feed particles or draw solute into the support layer (porous) of FO membrane. ICP resulting in water flux reduction. In OMBR case, the active layer facing feed side (AL-FS) presents a favored orientation to mitigate the higher ICP (Tang et al., 2010; Zhao and Zou, 2011; Aftab et al., 2015; Wang et al., 2016). FO membranes are also prone to fouling mechanism, though it is too low as compared to fouling in a conventional MBR due to lack of suction force requirement and lower operating flux conditions (Zhang et al., 2014; Wang et al., 2016; Yuan et al., 2015; Lutchmiah et al., 2014). But running with FO mode (OMBR having active layer facing mix liquor) membrane fouling nevertheless occur. Direct contact of mix liquor having variety of microorganisms including organic and inorganic foulants of highly complex feed with FO membrane leads to not only decline of the water permeability as membrane resistance increases but also raises the external concentration polarization (ECP) (Qiu and Ting, 2013; Wang et al., 2016; Yuan et al., 2015). Production of extra polymeric substances (EPS) and altered bacterial community within the bioreactor plays a vital role in biofouling development (Zhang et al., 2014; Qiu and Ting, 2013). Nguyen et al., (2016a) recently introduced



moving carriers to reduce suspended solids within the bioreactor to mitigate the problem of biofouling, while aeration intensity and modification of membrane surface were also found to be advantageous in lowering the fouling intensity in OMBR (Zhang et al., 2014; Qiu and Ting, 2013; Li et al., 2016).

Suspended solids in mix liquor can be retained by conventional membranes (ultra and micro) in MBR, but a substantial volume of particles may be permitted into the effluent through membrane. That is why there is no salt accumulation in the case of conventional MBR. However, high retention MBR systems (HRMBR) can hold maximum amount of dissolved solids and colloidal particles. This rejection not only provides highly precise effluent quality, but also raises the salt level with potentially adversative impacts on microbial growth and biological treatment. Biochemical and physical properties of the microorganisms required for biological treatment and also affected by high saline condition (Reid et al., 2006). Conventional microorganisms in domestic wastewater are generally not immune to halophilic conditions thus it is difficult for them to bear osmotic stress exerted by saline atmosphere. Especially some operational microorganisms, like denitrifying bacteria are apparently more sensitive under osmotic stress (Lay et al., 2010). Additionally, accumulated salinity eventually increases the amount of soluble microbial products (SMP) and extra polymeric substances (EPS) in mix liquor resulting in membrane fouling and flux reduction (Wang et al., 2014). High retention behaviour of FO membrane aiding reverse transport of draw solute further compounds the situation of feed solute accumulation, which consequently build-up the salinity content within the bioreactor (Aftab et al., 2015; Ge et al., 2012). This exalted saline condition is consequently an integral concern that high retention MBRs may demand to grapple with.

Researchers have introduced number of tactics to cop the challenge of salinity build-up throughout the OMBR process. Coupling of electrodialysis, UF/MF unit with OMBR process has been implemented as a solution to alleviate high salinity within the bioreactor. These MF/UF technology coupled with OMBR is not only capable to remove high saline content of mix liquor, but also permit the enriched nutrients like phosphorus to be mined for direct recovery from bioreactor (Qiu and Ting, 2013; Lu and He., 2015). Development of new salts (mixtures) or the use of alternative draw solutions instead of conventional one emerge as another affective strategy that promises to alleviate the salinity content (Qiu and Ting, 2013). Nguyen et al., (2015) and Nguyen et al., (2016a) used different mixtures (organic and surfactant) with inorganic salt as a novel DS which dramatically lowered down the salinity in bioreactor. Lower leakage of organic salts from DS into the reactor and their biodegradable nature results into lower salt accumulation. Additionally the leakage of organic salts increase carbon content as a food for microorganisms and also beneficial for the production of methane gas in anaerobic process (Qiu and Ting, 2013; Ansari et al., 2015). Divalent inorganic salts also show relatively less salinity buildup and better flux performance as compared to monovalent salts (Nguyen et al., 2015).

In present research work, performance of two divalent inorganic ( $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) and two organic ( $\text{NaOAc}$ ) and ( $\text{MgOAc}$ ) draw solutions were investigated in OMBR operation. Commonly used sodium chloride ( $\text{NaCl}$ ) was used as a base line to compare its performance with these salts. Cross-flow DCMD (Direct contact membrane distillation) process was used for the recovery of draw solute and production of pure water. OMBR setup integrated with DCMD process as a hybrid OMBR-MD (FOMBR-MD) system was continuously operated for the draw solutions till the fouling of membrane. This study aims to investigate the effect of salinity build-up by different salts on mixed liquor characteristics, membrane fouling, flux stability and pollutants removal

efficiency. Vital insight effects of organic and inorganic reverse solute on sludge characteristics were also discussed.

## **1.2 Objectives**

Effect of organic and inorganic draw solution on the viability of integrated OMBR and DCMD system while treating low strength wastewater is the principal objective of this study.

- Effect of different DS on water flux and salt accumulation on OMBR-MD system.
- Influence of elevated salinity upon sludge characteristics using different draw solution.

### 1.3 Scope of Study

Operation of **FO-MBR** was coupled with **DCMD** process to reconcentrate the diluted draw solution to check the stability of:

- Water flux
- Conductivity of Mix Liquor

Optimized operation with same molar concentration of 0.25M for different draw solutions.

- **Organic** ( MgOAc and NaOAc)
- **Inorganic** (MgCl<sub>2</sub>, CaCl<sub>2</sub> and NaCl)

The effects of salt accumulation on:

- Membrane biofouling
- Sludge Characteristics

The contaminant removal efficiency, product water quality and water productivity of the whole system with the FO-MBR operating with different DS will be studied.

## **Literature Review**

### **2.1 Membrane separation technique**

#### **2.1.1 Introduction**

With the passage of time the reserves of fresh water are getting inadequate because of high water demand so we need a new technique for the reclamation of clean water from wastewater. There are various techniques through which we get a separation process, membrane technology is best for material separation. The material that is separated from these techniques has advantages that these materials are not chemically nor thermally or biologically altered. The membrane technology is also used in the place of other water reclamation method, i.e. ion exchange, adsorption and sand filtration.

The membrane is a composition of the porous support layer and thin dense layer that acts as a barrier in separation techniques that blocks the unwanted particles and dissolved solutes and allow the minute particles and water particles to pass depends upon the type of membrane that is used in the process. This membrane technique is also used for the separation of solid particles, for example separation mix liquor for the treatment of low strength wastewater, up to the separation of molecular range material for example the dissolved salt retention in water desalination. Application of membrane techniques is shown in Figure 2.1

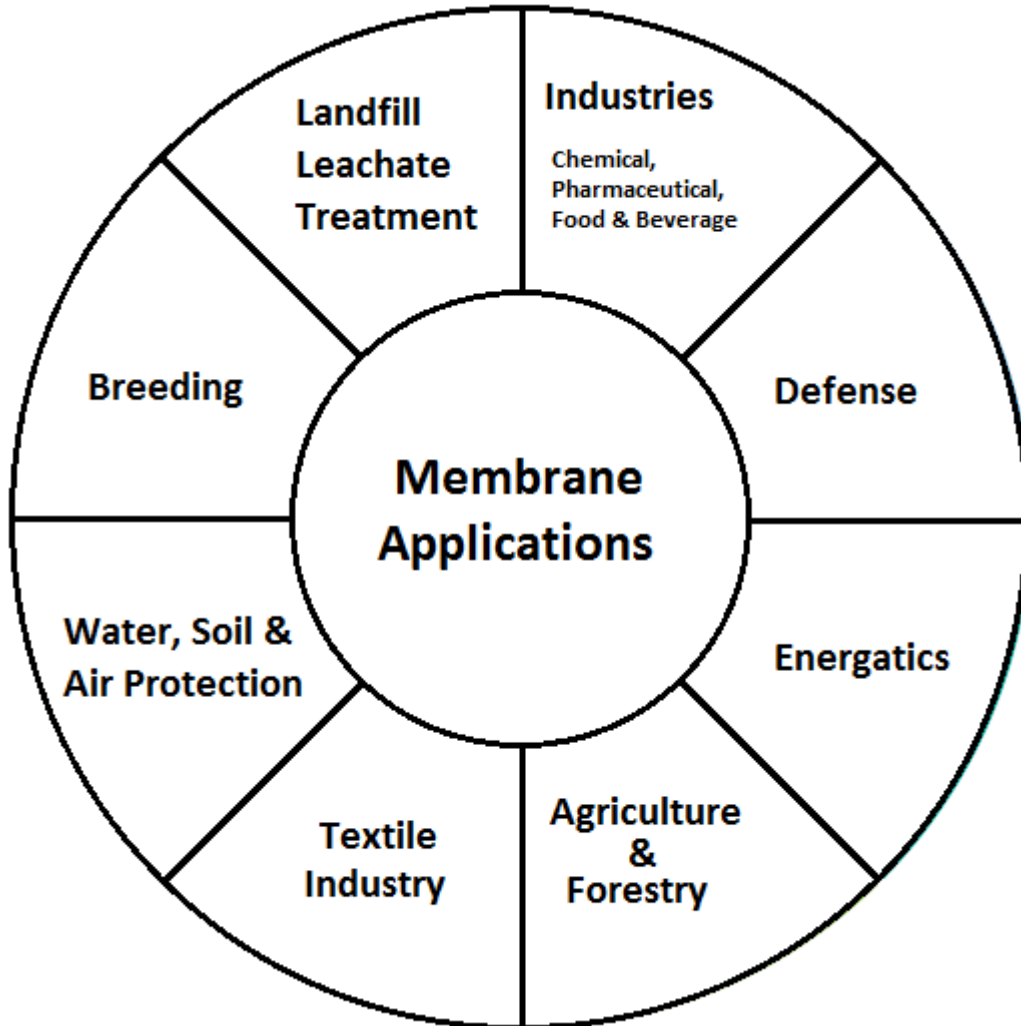


Figure 2.1. Membrane applications

According to orientation, there are two main membrane separation configuration, namely cross flow filtration and dead end filtration exist as shown in Figure 2.2.

The cross flow, which is also called tangential flow filtration because there is 90 degree angle between filtration flow and influent flow. Inlet flow passes over the surface cross flow membrane surface which resulted into two leaving fluid streams. Permeate fluid that contains some soluble and insoluble components by passing through the membrane and the fluid that doesn't pass from the membrane is called retentive fluid. The inlet turbulent flow hinders the gathering of particles

on the surface of membrane resulting in low fouling of the membrane. The influent flow is passing perpendicularly through the surface of the membrane in dead end flow, particles of larger size than the pore size of the membrane is retained by the membrane surface resulting in formation of cake layer on the surface of the membrane, the membrane is backwashed periodically to clean the surface of membrane otherwise with the passage of time cleaning efficiency is decreased due to membrane surface clogging. Dead end filtration with pressure drop and dead end filtration with constant flux are two main types of filtrations. In the filtration process with constant pressure drop, flux decreases because of membrane clogging, which keep the constant pressure drop across the surface of the membrane while in constant flux filtration the desired flux is attained by increasing the pressure drop across the surface of membrane.

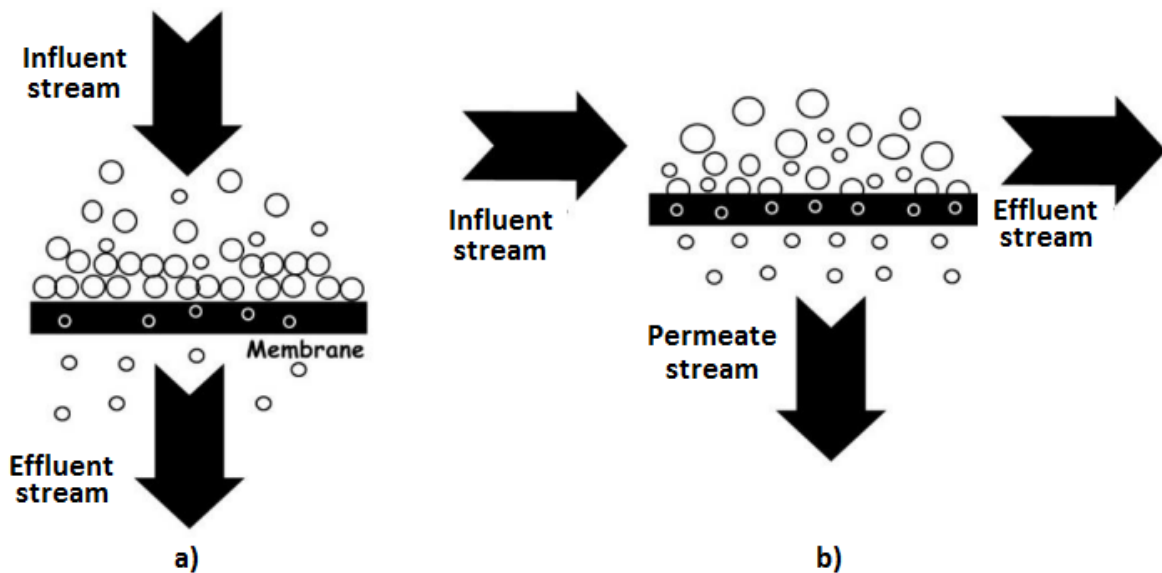


Figure 2.2. Filtration modes a) Dead end filtration b) Cross flow filtration

### **2.1.2 Types of membrane separation techniques**

Progressively membrane technology increasing its demand because of elimination of all types of micro-organism, bacteria, particles and neutral organic molecules which is existing in the water that carry out the disinfection byproduct into water by reaction with disinfectant and promulgate the color, taste and odor to it.

With the advancement and innovation in membrane technology, its operating method and its cost are gradually decreasing. There are four types of membrane method which are Reverse osmosis (RO), Nano filtration (NF), Microfiltration (M), Ultrafiltration (U) as shown in Figure 2.3.

#### **2.1.2.1 Micro filtration:**

In micro filtration pore size of the membrane is 0.3 to 10 microns which remove all the algae, salt, silt, giardia, cryptosporidium cysts, antiseptics like chlorine and other microbial classes. This membrane is prepared by the solution of polymer which absorbs water from the atmosphere and on drying the water is vaporized and produce a porous structure of the membrane. It has various applications, the leading role of micro filtration is in Membrane bioreactor (MBR) where the membrane separated the organic substance from biologically treated wastewater. This process retained the microbes and other organic matter larger than its porous size in bioreactor, resulted in the highly productive effluent water as compared to traditional activated sludge treatment method. This process may be used as a pretreatment for the ultrafiltration because of its decreased fouling rate and increased life time.



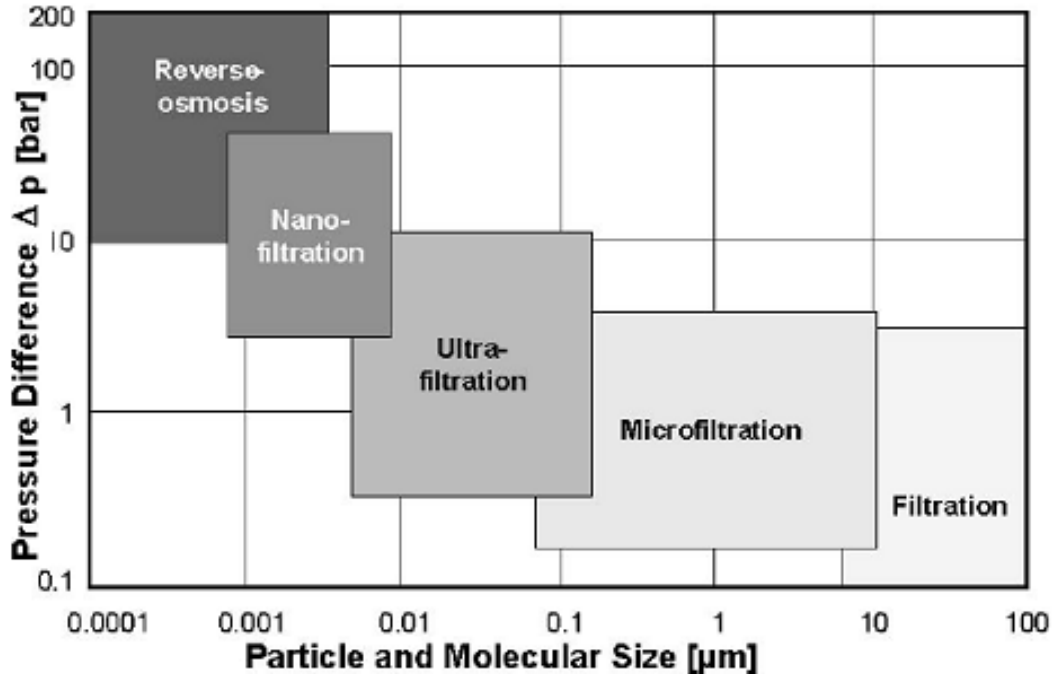


Figure 2.3. Different types of membrane filtrations

#### 2.1.2.2 Ultra filtration:

In ultra-filtration the membrane pore size is 0.002 to 0.1 microns is used which remove the microbes as well as the certain viruses and humic matter. This membrane operates at high pressure of 30 psi to 100 psi (200 kPa to 700 kPa). The pore size is the only difference between micro filtration and ultra-filtration. This membrane is prepared by the Cellulose Acetate Polysulfone and Polyvinyl Chloride polymers (cheremisinoff 2002). The advantage of the UF membrane over the conventional treatment and post chlorination is that it gives the constant effluent quality, no compact plan is designed and no chemical is required.

