

**INFLUENCE OF BIOFILM CARRIERS ON MEMBRANE
FOULING TENDENCY AND TREATMENT PERFORMANCE
IN HYBRID MEMBRANE BIOREACTOR**



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2009-NUST-MSPHD-Env E-05

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Islamabad, Pakistan
(2011)**

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HYBRID MEMBRANE BIOREACTOR**

By

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Islamabad, Pakistan

(2011)

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*This thesis is dedicated to my ever-loving mother
and the living memories of my father*

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TABLE OF CONTENTS

Acknowledgements.....	iv
Table of Contents.....	v
List of Abbreviations	vii
List of Tables	ix
List of Figures	x
Abstract	xi
Introduction.....	1
1.1 Background.....	1
1.2 Objectives of Study.....	4
Literature Review.....	5
2.1 Membrane	5
2.1.1 Membrane Operational Modes	6
2.2 Membrane Bioreactor (MBR).....	7
2.2.1 Advantages and Disadvantages of Membrane Bioreactor.....	8
2.3 Membrane Fouling.....	9
2.3.1 Classification of Fouling	10
2.3.2 Stages in Membrane Fouling.....	10
2.4 Classification of Membrane Fouling	13
2.4.2 Irremovable Fouling	15
2.4.3 Irreversible Fouling	15
2.4.3 Factors Affecting Fouling.....	15
2.4.3.1 Extra Polymeric Substances (EPS)	16
2.4.3.2 Pore Size Distribution and pH.....	16
2.4.3.3 Role of Floc Size and Air Flow Rate	16
2.4.3.4 Microbial Consortium	17
2.4.3.5 Effect of Retention Time.....	17
2.5 Attached Growth Membrane Bioreactor (AG-MBR).....	18
Methodology.....	22
3.1 Experimental Set-up.....	22

3.2	Acclimatization of Sludge and Media with Synthetic Wastewater	25
3.3	Experimental Conditions	26
3.4	Analytical Methods	29
3.4.1	Specific Oxygen Uptake Rate (SOUR)	29
3.4.2	Extra Polymeric Substances (EPS).....	31
3.4.3	Soluble COD (sCOD).....	32
3.4.4	Specific Cake Resistance (SCR).....	32
3.4.5	Membrane Cleaning	34
3.4.6	Membrane Resistance Analysis.....	35
	Results and Discussions.....	37
4.1	Analysis of Membrane Fouling	37
4.2	Resistance Analysis	39
4.3	Sludge Filterability Characteristic (SCR)	41
4.4	Influence of Floc Morphology on Membrane Fouling	42
4.5	Influence of Particle Size Distribution on Membrane Fouling.....	44
4.6	Influence of Extracellular Polymeric Substance on Membrane Fouling	47
4.7	Biological Environment	51
4.7.1	General Appearance and MLSS/MLVSS.....	51
4.7.2	Performance Evaluation	52
	Conclusions and Recommendations	54
5.1	Conclusions.....	54
5.2	Recommendations.....	55
	References.....	56
	Appendix - A.....	64
	Appendix B	71
	Appendix C.....	75
	Appendix D.....	79

LIST OF ABBREVIATIONS

Abbreviation	Description
R_t	Total resistance
R_c	Cake resistance
R_m	Intrinsic membrane resistance
R_f	Resistance due to pore blocking
COD	Chemical oxygen demand
sCOD	Soluble COD
TN	Total nitrogen
PAOs	Phosphorus accumulating organisms
SND	Simultaneous nitrification and denitrification
sEPS	Soluble EPS
bEPS	Bound EPS
EPS	Extra polymeric substance
SOUR	Specific oxygen uptake rate
PSD	Particle size distribution
SEM	Scanning electron microscopy
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
DI	De-ionized water
f_t	Temperature correction
J	Operational flux
μ	Viscosity of permeate
CER	Cation exchange resin