#### 2.1.2.3 Nano filtration:

Nano filtration is the process in which membrane pore size is within the range of Ultrafiltration and Reverse Osmosis, which is approximately 0.001 microns, which remove all the material having greater size than the pore size like divalent or multivalent, all cysts, all humic matter, and

all disinfectants, viruses and bacteria beside this NF removes the hardness and alkalinity from the water so it is also called “Softening membrane”. A very high pressure of 90 psi to 150 psi (600kPa to 100kPa) is required for its operation than ultrafiltration membrane.

#### **2.1.2.4 Reverse osmosis:**

Reverse osmosis (RO) which is also called the hyper filtration is the method in which movement of water across the RO membrane, which is a semipermeable osmotic membrane is from high concentration solution to low concentration. In this process, we need a comparatively higher pressure than the osmotic pressure of feed water is required to move water through the membrane which act as a filter for dissolved solutes. This method removes the viruses, radium, bacteria, giardia and all organic substance. This method is environment friendly as it doesn't produce a high quantity of heat or any harmful chemical so it preserve all nutrients, protein and enzyme which are present in the liquid food (Merry et al., 2010).

This method removes all the substance that makes the water smell unkind, taste unwell and give unique color to the water, hence it is used for the production of drinking water on large and small scale for household purpose.

#### **2.1.3 Membrane fouling**

Performance of membrane was decreased due to fouling with the passage of time during the operation. The solute particles were deposited on the surface of membrane or imprisoned on the pore of membrane and block it .There are various foulants such as biological, colloidal and organic which are responsible for fouling.

Depending on the strength of binding foulants on the surface of membrane, fouling of the membrane was classified into two types Reversible Fouling and Irreversible Fouling. In the

reversible fouling membrane may be recovered by cleaning it physically and by back washing the membrane. Physical cleaning may be done by the shaking or aeration which must be done by giving some shear force to the membrane. Irreversible cleaning may be done only by the chemically, acidic and basic cleaning are responsible for the chemical cleaning.

#### **2.1.4 Types of membrane module:**

Generally membranes were manufactured in hollow fiber or flat sheet form, which are then molded into various configurations according to the requirement of membrane area for the respective system. There are four types of membrane modules as shown in Figure 2.4.

##### **2.1.4.1. Spiral wound:**

Spiral wound module type is associated with nanofiltration membrane and Reverse osmosis. In this module porous tube is wound by the set of flat sheet membranes, in each set of membrane two membrane are attached having spacer between them. These membranes operate in two modes that are outside in mode and inside out mode, in outside in mode water moves from outside of the membrane and comes in by passing through the membrane and vice versa for inside out mode.

##### **2.1.4.2 Hollow fiber:**

This configuration was developed in the 1960s and designed for the Microfiltration or Ultrafiltration. In hollow fiber membrane configuration, the fibers were arranged in horizontal and vertical pattern and each contain 10 to 1000 fibers in a module. Fiber generally consist of a small hollow porous tube which is made by polyacrylic (PAN) or polyvinylidene fluoride (PVDF). It can bear high pressure from the outside of the membrane, but less pressure can be bear from the inside of the membrane so backwashing is only occurred at low pressure. This membrane operates at both inside out and outside in mode.

### 2.1.4.3 Tubular membrane:

This membrane was under research from early 1920s and used by the industry since 1960s. Tubular membrane is associated with MF and NF. This structure is made up of micro porous substrate, membranes place inside the tube. Area per unit volume of membrane is relatively less than its configuration. This membrane shows high fluxes when it is working at high pressure and due to rugged construction they are less disposed to fouling. This membrane is backwashed easily at 50 psi.

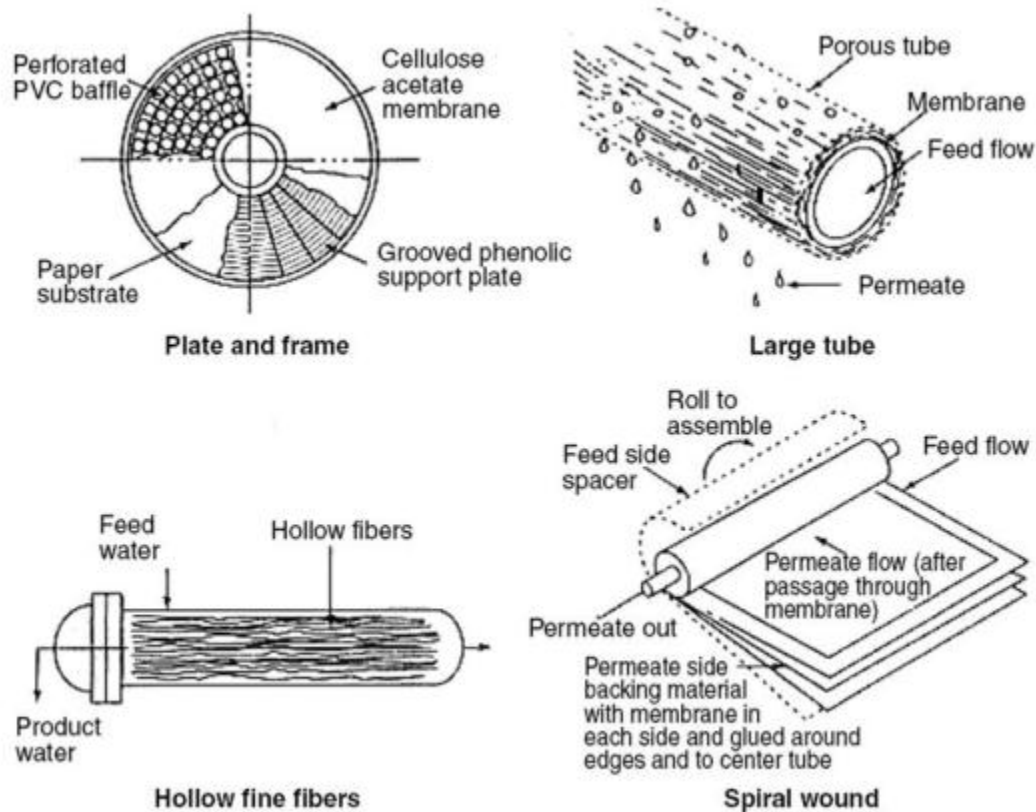


Figure 2.4 Different types of membrane modules

[http://www.separationprocesses.com/Membrane/MT\\_Ch04a.htm](http://www.separationprocesses.com/Membrane/MT_Ch04a.htm)

#### **2.1.4.4 Plate and frame:**

These modules of membrane are constructed for the flat sheet membrane, in this formation flat membrane sheet is attached to plate like structure supported by frame to provide mechanical support. This configuration is of two type cross flow and dead end flow. In cross flow filtration due to the perpendicular flow of water the membrane is less prone to fouling because of its scouring effect. While in a dead end filtration buildup of cake layer on the membrane surface increase the filtration of feed solution due to the reduction in pore openings.

#### **2.1.5 Membrane market:**

Globally the demand of membrane is increasing day by day because of its widespread application for both commercial and industrial use. Its market value increased with the increased demand of water. Market of membrane for both wastewater and industrial field is increasing from \$2.3 to \$5.5 billion from 2008 to 2015 with 13% of annual growth rate. The membrane that contain highest contribution of the whole membrane market is a Microfiltration membrane because of its widespread industrial and commercial use. Membrane marketing of MF from 2008 to 2015 is shown in Figure 2.5.

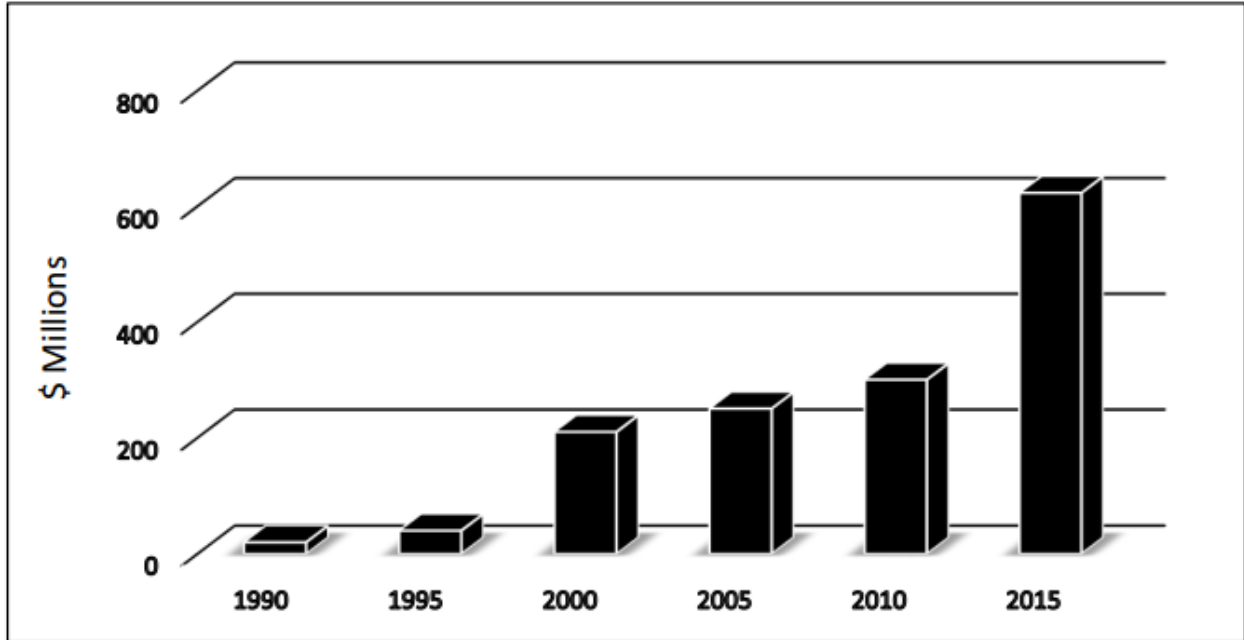


Figure 2.5 Global market of MF membrane (BCC Research)

## 2.2 Forward Osmosis:

### 2.2.1 Introduction:

It is a natural process of solvent (water) tend to pass through the selectively permeable forward osmosis membrane from high water concentration region to lower one. Osmotic pressure is responsible for the movement of water molecules from high to low region is generated by draw solute. The movement depends upon the concentration gradient means higher difference in gradients between solution higher water flux and depend upon the concentration of draw solute and type of draw solute.

For the water transport forward osmosis membrane plays a vital role because it allows only water to pass and keep outside all soluble solid. The osmotic process stopped, when the concentration gradient becomes equal and its osmotic pressure decreased between the two solutions.

The phenomenon of forward osmosis is illustrated in Figure 2.6.

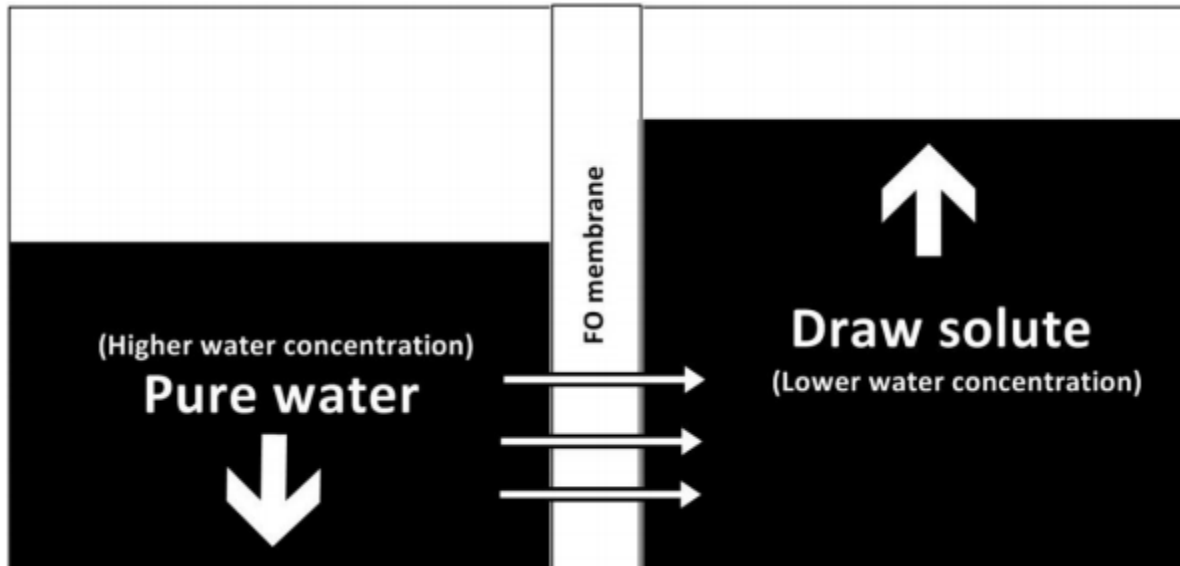


Figure 2.6 Process flow illustration of FO system

This figure shows that osmotic pressure takes the water molecule from a region of high water concentration to lower water concentration which is generated by the draw solute. The increase of flux is also depending upon the molarity of draw solute and molarity differs from salt to salt. Osmotic pressure depends upon the salt concentration and each salt show different behavior.

### 2.2.2 Draw solutes used in OMBR:

Due to gradient difference the movement of water molecules from low to high TDS concentration region between the draw side and feed side is due to osmotic pressure which is generated by the draw solute as mentioned earlier. Different osmotic pressures were generated by different solutes at different concentration.

The physical and chemical properties of each salt depend upon the features and the behavior of salt because some solute shows the high osmotic pressure at low concentration while some other salts were highly rejected by the FO membrane and some solutes show high reverse fluxes so it totally depend upon the solute selection.

For the ideal draw solution different researchers used different draw solutes for the applications of forward osmosis in their studies.

Neff et al., (1964) reported the regeneration of Ammonia and carbon dioxide used as draw solution by simple heating as a patent study, which resulted in the production of carbon dioxide and ammonia as byproducts again.  $\text{SO}_2$ , as a volatile solute was also employed by Batchelder et al., (1965) in the FO system act as a first step towards FO desalination. This DS was regenerated by using simple air stripping and heating method.

Frank et al., (1972) reported the reconcentration of  $\text{Al}_2\text{SO}_4$  used as draw solution in the FO system by precipitation using  $\text{Ca}(\text{OH})_2$ . Kravath and Davis reported the use of glucose in the FO system (Kravath and Davis, 1975). Loeb et al., (1997) used  $\text{MgCl}_2$  as draw solution in the FO system with flat and sheet module. McGinnis et al., (2007) regenerated the  $\text{SO}_2$  and  $\text{KNO}_3$  by using standard methods when used as DS. McCutcheon et al., (2005) employed  $\text{NH}_3$  and  $\text{CO}_2(\text{NH}_4\text{HCO}_3)$  as a draw solute in osmotic system and regenerate it by modest heating at  $60^\circ\text{C}$ .

Addition to this, the magnetic field was also used for the regeneration of draw solution, namely magnetic nanoparticles employed in forward osmosis setup (Adham et al., 2007). They also reported the use of dendrimers as a DS in FO and pH adjustment with ultrafiltration was applied for regeneration. Adham et al., (2007) also use solidification and denaturing for the regeneration of albumin employed as a DS in the forward osmosis system. Use of ethanol as draw solution and its regeneration by pervaporation was reported by McCormick et al., (2008). Yen et al., (2010) observed the performance of 2-methylimidazole-based solutes as DS on FO system, which is then regenerated by simple distillation process.



The use of polymer hydrogel as a draw solution and its regeneration by deswelling was reported by Li et al., (2011). Fertilizers were also used as draw solution by Phuntsho et al., (2011), these diluted draw solutions were also being used for the fertigation purpose. Lyer et al., (2011) apply the fatty acid-polyethylene glycol as a DS in osmotically driven FO system. Su et al., (2012) use nanofiltration for the regeneration of sucrose based draw solution in FO system. Stone et al., (2013) observe the performance of the organic draw solution like MgOAc, reverse osmosis system was used for its regeneration.

Ansari et al., (2015) observe the performance of different organic and inorganic salts to facilitate the integration of FO with an anaerobic system to produce methane gas. Holloway et al., (2015) use different mixtures of draw solutions with NaCl and MgCl<sub>2</sub> in FO to reduce the effect of high reverse salt flux.

### **2.2.3 Applications of forward osmosis:**

This process requires no energy for the movement of water from a region of low TDS concentration to the region of high TDS concentration by the help of osmotic pressure which is generated by draw solute. Demand of forward osmosis is increasing with the passage of time for both domestic and industrial use because of its green technology nature.

Applications of FO are the following:

- Landfill leachate treatment
- Complex stream treatment
- For food and beverage concentration
- Membrane brine concentrator (MBC) is done by FO
- At domestic level waste water treatment is done by MBC

- Desalination

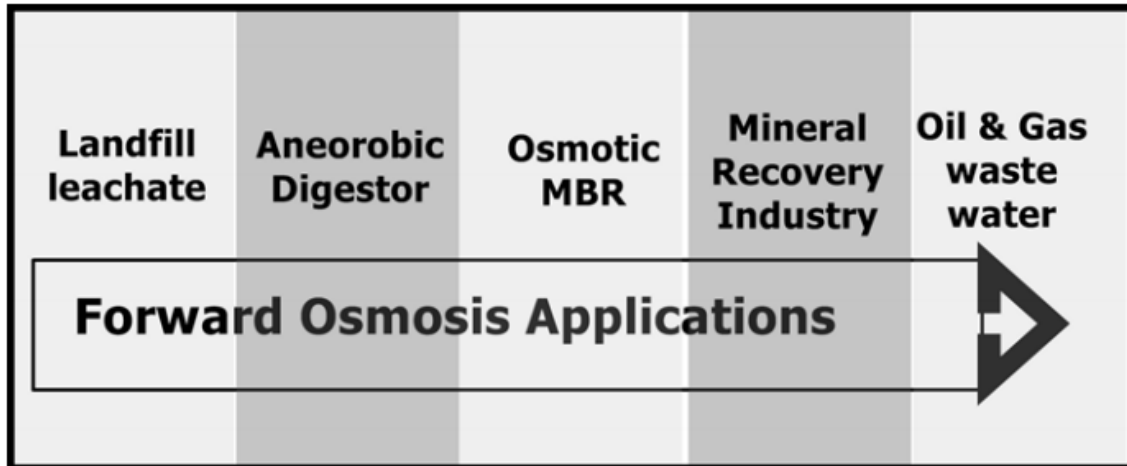


Figure 2.7 Application of FO process

#### 2.2.4 Forward Osmosis Membrane:

Different FO membranes are trying to develop by different researchers, but the most common membrane is FO membrane which is manufactured by the hydration technology innovation (HTI), Albany or Unites states. The nature of these membranes is hydrophobic and having a thickness not than 50 $\mu$ m (McCutchen et al., 2006). Cellulose acetate braced, which is embedded by the polyester mesh are the manufactured material of these membranes. These membranes have an asymmetric structure which is given by the porous support layer and a thick selective layer. Selective layer behaves like an Active layer and the dense layer having pores gave the mechanical support to the membrane.

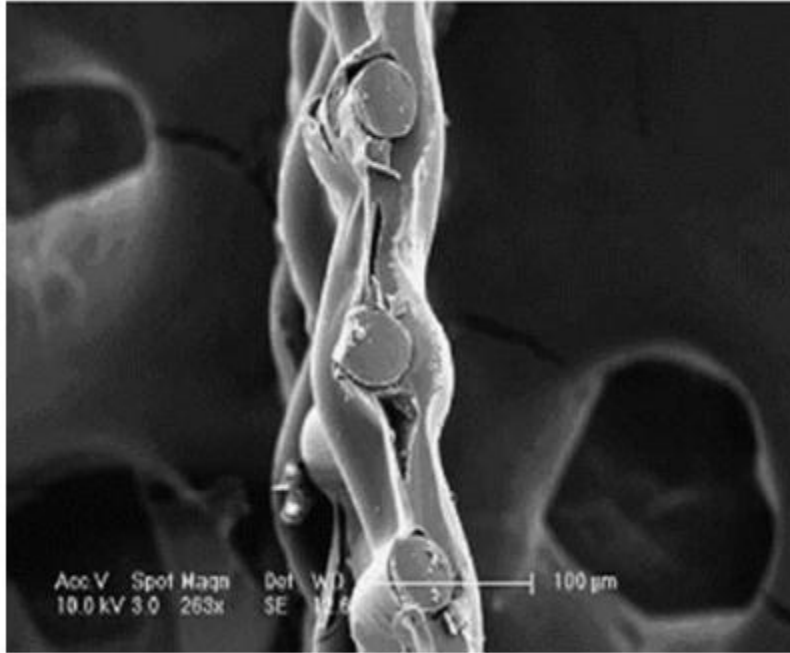


Figure 2.8 SEM image of CTA-FO membrane (McCutchen et al., 2006)

These membranes have 76 and 87 degree contact angle for both two layers respectively. Roughness of membrane is approximately 36nm shown by the Atomic Force Spectrometric analysis. High rejection shown by the FO membrane as compared to the RO membrane which allow only the water to pass. Some HTI outperforms of membrane are shown in figure 2.9.

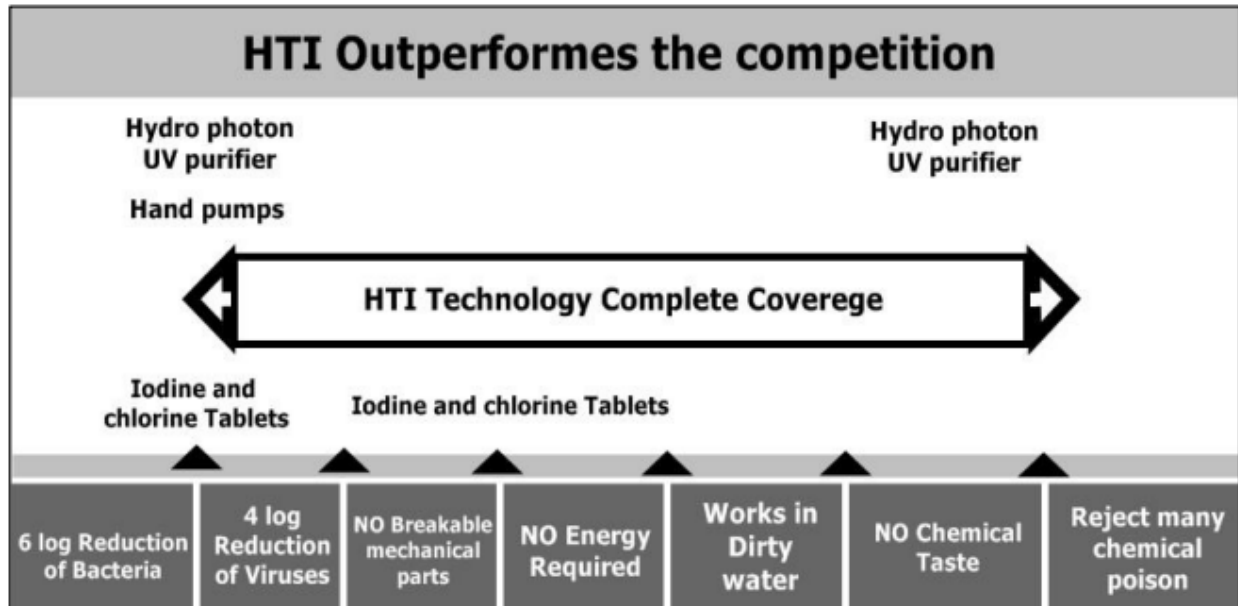


Figure 2.9 Outperformance of Hydration Technology Innovation

### 2.3 Membrane bioreactor:

It is the combination of the membrane separation technique and bioreactor or the membrane bioreactor is the combination of conventional acclimatized biomass treatment which is followed by the membrane filtration (Gunder et al., 1998). To separate the sludge from the stabilized water we use a suction pump instead of gravity to draw stabilized water (Judd et al., 2006). The pore size of membranes for the filtration in MBR technique is range from 0.005 to 0.4m. Vacuum pressure to the membrane is created by the suction pump and the TMP meter is required to measure the Trans membrane pressure (TMP). The MBR schematic diagram is shown in 2.10.

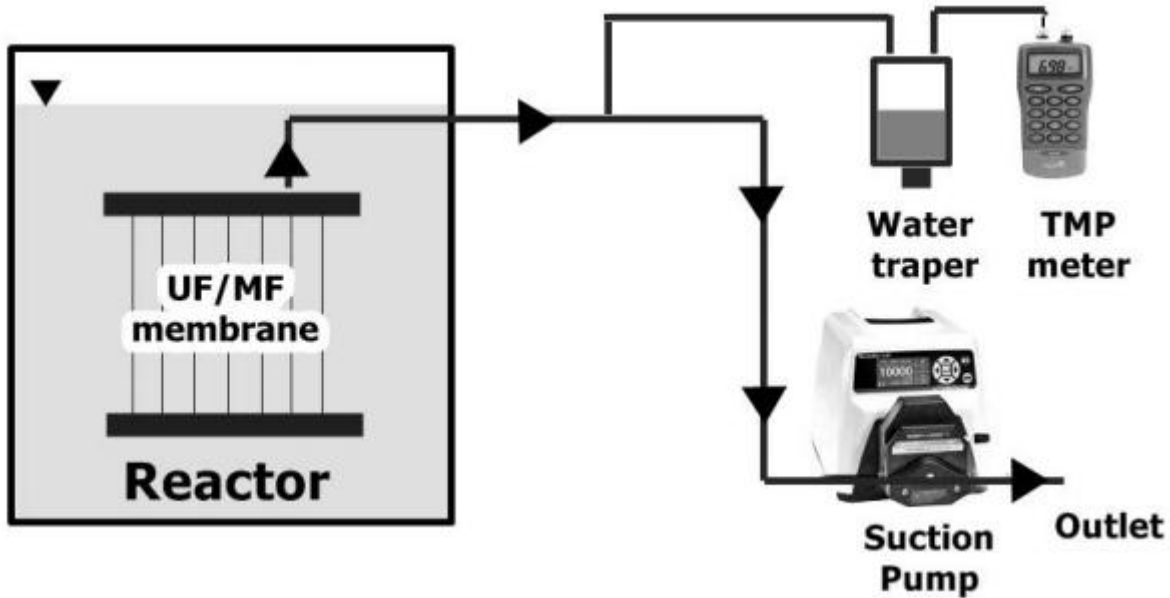


Figure 2.10 Flow chart diagram of simple MBR system

### 2.3.1 Advantages of membrane bioreactor:

MBR is dominant over CAS waste water treatments, because of its compact size so it requires less space. For better biological performance MBR has high effluent as compared to CAS because of its high (Mix Liquor Suspended Solids) MLSS, MBR is operated at low (Hydraulic Retention Time) HRT when we have high MLSS. As compared to CAS, MBR produces lesser amount of excess biomass, so as a result, it has a low cost to handle the excess biomass. Because of its UF membrane and MF membrane, MBR produces high class effluent by helping the solid liquid separations. For the stability of microbes in the tank we need a constant flux because stability defines the effluent quality of operated system.

### 2.3.2 Disadvantages of membrane bioreactor:

The capital cost of CAS was lower than MBR, because the high concentration of MLSS in MBR requires more aeration as compared to the CAS. For the separation of liquid and solid in MBR, we

need a suction pump which increases its operating cost as compared to the CAS. Membrane fouling is also the disadvantage of MBR, backwashing and cleaning of membrane is require to overcome the Trans membrane pressure of the membrane which increase with the operation of membrane.

### 2.3.3 MBR configuration:

In two different configuration membrane is attached to bioreactor (a) Side stream MBR (S.S.MBR)

(b) Submerged MBR (S.MBR)

#### a) Side stream MBR

In this case module of membrane is placed outside the bioreactor, membrane is more disposed to fouling and to overcome the deposition of suspended solid on membrane we need a high energy which circulate the water at a high cross velocity (Clech et al., 2005).

#### b) Submerged MBR

In this case membrane is placed inside the bioreactor, for the growth of sludge and to scour the membrane low air pressure is required, so this case is less disposed to fouling (Van der Roest et al., 2004).

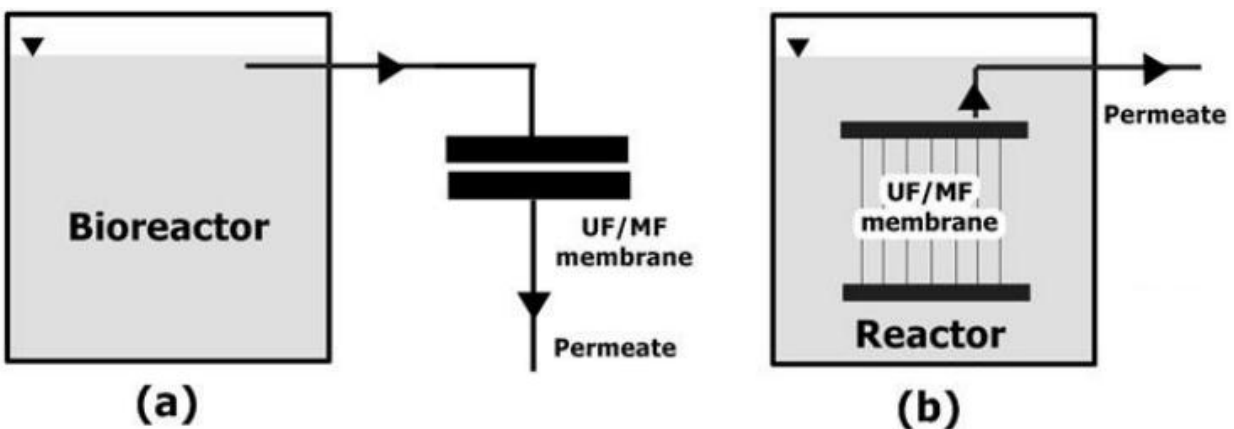


Figure 2.11 a) Side stream MBR b) Submerged MBR

**Table 2.1 Comparison of side stream and submerged configuration of MBR**

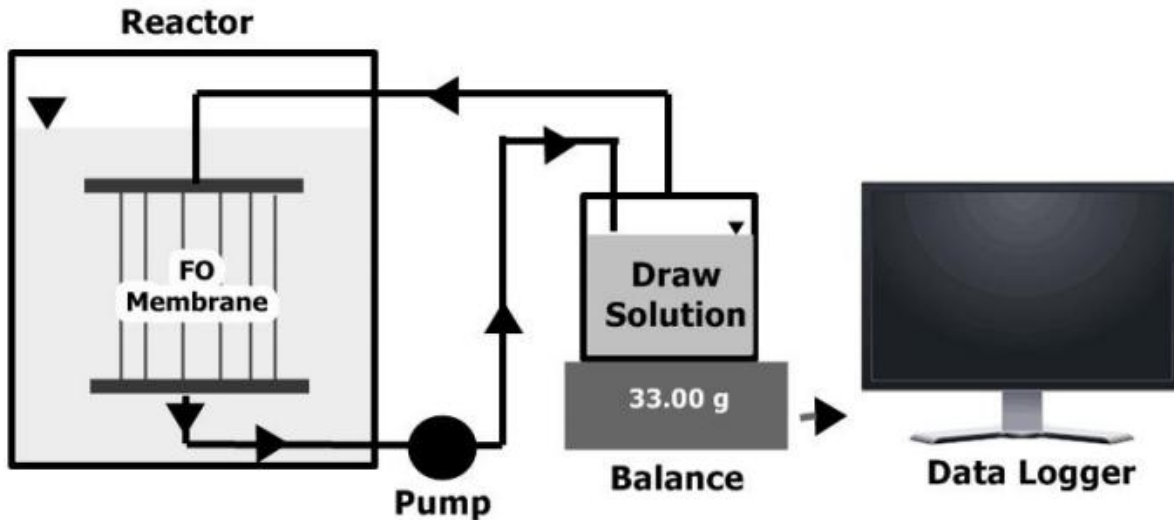
<b>Constituents</b>	<b>S.S-MBR</b>	<b>S-MBR</b>
<b>Mode of Operation</b>	Crossed flow	Submerged
<b>Operational flux</b>	55 - 105	10 – 30
<b>Operational cost</b>	High	Low
<b>Operating pressure</b>	200-600	5-30 (negative)
<b>Investment cost</b>	Comparatively High	Low
<b>Membrane cleaning</b>	Easy	Hard
<b>Membrane Configuration</b>	Plate & Frame	Hollow Fiber

## **2.4 Forward Osmosis Membrane Bioreactor**

### **2.4.1 Introduction:**

FO-MBR which is also known as osmotic membrane bioreactor is the combination of membrane bioreactor and osmotic process as shown in figure 2.12. In this process organic matter is stabilized by the membrane bioreactor and with the help of osmotic force FO membrane separates the stabilized organic matter. This osmotic force is actually induced by DS which is circulated through the one side of membrane. Separation technique is a major difference between MBR and OMBR, microfiltration and ultrafiltration membrane is used in MBR and through the suction pump water

is separated from the bio tank while osmotic membrane is used in the OMBR with the help of natural osmotic force water is separated from bio tank, bioreactor's role is same for both processes.



**Figure 2.12 Schematic flow chart of OMBR**

The FO membrane module is submerged in a bio tank in the OMBR process and from the draw tank draw solute is circulated within the membrane module, draw the water from reactor and flow back to draw tank. To separate the treated water from draw solute we need a post treatment technique which can be membrane distillation or reverse osmosis process.



A general comparison between conventional membrane bioreactor and osmotic membrane bioreactor is shown in table 2.2.

**Table 2.2 General comparison between OMBR and conventional MBR**

<b>Constituents</b>	<b>OMBR</b>	<b>MBR</b>
<b>Operating configuration</b>	Submerged/ Side stream	Submerged/ Side stream
<b>Operational flux</b>	3 - 10 LMH	>30 LMH
<b>Operational cost</b>	Low	High
<b>Operating pressure</b>	Osmotic pressure	Suction pressure
<b>Operating OLRs</b>	Can encounters the High OLRs	Best for low OLRs
<b>HRT (hrs.)</b>	Aug-42	< 12
<b>Fouling</b>	High	Less

#### **2.4.2 Advantages and the limitation:**

No need of suction force is required in OMBR as compared to conventional MBR, because of the natural process of osmotic gradient that is generated by draw solutes.

As osmotic membrane bioreactor runs on the mechanism of osmotic pressure and available osmotic membranes works on low water flux, so higher HRT was witnessed in OMBR generally as compare to conventional MBR. These longer HRTs in OMBR systems were helpful for better removal of nutrients and pollutants in contrast with MBR.

Reverse salt diffusion into the bioreactor is the most dynamic limitation, which not only affect the microbial growth, but also disturb the removal efficiency of OMBR system. So the need of an optimized draw solution is required, which is able to produce less reverse flux in OMBR system.