AG-MBR	Attached growth membrane bioreactor
SBR	Sequencing batch reactor
HF	Hollow-fiber
CMBR	Conventional suspended growth MBR
SND	Simultaneous nitrification and denitrification
SMBR	Submerged membrane bioreactor
NTU	Naphthalometric turbidity unit
RBC	Rotating biological contactor
SMP	Soluble microbial product
F/M	Food to microorganism ratio
TMP.	Trans-membrane pressure
NLR	Nitrogen loading rates
DO	Dissolved oxygen
HRT	Hydraulic retention time
SRT	Sludge retention time
OLR	Organic loading rate
MBBR	Moving bed biofilm reactor
CASP	Conventional activated sludge process
MBRs	Membrane bioreactors
C-MBR	Conventional Membrane bioreactor
MB-MBR	Moving biofilm Membrane bioreactor

LIST OF TABLES

Chapter 2

Table 2. 1: Comparison of Attached growth systems with other systems 18

Table 2. 2: Comparison of different media used in MBR studies 20

Chapter 3

Table 3. 1: Hollow-fiber (HF) membrane characteristics 23

Table 3. 2: Specific properties of sponge media 24

Table 3. 3: Chemical Composition of Synthetic Wastewater..... 26

Table 3. 4: Analytical parameters, methods and equipment 30

Chapter 4

Table 4. 1: Resistance Analysis of both MBR 40

Table 4. 2: Treatment Performance of both MBRs 53

Appendices

Table A- 1: CER buffer solution constituents..... 65

Table B- 1: MLSS and MLVSS concentrations in C-MBR and MB-MBR. 72

Table B- 2: sEPS and bEPS concentrations in the MB-MBR. 73

Table B- 3: bEPS concentrations in the C-MBR. 73

Table B- 4: Particle size distribution of MBR systems 78

Table C- 1: COD concentrations and removal efficiencies in MBR 76

Table C- 2: Nitrogen balance in MBR's. 77

Table C- 3: Phosphorous balance in MBR's..... 78

Table D- 1: Specific Cake resistances of MBR systems..... 81

LIST OF FIGURES

Chapter 2

Figure 2. 1: Perm- Selective Membrane	5
Figure 2. 2: Schematic of Membrane.....	6
Figure 2. 3: Dead-end filtration mode.....	6
Figure 2. 4: Cross flow filtration.....	7
Figure 2. 5: Membrane Bioreactor.....	8
Figure 2. 6: Diagram showing a fouled membrane.....	10
Figure 2. 7: Stages of fouling at constant flux operation.....	11
Figure 2. 8: Fouling stages for MBR operated at constant flux.....	12
Figure 2. 9: Fouling Mechanism in MBR.....	14

Chapter 3

Figure 3. 1: Schematic diagram of AG- MBR.....	25
Figure 3. 2: Schematic diagram of the experimental study	27
Figure 3. 3: Detailed plot of study	28
Figure 3. 4: Specific Cake Resistance apparatus set up.....	33

Chapter 4

Figure 4. 1: Four successive TMP profiles of C-MBR and MB-MBR.....	37
Figure 4. 2: Two-hour comparison of TMP rise after 24 hours of filtration	39
Figure 4. 3: Co-Relation of SCR with R_c in MBR.....	42
Figure 4. 4: Mean Particle size in MBR	45
Figure 4. 5: Particle sizes in the MBRs sludge distributed into four ranges.....	46
Figure 4. 6: Averaged EPS concentration in both MBR.....	48
Figure 4. 7: Protein and carbohydrate fractions of soluble EPS in MBR systems	49
Figure 4. 8: Carbohydrate and protein fractions of bound EPS in MBR systems	50
Figure 4. 9: MLSS & MLVSS concentration in both MBR systems	52

Appendices

Figure A- 1: Standard curve of carbohydrate	66
Figure A- 2: Standard curve of protein (BSA).....	69

ABSTRACT

In moving biofilm membrane bioreactor (MB-MBR) sponge carriers for biofilm growth were coupled with conventional submerged membrane bioreactor (C-MBR). This study compared the fouling propensity of C-MBR with MB-MBR and investigated the factors affecting fouling variation in both the systems. Membrane fouling tendencies were monitored in terms of transmembrane pressure (TMP) and the fouling characterization included membrane fouling resistances in situ and specific cake resistance (SCR) in batch filtration cell. Comparison of TMP profiles depicted prolong filtration periods in MB-MBR. The cake layer resistance (R_c), pore blocking resistance (R_p) as well as SCR were higher in C-MBR. The study reveals that hybrid biomass in MB-MBR creates a relatively more porous cake structure in the absence of filamentous bacteria which were found in abundance in C-MBR. The filamentous bacteria were also responsible for the release of high concentration of carbohydrates in the form of soluble extra polymeric substance (EPS) contributing to higher R_p in C-MBR.

INTRODUCTION

1.1 BACKGROUND

Water will remain a critical and limiting resource for sustained economic development of the country (Ahmad, 2004). Pakistan is already one of the most water-stressed countries in the world; a situation which is going to degrade into outright water scarcity (World Bank, 2005). The need of the day is to reduce the constantly growing stress on existing water resources for sustainable development. One possible solution to the problem is wastewater reclamation and reuse through treatment. Processes used to make water more acceptable for a desired end-use is termed as wastewater treatment. Groundwater recharging is one of the major benefits of waste water reclamation. The end product can be used for irrigation, industrial processes, and non potable purposes.

Activated sludge process is a conventional process that is successful in reducing the content of organic carbon up to 95–98%. The conventional activated sludge (CAS) process uses suspended growth biomass for removal of organic pollutants and it is considered an economical process. But the major drawback of this system including bulking and foaming problems of the sludge, large area requirements for aeration and sedimentation basins, large quantities of excess sludge, long hydraulic detention time (HRT) etc. and limit the use of these techniques. In the present era the trend of compact wastewater treatment plants is increasing having better quality of the effluent. The membrane bioreactor is an alternative way to achieve high quality effluent, compact plants and economical management (Ødegaard, 2000).

The Membrane Bioreactor (MBR) is a technology that is a combination of two processes i.e., biological treatment with physical separation. This idea was first commercialized in 1970's and since then MBR usage has widely increased. An MBR can replace the two physical processes in to one by filtering the biomass by using the membrane while in conventional activated sludge process the waste water undergoes two stages of treatment: primary sedimentation followed by aerobic degradation and finally secondary sedimentation to remove biomass (Judd, 2006).

The Membrane Bioreactor utilizes micro- or ultra filtration membranes with pore sizes ranging from 0.01–0.4 μm for solid/liquid separation instead of secondary clarifiers. The major advantages are that it enables the independent control of sludge retention time (SRT), hydraulic retention time (HRT) and retains a high concentration of sludge biomass (MLSS) in the reactors, less sludge production, good disinfection capability, higher volumetric loading, and better effluent quality (Engelhardt, 1998; Wang, 2006).

One of the major hurdles in the progress of MBR technology is membrane fouling. The membrane fouling can be defined as the undesirable deposition and accumulation of microorganisms, colloids, solutes, and cell debris within/on membranes. Fouling mechanisms are macromolecule adsorption, pore blocking and cake deposition. Clogging and sludge cake deposition on membranes is usually the predominant fouling component which reduces the permeate flux or increase the trans-membrane pressure (TMP) depending on operation mode (Lee *et al.*, 2001). Membrane fouling is the net result of solute/colloids adsorption on membrane, accumulation of sludge flocs of membrane surface, cake layer

formation on membrane surface and changes in foulant composition with time and space (Meng *et al.*, 2009).