Water flux of FO membrane in osmotic membrane bioreactor reactor system was actually depend on the concentration and type of draw solution, the osmotic pressure generated by the DS is much less than that of pressure created by suction force in MBR. That's why it is considered as a slow process.

Need of post separation method is required for the separation of draw solutes from treated water from OMBR effluent. Application of NF, RO and DCMD for the tertiary separation can be used according to the nature of DS employed.

#### **2.4.3 So far research on OMBR:**

Cornelissen et al., (2008) used different draw solutes in batch scale FO-MBR setup and observed high flux with low RSF by using divalent salts as DS as compared to monovalent, they further studied the effect of activated sludge on fouling of membrane, before and after activated sludge they used deionized water for testing FO membrane flux, and findings reveals that the activated sludge has no effect on membrane fouling.

Achilli et al., (2009) operated FO-MBR system with activated sludge by continuous feedings of wastewater and used meat extract as an organic source. FO-MBR has a high removal as compared to conventional MBR, it removed 99% of TOC and 98% of  $\text{NH}_4\text{-N}$ . Flux decrease was only observed due to salt accumulation in bio tank, no reversible and irreversible fouling was observed there.

Phuntsho et al., (2011) investigated the performance of fertilizers on FO system, an emerging technology with low energy consumption where there is no need of DS separation is required from FO effluent. Instead of separating the draw solutes from treated water, diluted DS can directly be employed to agricultural fields as fertigation.

Alturki et al., (2012) studied FO-MBR system for the removal of trace organics, with the help of biological degradation and FO membrane 23 out of 27 trace organics removed successfully and increase salt concentration of bio tank had disturbed biological properties.

Chen et al., (2014) run FO system with anaerobic sludge for the treatment of low strength wastewater. System was removed 100% of phosphorus, 92% of TOC and 62% of ammonium nitrogen that's removal higher than conventional anaerobic MBR. Effect of salinity was overcome by removing of supernatant after each cycle. Methane gas was also produced in sufficient amount which was used in FO-MBR for aeration.

Wang et al., (2014) investigate the SRT effect on fouling of FO membrane, system was operated at 10, 15 and 40 days SRT respectively. Results reveals that shorter SRT was helpful for the removal of accumulated salts from the sludge, longer SRT with high salt concentration effect microbial diversity of bio tank. For the removal of salts from bioreactor, Wang et al., (2014) introduced a microfiltration membrane in bio tank as shown in figure 2.13. Salts concentration in bio tank was maintained to a minimum level which increase the duration of cycle and helps a constant flux of FO as compared to conventional FO-MBR. Due to decrease in salinity of bio tank, TOC and ammonia removal were also increased.

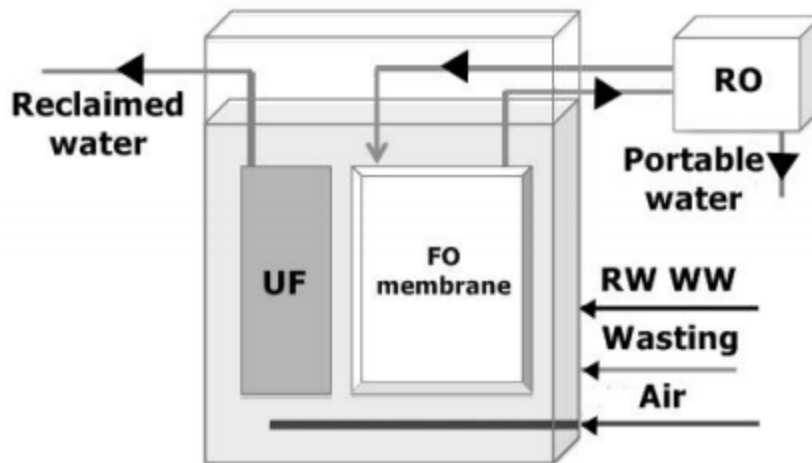


Figure 2.13 OMBR system integrated immersed UF membrane.

Holloway et al., (2014) used FO and UF membrane in the same tank and RO system applied on the permeate of FO. Salts from bio tank removed by the UF membrane which increase the performance of FO membrane. UF membrane was also remove phosphorus and give a nutrient rich permeate.

Holloway et al., (2015) by mixing the different draw solutions with commonly used NaCl, reported that by mixing the small amount of divalent ( $MgCl_2$  and  $MgSO_4$ ) salts with NaCl not only resulted into relatively less amount of reverse salt diffusion as compare to pure NaCl. But also the high water flux was observed in case of mixed draw solution at same osmotic pressure.

Nguyen et al., (2015) investigate the ideal draw solution in a hybrid MBBR-OMBR system for the treatment of synthetic wastewater, by using Na-EDTA mixed with Triton X-100. They reported that with the help of newly invented trivalent draw solution, negligible reverse salt flux, stabilized water flux and better removal of nutrients/pollutants were achieved.

Ansari et al., (2015) assessed the performance of organic and inorganic draw solutes on FO system integrated with anaerobic system. They observed that organic draw solutions were more suitable for anaerobic process because of lower reverse salt flux in to the bioreactor. No hindrance in gas production with organic DS was observed as compare to inorganic salts.

**Table 2.3 Use of different organic and inorganic DS at a constant osmotic pressure.**

<b>Draw Solutions</b>							
Salt	Formulae	Molar Mass (g/mole)	Concentration (M)	Osmotic Pressure (Mpa)	Water Flux (L/m <sup>2</sup> h)	Reverse Solute Flux (g/m <sup>2</sup> h)	References
<b>Organic</b>							
Sodium acetate	CH <sub>3</sub> COONa	82.03	0.72	3	3.28	0.72	Ansari et al. (2015)
Magnesium acetate	Mg(CH <sub>3</sub> COO) <sub>2</sub>	142.39	0.84	3	3.5	0.5	Ansari et al. (2015)
Sodium formate	HCOONa	68.01	0.68	3	9.36	6.04	Bowden et al. (2012)
Sodium propionate	C <sub>3</sub> H <sub>5</sub> NaO <sub>2</sub>	96.07	0.68	3	8.67	1.47	Bowden et al. (2012)
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	180.16	1.13	3	2.3	0.38	Yong et al. (2012)
<b>Inorganic</b>							
Magnesium chloride	MgCl <sub>2</sub>	95.21	0.36	3	8.38	4.8	Achilli et al. (2010)
Calcium chloride	CaCl <sub>2</sub>	110.98	0.4	3	9.5	7.9	Achilli et al. (2010)
Sodium bicarbonate	NaHCO <sub>3</sub>	84	0.76	3	8.89	1.7	Achilli et al. (2010)
Potassium sulfate	K <sub>2</sub> SO <sub>4</sub>	174.2	0.58	3	9.27	3.7	Achilli et al. (2010)
Sodium sulfate	Na <sub>2</sub> SO <sub>4</sub>	142.04	0.6	3	7.7	2.4	Achilli et al. (2010)

## Material and methods

### 3.1. Description of experimental set-up:

A laboratory scale hybrid OMBR-MD setup was used for this research work as shown in figure 3.1. The system consisted of feed tank, bioreactor having submerged FO membrane module, draw tank and DCMD unit for the recovery of draw solutes and production of pure water. Luo et al. (2016) observed that energy consumption (hydraulic pressure) as well as the capital cost of hybrid OMBR-RO compromised the paybacks over conventional MBR. Lower capital and operational cost, precise permeate quality, less effect of salinity on flux and specifically low grade heat utilization by MD membrane emerge as a good option to recover DS as compare to NF, RO and electro dialysis (Luo et al., 2014). So the continuous DCMD process was used in this study for the recovery of DS.

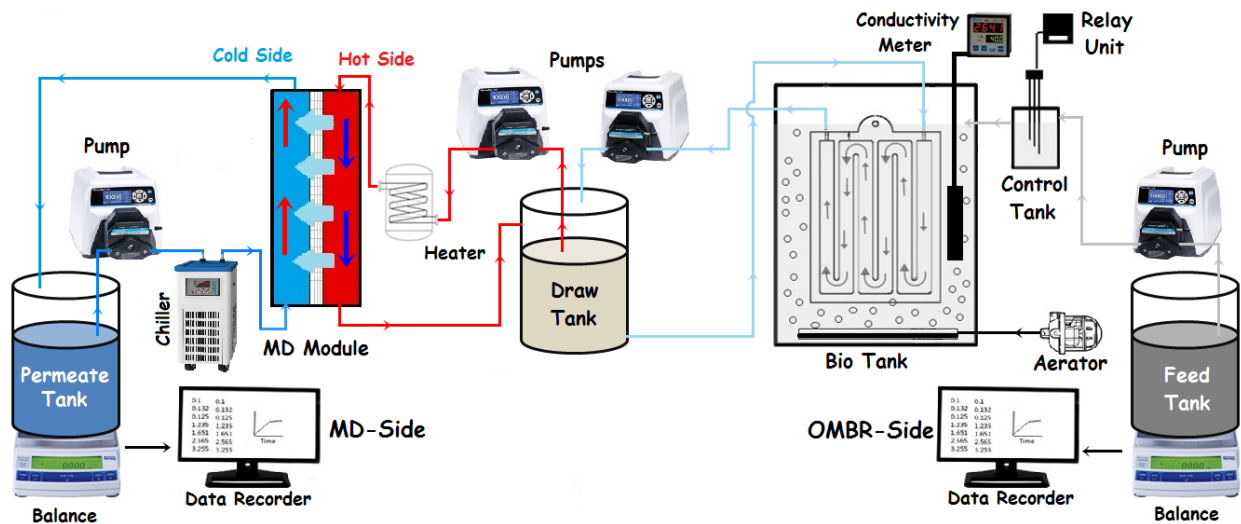


Figure 3.1 : Process flow diagram of hybrid OMBR-MD system.

At OMBR side, feed tank was placed on a top loading balance (UX6200H, Shimadzu, Japan) attached with computer to determine the flux of FO membrane. A peristaltic pump (Cole Parmer, 77200-62, Masterflex, USA) attached with relay unit (Omron Floatless Level Switch, 61F- Japan) was installed to feed the bioreactor. Plate and frame type FO membrane module made of acrylic sheet with length, width and height of 30cm, 30cm and 1.5cm respectively was submerged in bioreactor. Module was also provided with 10 baffles each of 0.6cm thickness to increase the contact time of DS with in the module. Flat sheet cellulose triacetate (CTA) FO membrane from Hydration Technology Innovations (HTI) USA with effective membrane area of  $0.12\text{m}^2$  was attached on module to seal the DS flow channel. Membrane active layer was facing the feed side (AL-FS) during the OMBR operation as this configuration cause less fouling in comparison with active side facing DS (AL-DS) (Aftab et al., 2015). Continuous dissolved oxygen of 3-4mg/L was provided for the active growth of microorganisms and membrane scouring by using an air pump. Conductivity due to increased salinity in bioreactor was monitored by using in-line conductivity meter. Peristaltic pump (Cole Parmer, 77200-62, Masterflex, USA) was used for the circulation of DS with cross-flow velocity of 500mL/min from draw tank to the FO membrane module. Figure 3.2 shows OMBR setup installed in water and wastewater lab, IESE, NUST.

Draw tank was used for integration of OMBR and MD systems to make hybrid OMBR-MD unit. Draw tank not only collected the treated water from OMBR side but also served as a feed reservoir for MD side. DCMD unit comprised of acrylic flat sheet module for hydrophobic membrane having two flow channels. Hydrophobic flat sheet microporous PTFE (Polytetrafluoroethylene) membrane from Porous Membrane Technology, Ningbo, China with an effective area of  $0.005\text{m}^2$  was used for the DCMD set-up.



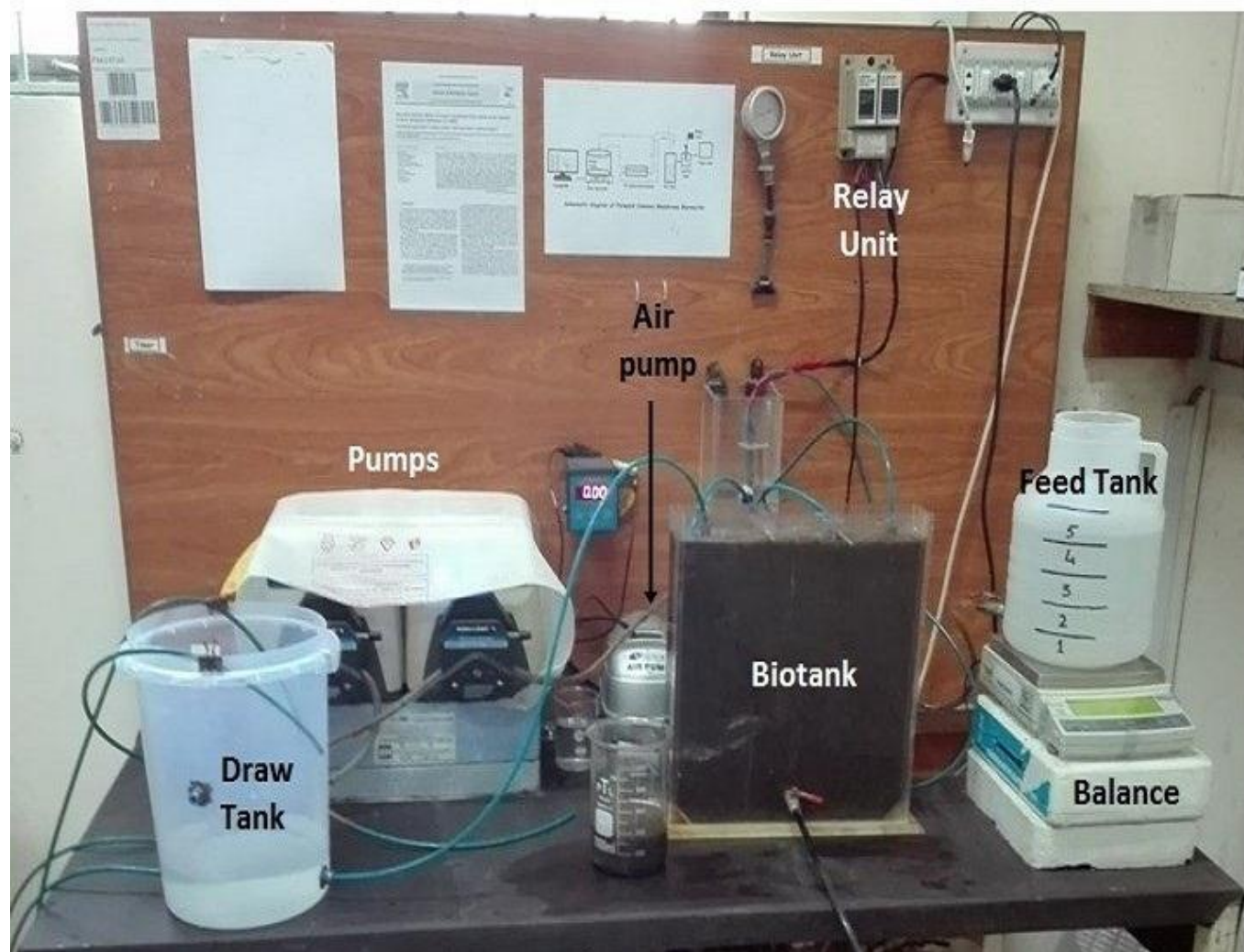


Figure 3.2 OMBR setup at IESE NUST

Two peristaltic pumps (Cole Parmer, 77200-62, Masterflex, USA) were used for the circulation of feed (i.e. Draw Solution) and permeate in a countercurrent manner through each channel providing the same circulation velocity on both sides. To heat the feed solution for hot MD side, heater containing stainless steel heat exchanging coil immersed in hot water reservoir was used.

Two temperature sensing devices (SANHNG-TPM-900, China) were installed to measure the temperature of incoming and exit temperature of feed side (i.e. Hot Side). HACH (sensION), USA TDS meter was used to measure the feed (i.e. DS) TDS. Permeate pass through the chiller to maintain temperature gradient between cold and hot side. In-line TDS meter with temperature sensor (KOMATSU) was installed on cold side (i.e. Permeate side) to record effluent TDS and temperature. Permeate tank was placed on a top loading balance (UX6200H, Shimadzu, Japan) attached with computer to measure the flux of MD membrane. Figure 3.3 shows DCMD setup installed in water and wastewater lab, IESE, NUST.

### **3.2. Draw solutions and feed:**

Nawaz et al. (2013) found that divalent salts ( $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) were more supportive to the growth of microbial community as compared to the monovalent salts. Therefore, commonly used divalent  $\text{CaCl}_2$  and  $\text{MgCl}_2$  were selected as inorganic DS for this study to operate in OMBR system. Divalent salts, due to their large hydrated radii produce better flux performance and less reverse salt transport than monovalent salts ( $\text{NaCl}$ ) (Nguyen et al., 2015; Khanzada et al., 2016; Holloway et al., 2015).

Similarly sodium acetate ( $\text{CH}_3\text{COONa}$ ) and magnesium acetate ( $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) were carefully chosen from organic family due to their wide use in FO to control salinity. These salts of acetate are highly degradable and capable of achieving a stabilized flux as they have less reverse salt flux than  $\text{NaCl}$  (Ansari et al., 2015; Bowden et al., 2012). Performance of these four salts was investigated against the commonly used  $\text{NaCl}$  in OMBR system at 0.25 M concentration of each DS. The DS was prepared by dissolving 0.25M concentration of each salt in DI water.

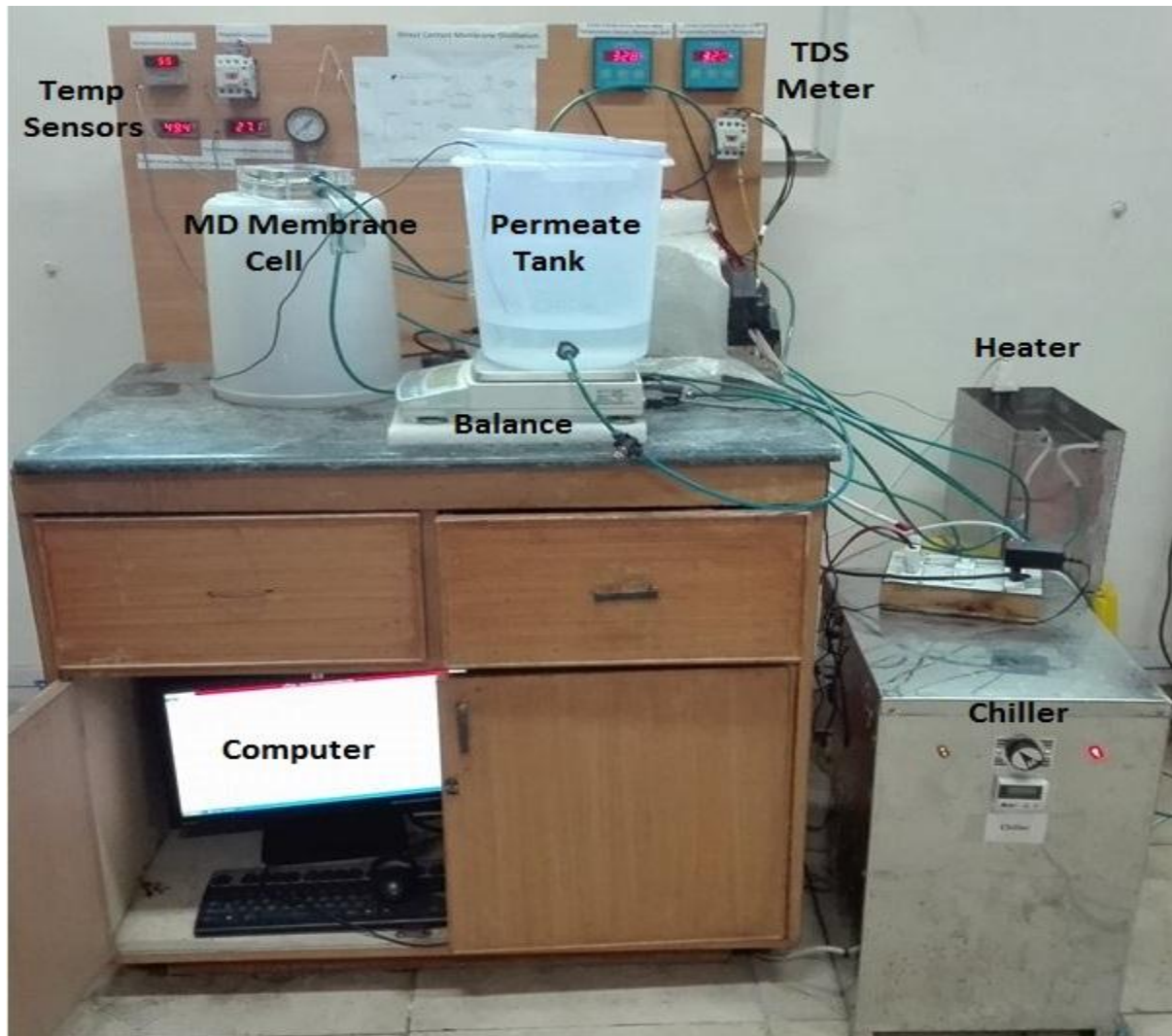


Figure 3.3 DCMD setup at IESE NUST

Synthetically prepared feed solution was used to simulate the domestic wastewater. Recipe of synthetic wastewater include Potassium dihydrogen orthophosphate, glucose, ammonium chloride and trace nutrient as described in Table 3.1.

**Table 3.1: Composition of synthetic wastewater.**

<b>Composition</b>	<b>Formula</b>	<b>Unit</b>	<b>Concentration</b>
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	mg/L	308.4
Ammonium Chloride	NH <sub>4</sub> Cl	mg/L	114.6
Potassium Phosphate	KH <sub>2</sub> PO <sub>4</sub>	mg/L	44.0
Magnesium Sulfate	MgSO <sub>4</sub> . 7H <sub>2</sub> O	mg/L	2.92
Calcium Chloride	CaCl <sub>2</sub>	mg/L	2.92
Ferric Chloride	FeCl <sub>3</sub>	mg/L	0.88
Manganese Chloride	MnCl <sub>2</sub> . 4H <sub>2</sub> O	mg/L	0.60
Sodium Bicarbonate	NaHCO <sub>3</sub>	mg/L	69.71

### **3.3. Operational protocol:**

OMBR-MD operation was carried out by using five different DS individually having concentration of 0.25M each. Bioreactor with 4.5L working volume having submerged FO membrane module was continuously aerated. Activated sludge having 7-8 g/L MLSS from NUST MBR Plant, Islamabad was used as a seed sludge for OMBR-MD continuous operation. Sludge was further acclimatized with synthetic wastewater used in this study for 8-10 days, prior to feeding the OMBR-MD system. New sludge was taken from MBR plant every time for each DS, as the reverse solute of previous DS in sludge suspension may interfere the performance of next DS. Initial hydraulic retention time (HRT) of five different DS were in the range of 7-10hrs and was measured from initial water flux of FO membrane. As a function of time, HRT increases with the decrease in water flux. The OMBR system was operated at constant solids retention time (SRT) of 20 days under each DS condition. Maintenance of SRT was also helpful to alleviate the salinity build-up

in bioreactor to a certain extent that is beneficial for biomass growth (Aftab et al., 2015; Luo et al., 2016). To concentrate the DS continuously, MD system was run parallel to OMBR system with initial circulating velocity of 1000mL/min on both sides (i.e. Hot and cold side). Suitable temperature on trial and error basis was selected for every DS recovery on hot side and 10 °C for cold side was maintained throughout the study. Behaviour of water transfer rate at MD side was dependent on the water flux of FO side. Water transfer rate of MD side was adjusted on the daily basis to match with transfer rate of OMBR side by changing the circulating velocity of MD system as reported earlier by Luo et al. (2016) where the FO membrane flux was adjusted with RO system by changing the hydraulic pressure. Additionally the velocities of both sides remained identical throughout the study. TDS in draw tank was continuously measured to maintain 0.25M concentration of each DS.

To stabilize the condition of increasing TDS concentration in the draw tank, circulating velocity was reduced. Whenever the TDS concentration in draw tank decreased due to the salt deposition on hot side, MD membrane was flushed with DI water. Previously, Xie et al. (2014) flush the FO membrane for the adjustment of flux in FO-MD system. DI water was circulated on both side of MD membrane for the flushing purpose with cross flow velocity of 20 cm s<sup>-1</sup> at 25 °C for one hour. After flushing, the MD system was again attached with the OMBR setup to achieve continuous recovery of draw solute to maintain TDS concentration in the draw tank. OMBR-MD system operation was terminated when the flux of FO membrane declined up to 20% of the initial flux.

#### **3.4. Analytical Methods:**

For each salt sludge characteristic were observed in term of mix liquor suspended solids (MLSS), mix liquor volatile suspended solids (MLVSS), capillary suction time (CST) and particle size distribution (PSD). While the treatment analysis in terms of chemical oxygen demand (COD),

Phosphate-P ( $\text{PO}_4^{3-}\text{P}$ ) and Ammonium-N ( $\text{NH}_4^+\text{-N}$ ). All these analysis were performed as per Standard Method (APHA, 2012).

Mean particle size of sludge floc was measured by using particle size analyzer (LA-300, HORIBA, Japan). CST apparatus (304B-CST, Triton, Canada) was used to analyze the filterability and conditioning of sludge in terms of capillary suction time (CST). In this process, water is gulped from sludge by using a standard filter paper and the rate at which water permeates through paper depends on sludge quality. Two electrodes were positioned at standard interval from funnel, time taken by water front to travel between these two poles is the capillary suction time to suck water from sludge.

### **3.5. EPS extraction and quantification:**

Cation exchange resin method was used to extract the Extracellular Polymeric Substances from the sludge (Froland et al., 1996). Concentrations of proteins and polysaccharides were used to measure the quantity of SMP (soluble microbial products) and EPS (extracellular polymeric substances). Standard curve for protein (PN) was developed by using various concentrations of Bovine Serum Albumin (BSA). Lowery method (Folin-Ciocalteu's phenol reagent) was used to measure the concentration of protein (PN), using spectrophotometer (T60-UV/VIS, PG-Instrument, Britain) where absorption was measured at the wavelength of 750 nm (LOWRY et al., 1951). Concentration of PS (carbohydrate or polysaccharide) were measured by using Dubois method (Phenol-Sulfuric Acid), wavelength of 470 nm was used to measure the absorption of solution (DuBois et al., 1956). Standard curves of PS was developed using analytical grade glucose.

## Results and discussion

### 4.1 Water flux of FO membrane:

Figure 4.2 illustrates the water flux as a function of time for each draw solution. Among five different DS,  $\text{CaCl}_2$  and  $\text{NaCl}$  produce highest initial flux followed by  $\text{NaOAc}$ ,  $\text{MgCl}_2$  and  $\text{MgOAc}$  respectively at a constant molar concentration. These results were also correlated with previous findings (Achilli et al., 2010; Ansari et al., 2015; Bowden et al., 2012).

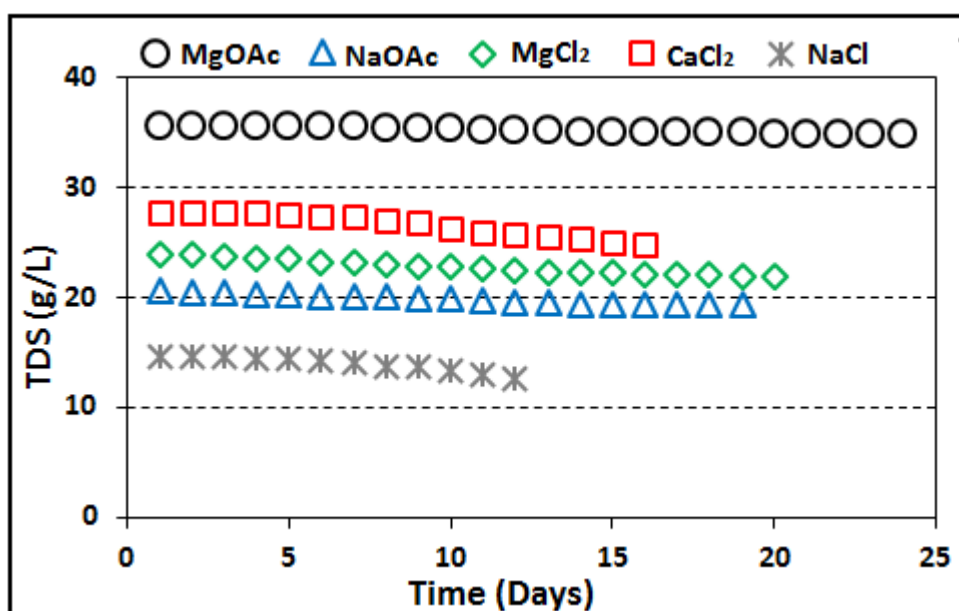


Figure 4.1 TDS concentration in draw tank for each draw solution

Providing high salt rejection (>98%) by MD membrane, a minute decrease in DS concentration was observed at the end of each filtration run as shown in Figure 4.1. So the decreased in water flux was due to membrane fouling or either by raised salinity level in bioreactor. Decline in flux for each inorganic salt ( $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) was actually due to the accumulation of salt, as a result of which salinity level raised with in the bioreactor. In the case of inorganic salts, rapid flux decline was observed with  $\text{NaCl}$  (Figure 4.2) within 12 days as filtration run was terminated when

flux decreased up to 20% of initial flux. The filtration run with  $\text{CaCl}_2$  and  $\text{MgCl}_2$  as DS was ended up within 16 and 21 days respectively at same molar concentrations. These results were mainly attributed to the values of specific reverse salt diffusion (Table ) of each DS. Achilli et al. (2010) and Bowden et al. Bowden et al., (2012) found that specific reverse salt diffusion ( $J_s/J_w$ ) is a valuable parameter for DS performance because lower value of  $J_s/J_w$  indicates minimum salt loss or less reverse transport of solute. Independent of the concentration, the values of specific reverse salt diffusion ( $J_s/J_w$ ) remains relatively constant for each salt and this ratio is helpful for the estimation of reverse solute transport during FO process (Achilli et al., 2010; Bowden et al., 2012; Phillip et al., 2010). Draw solutions that exhibit higher ratios of specific reverse salt diffusion, reflects lower efficiency of process in term of water flux and decrease in membrane selectivity due to the effect of ICP (Internal concentration polarization) at supporting layer of FO membrane (Achilli et al., 2010; Ansari et al., 2015; Hancock and Cath, 2009). Table depicts that  $\text{CaCl}_2$  and  $\text{NaCl}$  has high values of specific reverse salt diffusion which resulted in higher salinity content (section 4.2) as compare to other salts.



**Table 4.1 Specific reverse salt diffusion ( $J_s/J_w$ ) for each DS at same molar concentration.**

<b>Draw Solution</b>	<b>Concentration (moles/L)</b>	<b>Concentration (g/L)</b>	<b>Specific Salt diffusion <math>J_s/J_w</math> (g/L)<sup>a</sup></b>
Mg(CH <sub>3</sub> COO) <sub>2</sub>	0.25	36	0.11
CH <sub>3</sub> COONa	0.25	21	0.26
MgCl <sub>2</sub>	0.25	24	0.59
CaCl <sub>2</sub>	0.25	28	0.83
NaCl	0.25	15	0.74

<sup>a</sup> Data from Achilli et al. (Achilli et al., 2010) and Bowden et al. (Bowden et al., 2012)

Moreover, the salinity build-up in bioreactor decreases the osmotic pressure gradient between DS and feed, which resulted in rapid flux drop in case of CaCl<sub>2</sub> and NaCl in comparison with MgCl<sub>2</sub>. A sticky gel like fouling layer was apparently observed at the end of filtration run with each of the inorganic DS. This fouling layer on the surface of membrane was due to enhanced release of SMP (soluble microbial products) due to increased osmotic stress on FS side, as reported elsewhere (Aftab et al., 2015; Zhang et al., 2014). DS producing more saline stress condition in bioreactor results in rapid flux decline, due to higher  $J_s/J_w$  ratio, more reverse salt flux and more severity of fouling.

On the other hand, prolong and stable filtration run was observed (Figure 4.2) for both organic draw solutions (MgOAc and NaOAc) as compared to inorganic salts. Considerably less salinity build-up resulted for each organic DS, as they exhibit significantly lower values of  $J_s/J_w$  (Table ) in contrast with inorganic DS. In case of inorganic DS, flux decline resulted mainly due membrane fouling than salt accumulation within the reactor. A significant prolonged filtration run for 24 days

with MgOAc was observed as compare to NaOAc at same molar concentration that ended within 19 days. Even with less salinity build-up, NaOAc has a noticeable decline in flux (Figure 4.2) in comparison with MgCl<sub>2</sub> because of severe membrane fouling. Attachment of biomass on membrane surface was observed at the end of filtration run with MgOAc and NaOAc,