There are three types of fouling. 1) removable fouling 2) irremovable fouling and 3) irreversible fouling. The removable fouling can be easily eliminated by implementation of physical cleaning (e.g., backwashing) while the irremovable fouling needs chemical cleaning to be eliminated. The removable fouling is caused by loosely attached foulants however; irremovable fouling is caused by pore blocking and strongly attached foulants during filtration. The irreversible fouling is a permanent fouling which cannot be removed by any of the approaches.

The addition of biofilm media in MBR is an attractive alternative to conventional MBR which may reduce membrane fouling (Leiknes and Ødegaard, 2001). Supporting media aids in membrane surface scouring and the biofilm growth on the support media improve the nutrients removal efficiency. Basu and Huck. (2005) studied the effect of support media in integrated biofilter submerged membrane system. It was found that the membrane fouling rate doubled in the absence of support media. Different biofilm support materials are granular activated carbon, zeolite, blasted clay granules and Kaldnes carriers. Research has been done on different growth media like polyurethane cubes, polystyrene beads, polyethylene carriers (Kaldnes), activated carbon (granular and powdered), and sponge in MBR (Lee *et al.*, 2006; Yang *et al.*, 2006).

Porous sponge is a mobile carrier for retaining active biomass and by favoring a hybrid growth system including both their attached and suspended growth environments. It has been considered as a feasible attached growth media and reduces fouling of the membrane (Chae *et al.*, 2004).

Even though widespread work has been done on optimization of operating conditions like organic loading rate, SRTs, HRTs, DO concentration in MBRs to control fouling but limited research has been carried out on effects of media on fouling propensity. In this study, fouling phenomenon will be evaluated and discussed in conventional MBR versus hybrid MBR containing sponge as a moving media operated under different hydrodynamic environments.

1.2 OBJECTIVES OF STUDY

Objectives of study were:

- To compare treatment performance of conventional Membrane bioreactor (C-MBR) with moving biofilm Membrane bioreactor (MB-MBR)
- To compare fouling tendency of conventional Membrane bioreactor (C-MBR) with moving biofilm Membrane bioreactor (MB-MBR)
- To compare cake resistance in batch dead end filtration versus continuous membrane filtration

LITERATURE REVIEW

2.1 MEMBRANE

Membrane is a material that behaves as a selective barrier allowing some physical or chemical components passing through it showing its perm selective nature.

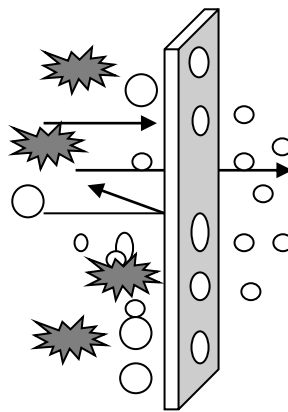


Figure 2.1: Perm- Selective Membrane

The degree of selectivity is mainly dependent on the pore size of the membrane. Membranes commercialization began in early 1990's and since then it is being used in specialized applications in water and wastewater treatment. Wastewater recycling and reuse solutions are best possible by the use of membrane. Up to 15% annual growth in wastewater treatment has been recorded (Leikens, 2006). With time stringent effluent discharges and legislation for conserving water quality, effective treatment, recycling and reusing the wastewater are the key drivers for the advancement of this technology.

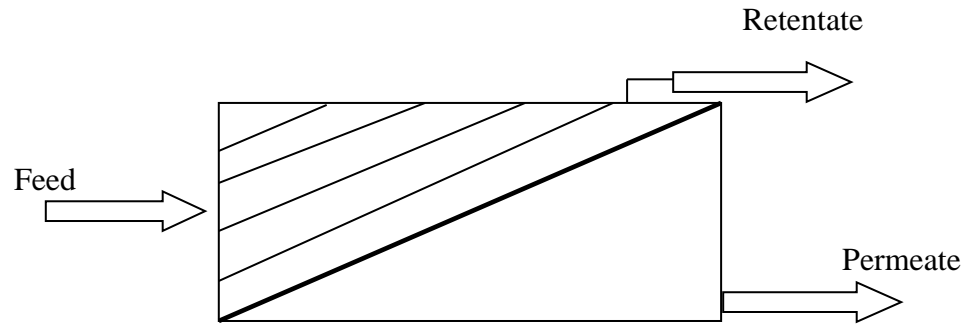


Figure 2.2: Schematic of Membrane

2.1.1 Membrane Operational Modes

Membrane can be operated either under dead-end filtration or cross-flow filtration mode depending upon the nature of use.