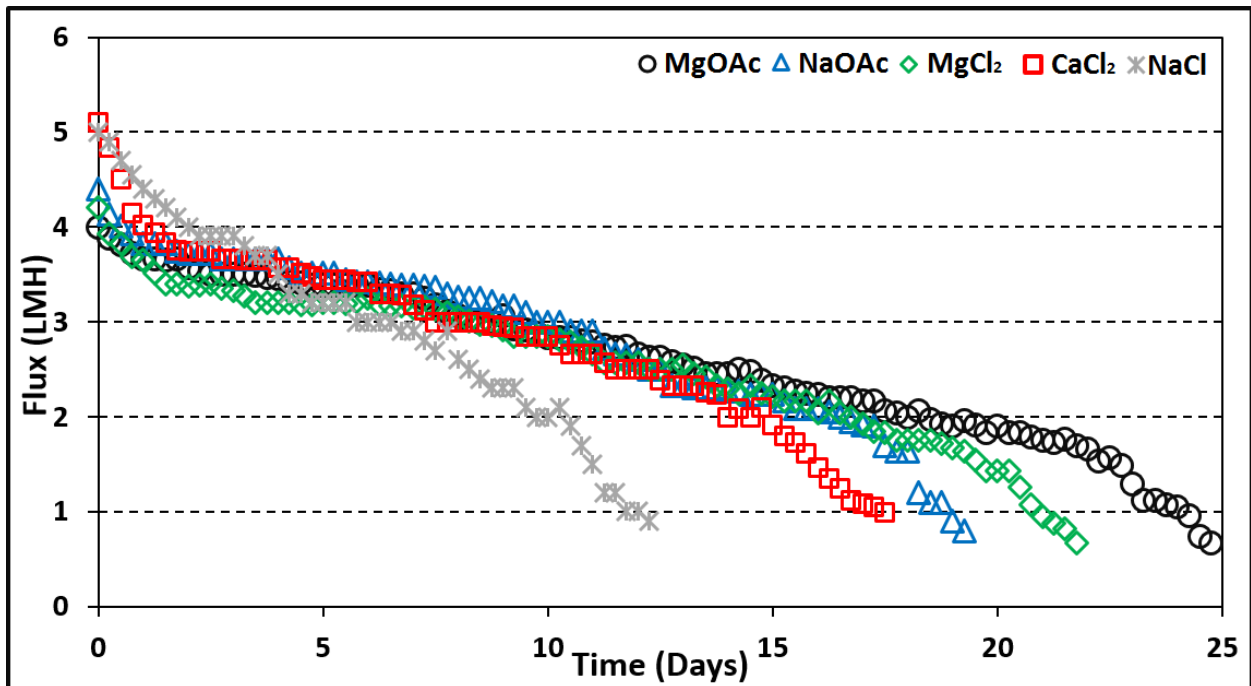
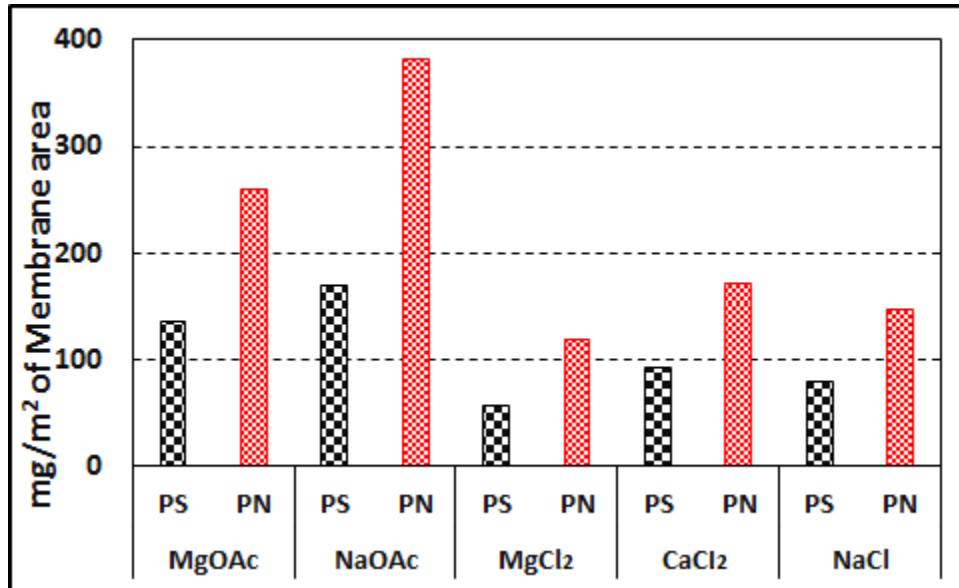


Figure 4.2. Water flux with organic and inorganic DS using OMBR system.

as organic reverse salt flux (Acetate ion) acted as a carbon/food source for microbial growth resulting in biofilm formation on membrane surface (Ansari et al., 2015; Luo et al., 2016). Figure 4.3 presents the EPS of biomass attached on membrane surface, infers that NaOAc has severe fouling than MgOAc and other inorganic salts, due to that reason rapid decline in water flux was observed for NaOAc. Luo et al., (2016) has also experienced that due to higher organic reverse salt flux of NaOAc, high values of biofilm EPS was observed with NaOAc in contrast with other organic salts. So intense fouling was attributed for NaOAc. Attached biomass for NaOAc that

contains higher PN content within the EPS (Figure 4.3), also exhibits higher hydrophobicity resulting in severe membrane fouling.



**Figure 4.3 Protein and carbohydrate contents in fouling layer found on the surface of FO membrane.**

#### **4.2 Salt accumulation in bioreactor:**

A natural phenomena associated with OMBR system is accumulation of salts within the bioreactor due to high rejection features of FO membrane and reverse transport of draw solute acting as a major source for salinity build-up. Elevated TDS concentration within the bioreactor decreases the driving force for water flux as osmotic gradient decreases between feed and DS side (Holloway et al., 2014). Trend of mix liquor conductivity within the bioreactor is shown in (Figure 4.4) for each DS. Significantly less amount of salinity build-up was observed in bioreactor with Na-Ace and Mg-Ace as expressed by the electrical conductivity (mS/cm). In the case of organic DS, conductivity approx. increases from 0.8 to 9 mS/cm and 0.7 to 6.8 mS/cm with NaOAc and MgOAc, respectively. Due to the low salt accumulation in bioreactor, less decrease in osmotic gradient was observed which resulted in prolonged filtration runs for both organic DS at similar

molar concentration as compared to  $\text{CaCl}_2$  and  $\text{NaCl}$  (Figure 4.2). Specific reverse salt diffusion (or ratio of reverse salt flux to the water flux) reported in Table also manifested that due to lower ratios of  $J_s/J_w$  for organic salts, low reverse salt flux was produced which resulted into less salinity build-up in bioreactor as compared to inorganic salts (Achilli et al., 2010; Bowden et al., 2012).

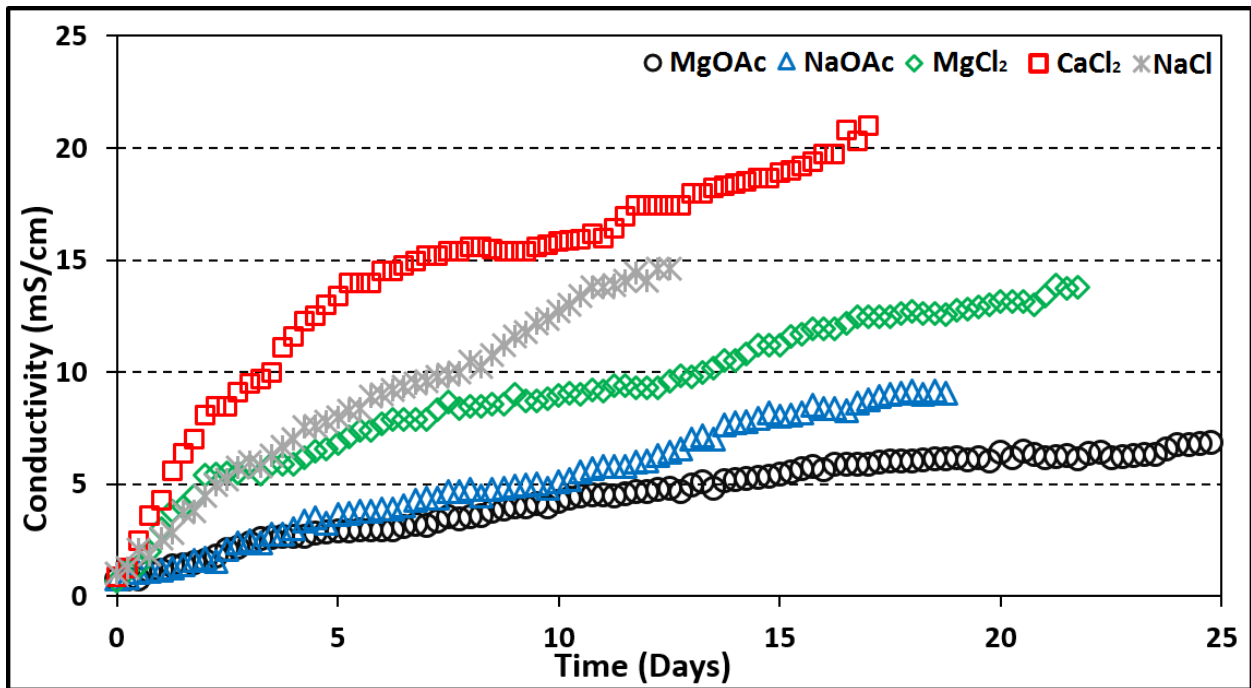


Figure 4.4. Conductivity of mix loquor in bioreactor with each draw solute.

These results were also attributed to the size of hydrated diameter (Table 4.2) of respective anions and cations of DS tested in this study. Achilli et al. (2010) found out that the draw solutions with larger hydrated size of anions produce lower reverse salt flux, irrespective of the size of their corresponding cations. Acetate ion ( $\text{CH}_3\text{COO}^-$ ) with both of its corresponding cations ( $\text{Mg}^{2+}$  and  $\text{Na}^+$ ) gives lowest specific reverse salt diffusion ( $J_s/J_w$ ) as compared to each inorganic salt having chloride ion ( $\text{Cl}^-$ ). These results were credited to the larger hydrated diameter of acetate ions (Table 4.2) in contrast with chloride ions.

On the other hand, when we consider only organic salts, NaOAc produces slightly high conductivity and rapid decline in flux as compared to MgOAc as shown in (Figure 4.4).

**Table 4.2 Hydrated diameter of ions used in this study**

<b>Ions</b>	<b>Hydrated diameter (picometer)<sup>a</sup></b>
<i>Anions</i>	
Cl <sup>-</sup>	300
CH <sub>3</sub> COO <sup>-</sup>	450
<i>Cations</i>	
Na <sup>+</sup>	450
Ca <sup>2+</sup>	600
Mg <sup>2+</sup>	800

<sup>a</sup> **Data from Achilli et al. (2010) and Kielland (1937)**

This is actually due to the smaller hydrated diameter of sodium ion (Na<sup>+</sup>) than that of magnesium ion (Mg<sup>2+</sup>) as monovalent ions (because of small hydrated radii) can be easily diffused across the FO membrane from DS side to feed side as compared to divalent ions (Nguyen et al., 2016b). Similar behaviour was observed in the case of inorganic draw solutions for NaCl and MgCl<sub>2</sub>. As the inorganic DS have same anions but different in their impact on water flux and conductivity was due to the dissimilarity in the size of their hydrated cations. Additionally, an exception was also observed that even due to divalent nature of CaCl<sub>2</sub>, its conductivity increases from 0.86mS/cm to 21.02 mS/cm as compared to MgCl<sub>2</sub> from 0.66 to 13.78 mS/cm. The reason behind this exception was high reverse solute flux of CaCl<sub>2</sub> due to smaller hydrated diameter of calcium ion

(Ca<sup>2+</sup>) in contrast with magnesium ion (Mg<sup>2+</sup>) (Achilli et al., 2010; Nguyen et al., 2016b). Effect of these salt accumulations on sludge characteristics and removal efficiencies will be discussed in the later sections.

### **4.3 Basic performance:**

#### **4.3.1 Build-up and removal of organic matter:**

Regardless of the draw solute, high retention features of FO membrane and reverse salt flux of each DS resulted in the accumulation of organic content within the bioreactor. Fig. 3.5 represents the build-up of organic content in bio-tank and removal efficiency in permeate for each DS. More than 98% removal of COD was observed in permeate with each DS as shown in Fig. 3.5, because of synergistic effect of dual barriers of high retention membranes (FO and MD) and biological treatment. Accumulation of COD within the bioreactor was observed with both organic and inorganic draw solutions, which is consistent with the previous studies (Aftab et al., 2015; Luo et al., 2016; Qiu and Ting, 2013).

For each inorganic draw solution (NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>) a much higher amount of COD (organic matter) build-up within the bioreactor (Fig. 3.5) was observed as compared to organic salts. CaCl<sub>2</sub> with highest reverse salt flux and salinity build-up, produced high amount of organic accumulation. Similar behaviour was observed with NaCl also. Increased concentration of organic content in bio-tank reflect the decrease in biodegradation of organics by microbial consortium. Majority of microbes involved in wastewater treatment process, such as activated sludge process are non-halophilic in nature. These microbial communities do not possess the ability to survive in highly saline environment. Osmotic stress on the feed side compels the intercellular water to move outside, subsequently cause cell dehydration which results into cell plasmolysis and deteriorate the cell activity for microbes (Lay et al., 2010; Yogalakshmi and Joseph, 2010). Hence, this

deteriorated condition gradually accumulates the organic matter within the bioreactor. Gradual increase of supernatant COD with inorganic DS was actually due to salinity build-up, which initiated the gathering of non-biodegradable DOM (Dissolve organic matter) in bio-tank (Qiu and Ting., 2013). Elevated salinity not only deteriorates the metabolic activity of bacterial community, it also increases the level of DOM that attribute the release of soluble microbial products (to be discussed in section 4.4.2) with in the activated sludge (Luo et al., 2016; Qiu and Ting, 2013; Yogalakshmi and Joseph, 2010).

Likewise, both organic draw solutions also show the accumulation of COD in bio-tank (Fig. 3). As already discussed (section 4.1), that lower reverse salt diffusion of organic DS not only mitigate the problem of high salt accumulation, it also provide a carbon source for bacterial growth. These results were attributed to the organic nature of acetate ion as reported elsewhere (Ansari et al., 2015; Luo et al., 2016). Resulting in accumulation of organic content in bioreactor. Readily degradable nature of organic draw solutions credited to their osmoprotectant features, reduces the osmotic stress on microbial flora (Oh et al., 2008).

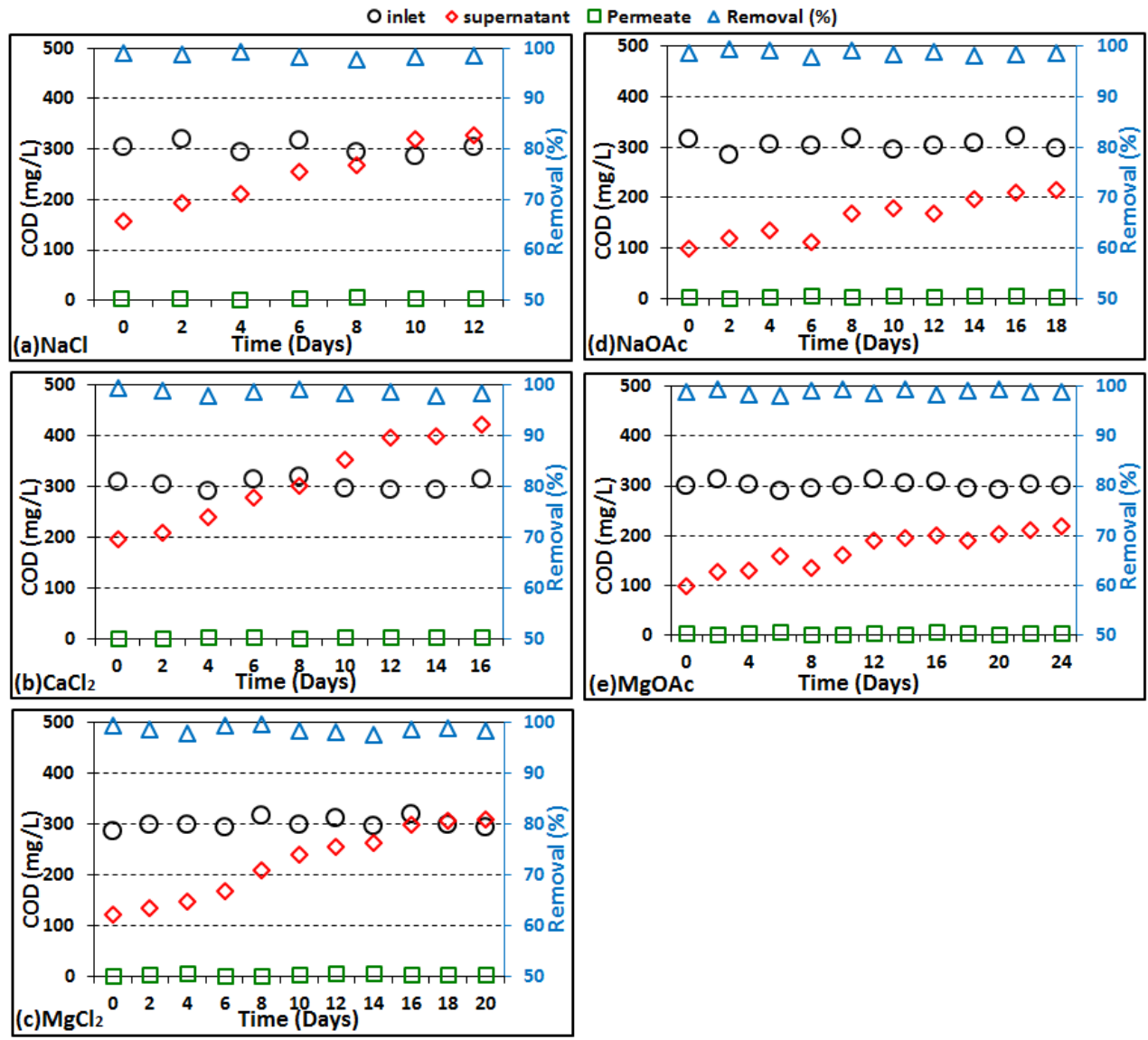


Fig. 3.5 Concentration of COD in bio tank and permeate with each draw solution.

However, the reduced osmotic stress on the feed side enhance the methane production by providing them additional carbon source for the better growth of microorganisms (Ansari et al., 2015). It was also observed that inorganic DS adversely affects the production of gas due to cell dehydration of bacterial community.



#### **4.3.2. Nutrient removal in high saline environment:**

Removal of phosphorus and nitrogen using microbes are generally termed as biological nutrient removal. For nitrogen removal there are two process, firstly in nitrification conversion of nitrogen compounds into its oxidized forms of nitrates ( $\text{NO}_3^-$ ) and nitrites ( $\text{NO}_2^-$ ). Secondly, denitrification convert these nitrates and nitrites into the form of final nitrogen ( $\text{N}_2$ ) gas. Nitrifiers and denitrifiers are the groups of microorganisms widely involved in these two processes (Lay et al., 2010; Qiu and Ting, 2013). On the other hand, phosphorus was biologically removed by utilizing the specific heterotrophic microbes known as PAOs (Phosphorus accumulating organisms) (Zuthi et al., 2013).