Dead-end filtration is also known as direct filtration in which the flow of direction is perpendicular to the membrane. The particles retained by the membrane result in cake formation on the membrane surface. The cake may damage and clog the pores of the membrane. Figure 2.3 illustrates dead-end filtration.

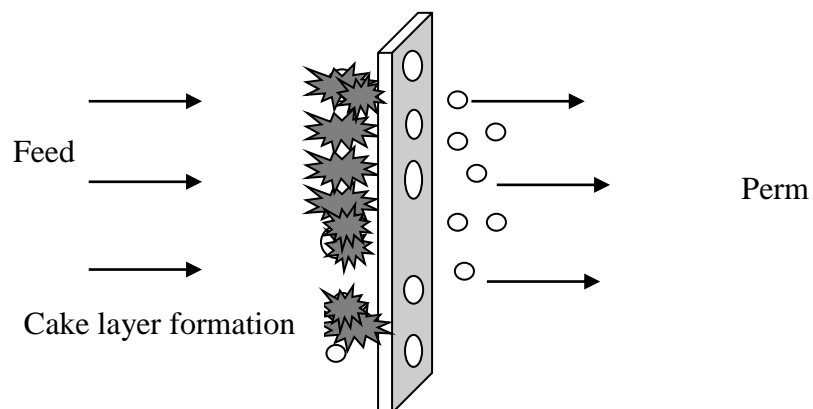


Figure 2.3: Dead-end filtration mode

In cross-flow filtration, the flow is tangential across the surface of the membrane. A portion of feed passes through the membrane which is called

permeate and the rest is rejected. Cross flow filtration opposes cake formation as it scours the membrane surface along with the flow, until adhesive forces binding the cake to the membrane are balanced. Upon this equilibrium a steady state is achieved resulting in higher permeate flow. Figure 2.4 shows mechanism of cross flow filtration.

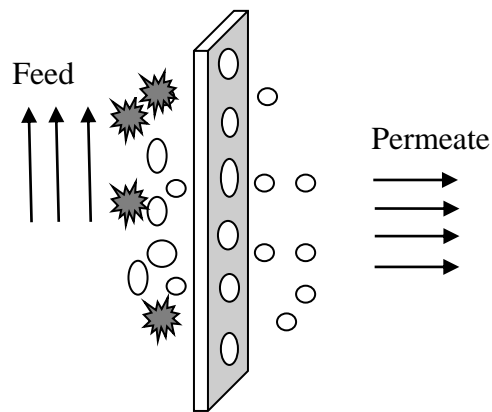


Figure 2.4: Cross flow filtration

2.2 MEMBRANE BIOREACTOR (MBR)

Membrane bioreactors (MBR) are commonly understood as the combination of membrane filtration and biological treatment using activated sludge (AS) where the membrane primarily serves to replace the clarifier in the wastewater treatment system (Gunder *et al.*, 1998).

An MBR can replace two physical processes in to one by filtering the biomass by using the membrane while in conventional activated sludge process the wastewater undergoes two stages of treatment: aerobic degradation followed by secondary sedimentation to remove biomass. (Judd, 2006)

A membrane bioreactor (MBR) is advancement to the conventional activated sludge process (CASP). There are two modes of operation for membrane bioreactor i.e., at constant flux and at constant trans membrane pressure (TMP).