##### **4.3.2.1. Phosphate enrichment and removal:**

OMBR performance in terms of phosphate ( $\text{PO}_4^{3-}\text{P}$ ) removal was evaluated with the five different draw solutions and their results are presented in Figure 4.6. Due to high retention properties of FO membrane, substantial enrichment of phosphate was observed within the bioreactor for each DS. Much lower amount of accumulated phosphate in bio tank was detected during filtration run with organic as compared to inorganic draw solutes. As shown in (Figure 4.6 (d)-(e)) with the average influent phosphate of 10 mg/L (approx.), phosphate concentration in mixed liquor raised up to 20mg/L with organic DS. This accumulation was credited to effective FO rejection due to negatively charged and larger hydrated diameter of ortho-phosphate ion (Luo et al., 2016, 2015). Addition to this, less buildup of phosphate with organic DS was because of higher biomass activity. Aftab et al., (2015) also reported that less accumulation of phosphate was observed due to increased microbial activity necessitating high phosphate to fulfill the nutrient demand of phosphorus accumulating organisms (PAOs). Increased bacterial growth was observed due to less salinity buildup (section 4.2) and lower osmotic stress on feed side with readily degradable acetate

ion as reverse solute. Hence, high bacterial activity lowers the phosphate accumulation in the bioreactor using organic salts.

However, the salinity buildup in case of inorganic draw solutions generate a detrimental condition for PAOs. It is generally hypothesized that salt accumulation within the cells not only adversely affect the sensitivity of PAOs but also reduces the phosphate accumulating ability of microbes by increasing the osmotic stress within the cells (Lay et al., 2010; Luo et al., 2016). In this contest, as high phosphate enrichment was observed for inorganic DS (Figure 4.6) when compared to organic salts. Using  $\text{CaCl}_2$  (Figure 4.6 (b)) up to 37 mg/L phosphate accumulation was observed at the end of filtration run, similar trend was also witnessed with  $\text{NaCl}$  and  $\text{MgCl}_2$ . Higher concentration of chloride ions ( $\text{Cl}^-$ ) also inhibit the performance of PAOs, which reduces the phosphate removal, as reported elsewhere (Bassin et al., 2011). Therefore, this increased amount of phosphate accumulation was actually due to high retention features of FO membrane and salinity buildup (Aftab et al., 2015; Lay et al., 2010; Qiu and Ting, 2014). Despite of accumulated phosphate within the bioreactor, more than 99% removal of phosphate was achieved in permeate water for each salt because of dual membrane barriers FO and MD.

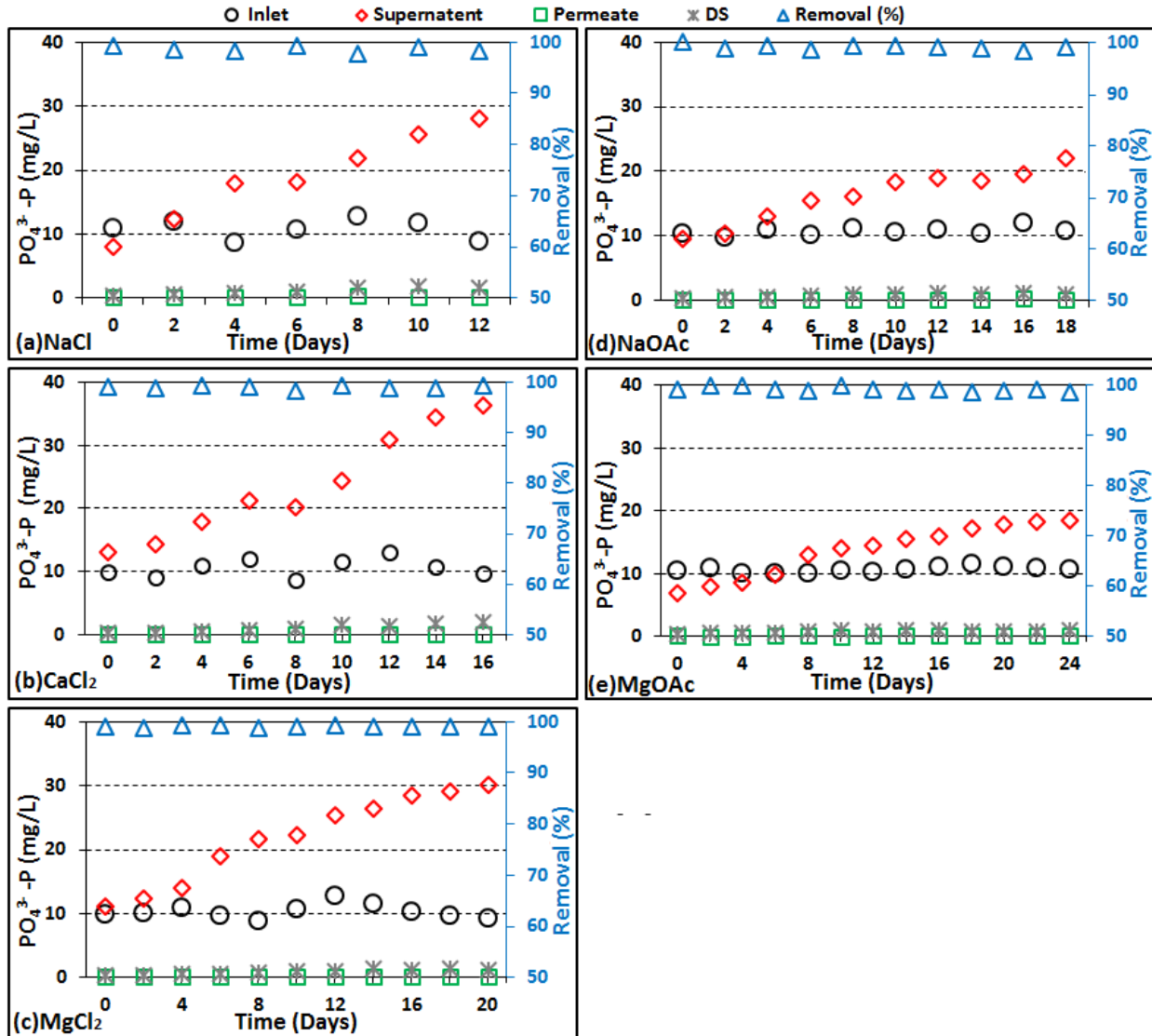


Figure 4.6 Concentration of  $\text{PO}_4^{3-}\text{-P}$  in bio tank and permeate with each draw solution.

#### 4.3.2.2. Nitrogen removal:

Nitrification is a very sensitive process as microbes (Nitrifiers) involved in this process are slow growing and highly susceptible to environmental circumstances like DO concentration, pH, temperature and salinity (Lay et al., 2010). It was reported that, less removal of biological nitrogen is generally due to deprived nitrification. Figure 4.7 demonstrate the removal and buildup of Ammonium-N for each salt used as a DS at same molar concentration. With high saline stress due

salt accumulation in bio tank, buildup of  $\text{NH}_4^+\text{-N}$  was also observed for each inorganic draw solute. These trends of  $\text{NH}_4^+\text{-N}$  are also in consistent with the previous studies (Aftab et al., 2015; Luo et al., 2015; Qiu and Ting, 2013). This increased concentration of  $\text{NH}_4^+\text{-N}$  within the bio tank was escorted by its transfer into draw tank as shown in (Fig (a)-(b)-(c)). Removal % of  $\text{NH}_4^+\text{-N}$  in draw tank continuously decreased noticeably from 98 to 72% with  $\text{CaCl}_2$  and from 98 to 79% for  $\text{NaCl}$ .  $\text{MgCl}_2$  when used as DS also shows the similar behaviour. These results were ascribed to the inhabitation of bacterial activity of AOBs (ammonia oxidizing bacteria), by high saline stress (Qiu and Ting, 2013). Hence, troubled the biological transformation of  $\text{NH}_4^+\text{-N}$  which further results into poor biological removal. In permeate, more than 98% of  $\text{NH}_4^+\text{-N}$  removal was achieved for each draw salt through the study. Since small amount of  $\text{NH}_4^+\text{-N}$  was transferred to draw tank across FO membrane, may be rejected by high retention MD membrane.

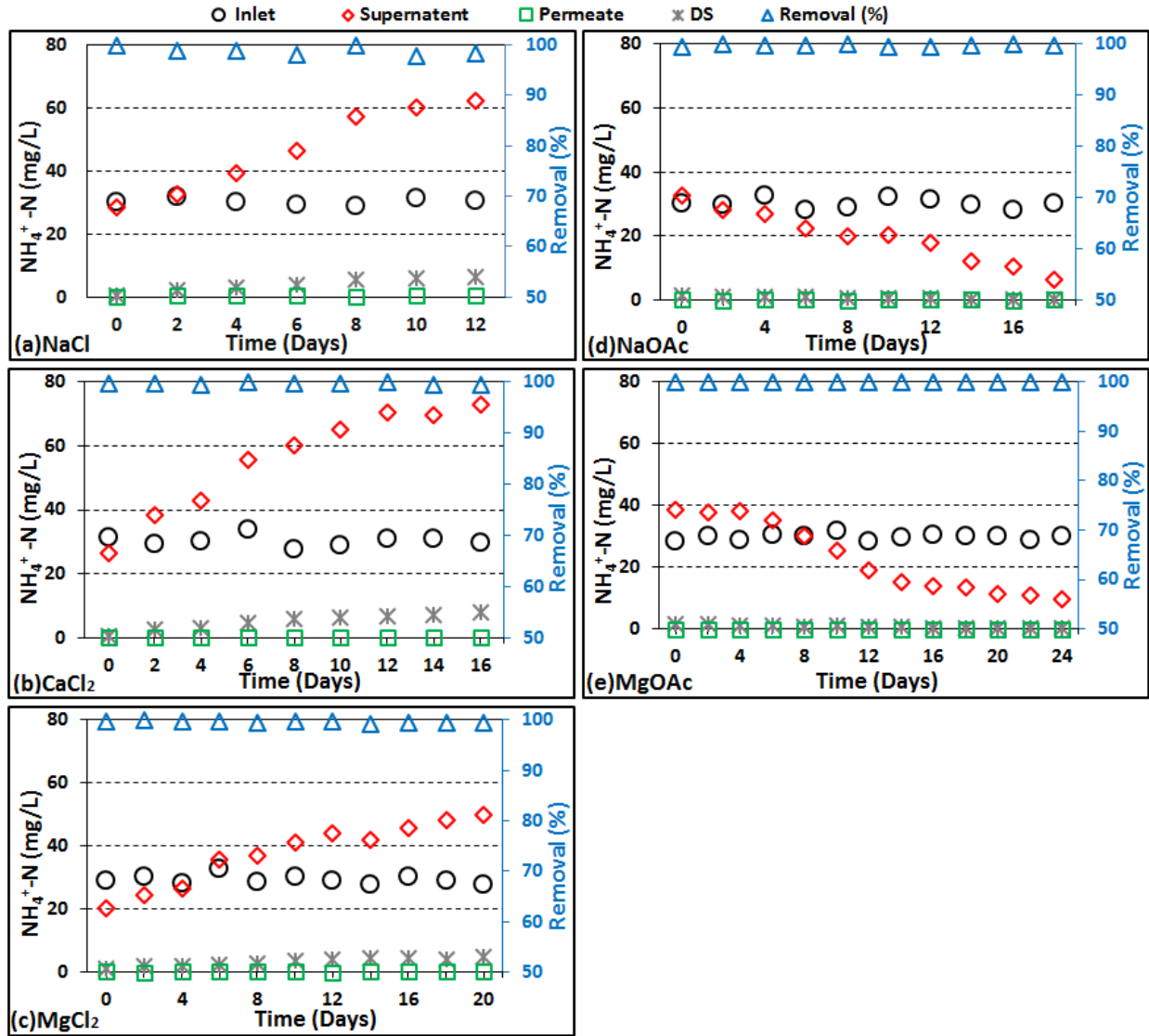


Figure 4.7 Concentration of  $\text{NH}_4^+\text{-N}$  in bio tank and permeate with each draw solution.

Contrary to all this, continuous decline in the concentration of  $\text{NH}_4^+\text{-N}$  within the bioreactor was observed (Figure 4.7 (d)-(e)) throughout the filtration run for both organic DS. Negligible amount of  $\text{NH}_4^+\text{-N}$  was observed in draw tank at the start of filtration run with both organic DS, which was further reduced to negligible value. Luo et al., (2016) also reported that degradation of  $\text{NH}_4^+\text{-N}$  increased in mix liquor with increased biomass activity in OMBR. Acetate ion as a reverse transported solute provide a source of carbon for bacterial growth due to its readily degradable

nature. This provides a suitable environment to microorganism for their growth and microbial activity that increase the rate of  $\text{NH}_4^+\text{-N}$  removal.

#### **4.4 Biomass Characteristics:**

In MBR operations, characteristics of biomass plays an important role in biological treatment. It not only governs the productivity of biological treatment, but also effect the membrane filtration processes (Holloway et al., 2014; Lay et al., 2010).

##### **4.4.1. Behaviour of suspended and volatile solids:**

Concentration of MLSS and MLVSS was plotted as a function of time as shown in Figure 4.8. Highly saline environment adversely affect the MLSS and MLVSS by decreasing their concentration continuously throughout the filtration run for each inorganic DS. Increased osmotic stress due to salinity build-up, inhibit the growth of microorganisms as biomass start decaying within the salty environment (Luo et al., 2016; Tadkaew et al., 2013). Figure 4.8 (a-b) clearly shows decline in the concentration of MLSS and MLVSS by using inorganic DS in OMBR-MD setup. MLVSS/MLSS ratio decreased from 0.69 to 0.62, 0.64 to 0.61 and 0.66 to 0.59 for  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{NaCl}$ , respectively throughout the filtration run. These results point out the decrease or death of biomass due to increased level of salinity in bio tank for each inorganic draw solute. Luo et al., (2015) also reported that due to increased osmotic stress on feed side, reduction in MLVSS/MLSS ratio was observed which decreased the concentration of active biomass in sludge. Active biomass decline in mix liquor not only reduce the biological treatment process, it also effect the characteristics of sludge. At same molar concentration, when we are talking about the use of organic draw solution in OMBR-MD, totally altered trends were observed as compare to inorganic

DS.

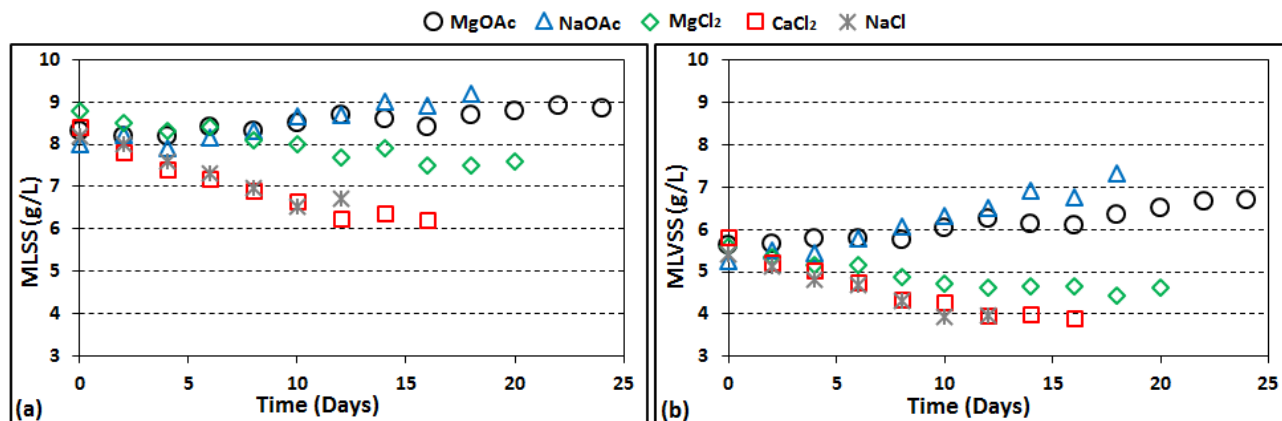


Figure 4.8 Temporal variation of MLSS and MLVSS in bioreactor.

In Figure 4.8, rise in the concentration of MLSS and MLVSS was observed with respect to time. Increase in MLVSS/MLSS ratio from 0.66 to 0.80 and 0.68 to 0.76 was observed with the employment of NaOAc and MgOAc as a DS respectively, indicating the increase in biomass growth within the bio tank. This increase in the concentration of active biomass was accredited to the reverse transport of acetate ion ( $\text{CH}_3\text{COO}^-$ ) as a reverse salt flux (Ansari et al., 2015; Luo et al., 2016). Readily degradable nature of acetate ion not only provides the additional organic substrate but also lowers the osmotic stress for the growth of microbes, resulting in the increase of active biomass.

#### 4.4.2. SMP and EPS in supernatant:

While talking about the organic foulants, soluble microbial products (SMP) and extracellular polymeric substances (EPS) noticeably act as the most substantial aspects liable for the fouling of membrane (Luo et al., 2015; Xie et al., 2014). SMP and EPS both are heterogeneous and generally comprises of proteins, humic acid, lipids, carbohydrates and nucleic acid. Proteins and carbohydrates are dominantly existing components naturally found in extracted SMP and EPS, so

the sum of proteins and carbohydrates were used to represent the SMP and EPS. Figure 4.9 (a-b) compare the temporal concentrations of SMP and EPS for each organic and inorganic salts employed as DS in OMBR-MD setup.

Salt accumulation within the bioreactor (section 4.2) increase osmotic stress on microbial activity, due to which a conspicuous increase in the concentration of SMP was observed (Figure 4.9 (a)) with chlorides of Na, Ca and Mg. These observations are in consistent with previously reported literature that salinity build-up in bio tank resulted in increased concentration of SMP in the supernatant of OMBR (Luo et al., 2015; Reid et al., 2006). This increase was ascribed to the accelerated endogenous respiration, which is escorted by the release of organic cellular components from cell lysis and by cell secretions (Reid et al., 2006). They also reported that this rapid increase in SMP fraction was due to chloride addition. Luo et al., (2015) also reported that accumulation of intermediate and unmetabolised constituents due to partial degradation of organic material in high saline environment led to an increase in the amount of SMP in mix liquor. Moreover, increased salinity within the bio tank could also accelerate the solubility of carbohydrate and protein contents of SMP, which might be an additional cause for the increased SMP contents in supernatant (Zhang et al., 2014).

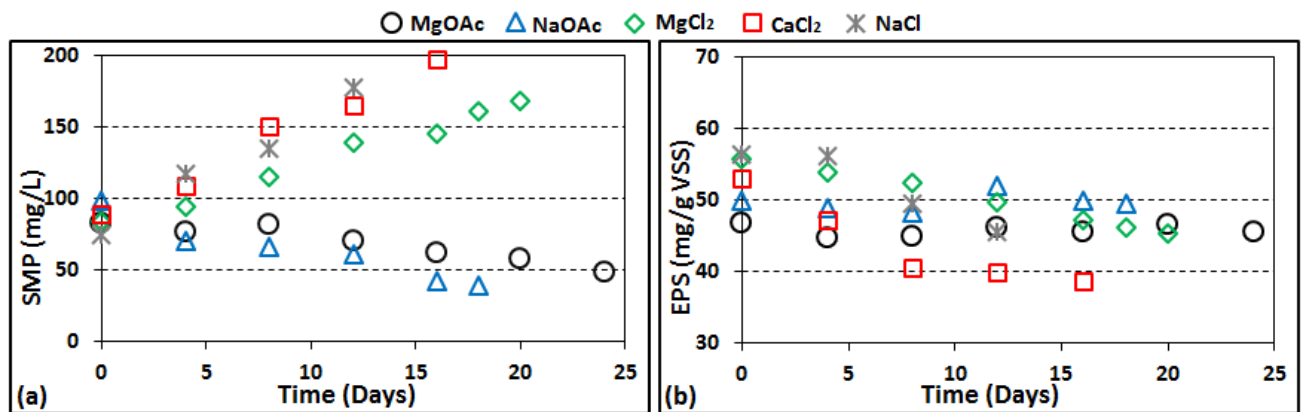


Figure 4.9 Variation in SMP and EPS production with organic and inorganic salts.



With increasing SMP concentration in supernatant with the use of inorganic salts, decrease in the concentration of EPS was observed as shown in Figure 4.9 (b) due to salinity buildup within the bioreactor. Lin et al., (2014) reported that environmental stresses and unfavorable conditions in bioreactor can disturb the contents of EPS and under such conditions, cell lysis and death of biomass is expected causing the release of carbohydrates and proteins contents in supernatant. Increased saline stress within the bioreactor due to high salt concentration can also elevate the risk of EPS extraction from sludge flocs (Zhang et al., 2014), as a result of which increase in the concentration of SMP was observed (Figure 4.9 (a)). Observed decrease in EPS concentration was also credited to the high solubility of EPS fragments (carbohydrates and proteins) with the increase in the salinity of mix liquor as reported elsewhere (Luo et al., 2015). Both released and extracted fractions of EPS were highly soluble because of salt accumulation, which further resulted in to decrease in EPS and increase in SMP production.

On the other hand, no significant change in the concentration of EPS was found (Figure 4.9 (b)) with the use of organic salts as draw solution. This is because of stabilized microbial growth due to the reverse transport of acetate ions providing a source of organic content within the bioreactor. Increased microbial growth balanced the hydrolysis and release of EPS concentration as reported elsewhere (Luo et al., 2016). Additionally, degradation of SMP content in supernatant with the use of organic DS was also observed as shown in Figure 4.9 (a). SMP degradation is probably due to the enhanced microbial activity in bio tank as a result of which decrease in the concentration of SMP in mix liquor was found. Menniti and Morgenroth, (2010) observed that SMP produced by the retained compounds in reactor operation is readily degradable. Methane producing properties of acetate also reduce the production of SMP (Barker and Stuckey, 1999). So increased biomass activity due to reverse acetate flux, degrade the SMP contents of mix liquor within the bioreactor.

#### **4.4.3. Sludge filterability and floc size:**

Sludge filterability in terms of capillary suction time (CST) was observed for each organic and inorganic salt as shown in Figure 4.10 (a). Increase in capillary suction time reduce the filterability of sludge, when inorganic salts were employed as draw solution in OMBR system. Deteriorated sludge filterability may be credited to the accumulation of SMP contents with the buildup of salinity level in bio tank (Reid et al., 2006). In case of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , CST increased from 22s to 45s and 25s to 37s, respectively. Whereas, while talking about the floc size of suspended sludge, it decreased with the increase of salt accumulation by using salts of chloride as DS. Figure 4.10 (b) shows the decrease in mean particle size that was evaluated on the basis of number of particles. The drop in particle size with salts of chloride ( $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) was attributed to the decrease in the amount of filamentous bacteria in activated sludge flocs with increased salinity (Jang et al., 2013). As these filamentous organisms are the backbone of sludge floc contributing in the development of larger flocs. Zhang et al., (2014) also reported that increased saline stress has detrimental effect on floc strength and flocculation of activated sludge. Extraction of EPS from flocs (section 4.4.2.) because of cell lysis and production of more SMP content in supernatant with the increased salinity may also deteriorate the settling and flocculating properties of mix liquor (Barker and Stuckey, 1999; Lin et al., 2014; Zhang et al., 2014). So, in case of inorganic salts smaller particle size might be a reason for increased CST reducing the sludge filterability.

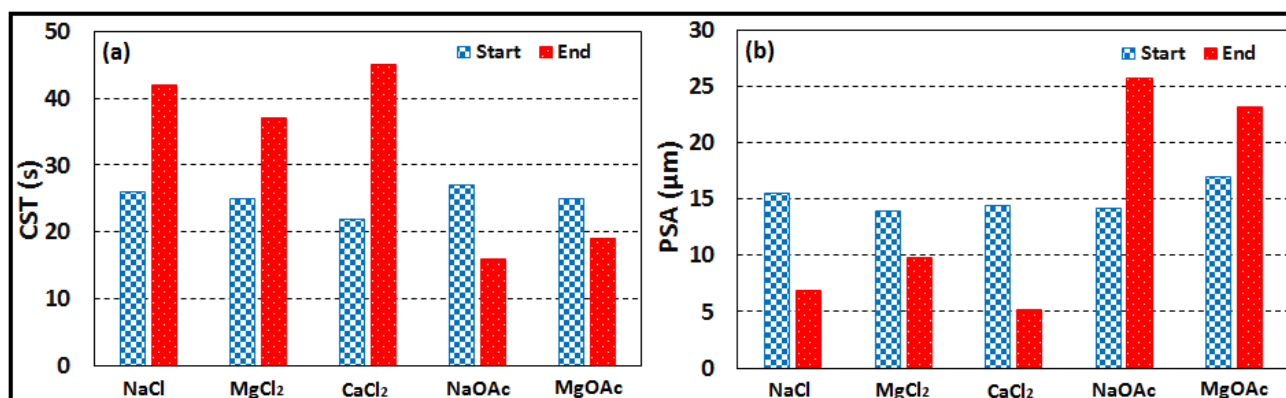


Figure 4.10 Sludge filterability and floc size distribution with each DS.

On the contrary, increase in particle size was observed (Figure 4.10 (b)) in case of organic draw solutes. Salts of acetate (NaOAc and MgOAc) are actually the source of carbon provider that increased the microbial growth in sludge. As already discussed that with increased biomass activity, degradation of SMP also increased and stabilized EPS production was observed. No change in EPS confirms the increase in mean particle size because stabilized EPS content increase the stability of floc size as reported elsewhere (Lin et al., 2014; H. Zhang et al., 2014). Particle size increased from 14.18 to 25.64  $\mu\text{m}$  with NaOAc and 16.91 to 23.20  $\mu\text{m}$  with MgOAc accompanied by decrease in CST (Figure 4.10 (a)) with organic draw solutes exhibiting microbial strength and improved filterability. By concluding this all, we came to the fact that increased saline stress within the bio tank not only deteriorated the floc size, it also increased the CST due to cell autolysis and dehydration. Whereas increase in particle size and reduction in CST was observed with the employment of organic salts as DS in OMBR system.

**Conclusions:**

This study appraised the organic and inorganic draw solutes flux performance and effect of reverse salt diffusion on mix liquor characteristics in OMBR system. Results showed that both organic salts (NaOAc and MgOAc) not only mitigate the bottleneck of salinity buildup in bioreactor, they also increase the microbial activity. Improved sludge characteristics with increase in sludge filterability and enhanced flocculation was achieved with the salts of acetate. Stabilized and prolonged filtration runs were witnessed with MgCl<sub>2</sub> (inorganic) and MgOAc (organic) at same molar concentration. Significant fouling with NaOAc was observed due to dense biomass attached on membrane surface. Short filtration runs but high initial water flux at same molar concentration was obtained with inorganic salts (NaCl and CaCl<sub>2</sub>). Moreover, salt accumulation with inorganic draw solutes decreased the removal efficiency of pollutants through biological processes. This accumulation with the salts of chloride significantly altered the characteristics of biomass, resulting in a decline of water flux and sludge production. Particularly, increased SMP production was observed with inorganic salts. In addition to this, chloride based salts also led to the stockpiling of numerous foulants like phosphate and ammonia within the bioreactor.

**Recommendations:**

- Different mixtures/combinations of acetate and chloride based draw solutions may be used in OMBR system and then compare the salinity buildup in bio tank with pure draw solutes.
- Real wastewater instead of synthetic composition may also be tested in OMBR system and its sludge characteristics should be compared with sludge of synthetic feed.
- Effect of salt accumulation on microbial community in bioreactor may be characterized biologically
- Energy consumption of OMBR-MD system may be compared with conventional MBR and hybrid OMBR-RO systems.

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## Protocols

### Extra polymeric substances (EPS) extraction and analyses

#### Cation exchange resin (CER)

The CER was required to be soaked for 1 h in the extraction buffer solution and dried in room temperature for 1 h before usage.

#### Buffer solution

Chemical name	Concentration	Amount in 1 L DI water
Na <sub>3</sub> PO <sub>4</sub> .12H <sub>2</sub> O	2 mM	$380 \times 2 / 1000 = 0.76$ g
NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O	4 mM	$156 \times 4 / 1000 = 0.624$ g
NaCl	9 mM	$58.5 \times 9 / 1000 = 0.5265$ g
KCl	1 mM	$74.6 \times 1 / 1000 = 0.0746$ g

#### EPS extraction

The EPS was measured in the form of soluble EPS and bound EPS. The two forms of EPS were extracted by the procedure outlined as follows:



- 1.** Take 50 mL sludge sample
- 2.** Centrifuge sample at 5,000 rpm for 15 min, 4°C
- 3.** Centrifuge sample at 5,000 rpm for 15 min, 4°C
- 4.** Supernatant stored at 4°C for Soluble EPS analysis
- 5.** Re-suspend settled sludge flocs in buffer solution to previous volume
- 6.** Stir sample at 300 rpm for 1hr
- 7.** Centrifuge sample at 5,000 for 15min
- 8.** Remove supernatant for LB-EPS
- 9.** Add resin 70 g/g VSS       $70\text{g} \times \text{MLVSS g/L} \times 0.05 \text{ L} = \text{g}$
- 10.** Stir sample at 300 rpm for 2h, room temperature
- 11.** Centrifuge sample at 5,000 rpm for 10min, 4°C
- 12.** Remove CER and floc components
- 13.** Centrifuge sample at 5,000 rpm for 20min, 4°C
- 14.** Remove remaining floc components
- 15.** Supernatant stored at 4°C for TB-EPS analysis

Carbohydrate and protein fractions of the soluble and bound EPS were measured by the colorimetric methods of Dubois et al. (1956) and Lowry et al. (1951), respectively using spectrophotometer.

### **Measurement of carbohydrate: Phenol-sulfuric acid method (Dubois method)**

#### **Principle**

Simple sugars, oligosaccharides. Polysaccharides and their derivatives give a stable orange yellow color when treated with phenol and concentrated sulfuric acid. Under proper conditions, the accuracy of the method is within 2%.

#### **Chemical reagents**

- 5 w% Phenol solution
- Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)
- D-Glucose for standard solution

#### **Procedure**

##### **Standardization:**

1. Make all measurements in duplicate
2. Pipette 2 mL of sugar solution (D-Glucose) containing 0, 5, 10, 15, 20, 25, 30, 35, 40 and 50 mg/L of glucose into test tubes

3. Add 1 ml of the 5% phenol solution and 5 ml of the concentrated sulfuric acid to the test tubes. The addition should be rapid. In addition, direct the stream of acid against the liquid surface, rather than against the side of the test tube for good mixing
4. Allow the tubes to stand 5 min.
5. Thoroughly mix the solutions using vortex machine.
6. Cool again by standing for 5 minutes.
7. Measure absorbance at 490 nm in HACH spectrophotometer.
8. Prepare a calibration curve of concentration of sugar (Glucose-D) versus absorbance.

**Analysis: (Sample for soluble and bound EPS)**

1. Soluble and bound EPS were determined with dilution factor 2 i.e. 1 ml sample and 1 mL deionized (DI) water were pipetted into the test tubes.
2. Remaining procedure was identical to the one followed for carbohydrate standardization mentioned above.
3. Measured absorbance of sample solution at 490 nm was correlated to the carbohydrate concentration in the sample using the carbohydrate standard curve and straight line equation.
4. Carbohydrate concentration was reported in mg/L for soluble EPS and mg/gVSS for bound EPS.

## Measurement of Protein: Lowry method

### Principle

This is a standard and quantitative method for determining protein content in a solution.

Lowry method is a reliable method for protein quantification and little variation among different proteins has been observed.

### Chemical reagents

- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- Sodium Citrate
- $\text{Na}_2\text{CO}_3$
- $\text{NaOH}$
- Folin-Ciocalteu phenol reagent
- Bovine Serum Albumin (BSA) for standard solution

### Solution A, 100 mL;

- 0.5 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- 1 g  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  (Sodium citrate)

### Solution B, 1L;

- 20g  $\text{Na}_2\text{CO}_3$
- 4 g  $\text{NaOH}$

**Solution C, 51 mL;**

- 1 mL solution A
- 50 mL solution B

**Solution D, 20mL;**

- 10 mL Folin-Ciocalteu phenol reagent + 10 mL DI water

**Procedure****Standardization:**

1. Make all measurements in duplicate
2. Pipette 0.5 mL of BSA solution containing 0, 20, 30, 40, 50, 60, 80 and 100 mg/L of BSA into test tubes
3. Add 2.5 mL solution C
4. Thoroughly mix the solutions using vortex machine and let them stand at room temperature for 5 min
5. Add 0.25 mL Solution D and thoroughly mix again.
6. After 20 min, measure absorbance at 750 nm in dark condition.
7. Prepare a calibration curve of protein (BSA) concentration (mg/L) versus absorbance.

### **Analysis: (Sample for soluble and bound EPS)**

1. Soluble EPS was determined with no dilution while bound EPS was determined with dilution factor 2 i.e. 1 mL sample and 1 mL deionized (DI) water were pipetted into the test tubes.
2. Remaining procedure was identical to the one followed for protein standardization mentioned above.
3. Measured absorbance of sample solution at 750 nm was correlated to the protein concentration in the sample using the protein standard curve and equation of straight line.
4. Protein concentration was reported in mg/L for soluble EPS and mg/gVSS for bound EPS.

### **Capillary Suction Time (APHA, 2012)**

#### **General discussion**

The capillary suction time (CST) test determines rate of water release from sludge. It provides a quantitative measure, reported in seconds, of how readily a sludge release water. The results may be used to assist in sludge dewaterability processes; to evaluate sludge conditioning aids and dosages.

## **Apparatus**

1. CST apparatus including reservoir 18 mm ID and 25 mm height.
2. CST paper
3. Thermometer
4. Pipet, 10 ml

## **Procedure**

1. Turn on and reset CST meter. Dry CST test block and reservoir.
2. Place a new CST paper on lower test block with rough side up and grain parallel to the 9 cm side.
3. Add upper test block, insert sludge reservoir into test block and seat it using light pressure and quarter turn to prevent surface leaks.
4. Measure and record temperature of sludge. Pipet 6.4 mL sludge into test cell reservoir; if pipetting is difficult because of sludge consistency, pour a representative sludge sample into cell until it is full.
5. The CST device will begin time measurement as liquid being drawn into paper reaches the inner pair of electrical contacts.
6. Timing ends when the outer contacts is reached.
7. Record CST on digital display.
8. Empty remaining sludge from reservoir and remove and discard used CST paper.

Rinse and dry test block and reservoir.

9. Temperature and sample volume may affect CST results. Ensure that all analyses are run under same conditions.