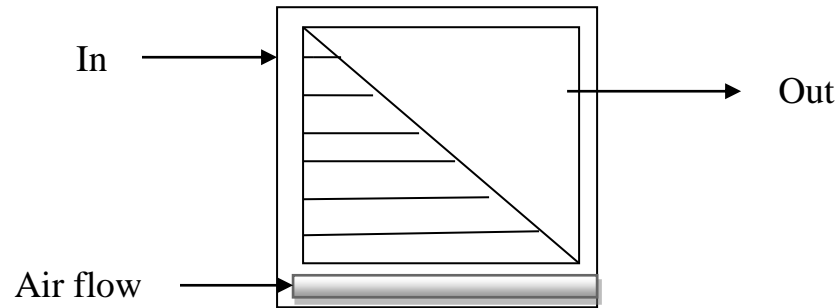


Figure 2.5: Membrane Bioreactor

2.2.1 Advantages and Disadvantages of Membrane Bioreactor.

Chang *et al.* (2002) and Le-Clech *et al.* (2006) have reviewed that MBR is the most effective technology used for waste water treatment to achieve higher effluent quality that is difficult to achieve with the conventional activated sludge process. In comparison with Activated Sludge Process, MBR has the following advantages:

- Reduction in capital cost because less space is required due to elimination of secondary clarifier.
- Membrane pore size of $\leq 0.4 \mu\text{m}$ retains all the biomass within the system resulting in high quality and largely disinfected effluent.
- High Mixed liquor suspended solid (MLSS) concentration can be attained unlike in CASP.
- All suspended solids (SS) larger than the membrane pore size are retained in MBR whereas in CASP, removal efficiency of SS depends on the settling characteristics which can be inconsistent.

- Long SRT resulting in less sludge production and growth of slow growing denitrifiers
- Nitrogen removal by Simultaneous nitrification and denitrification (SND)

Despite of several advantages of MBR, the process has certain limitations

- Greater process complexity i.e., membrane sensitivity to some chemicals, limitations of dissolved oxygen (DO) and pH.
- Higher capital cost of the membrane
- Membrane fouling, life of the membrane reduces with time due to chemical cleaning and internal pore blocking
- Pretreatment of the influent is required
- Higher operating and maintenance cost which includes frequent membrane cleaning and large aeration demand.

2.3 MEMBRANE FOULING

Membrane fouling is one of the major negative aspect of the technology, causing reduction in the permeate flux but can be mitigated by recurrent back washing to remove the deposited particles, frequent chemical cleaning resulting in increased operational cost and decreasing membrane life (Lyko *et al.*, 2008). Fouling can be explained as the coverage of the membrane surface either externally or internally by deposition which adsorb on the surface or simply accumulate during operation. Membrane pore blocking causes decline in permeate flux consequently requiring larger surface area or increase in cross flow pressure.

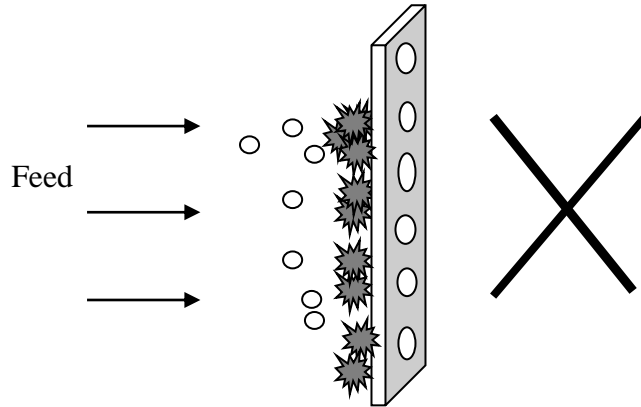


Figure 2.6: Diagram showing a fouled membrane

2.3.1 Classification of Fouling

Membrane fouling in MBRs can be attributed to both membrane pore clogging and sludge cake deposition on membranes which is usually the predominant fouling component (Lee *et al.*, 2001). Meng *et al.*, 2009 reported the membrane fouling can occur due to the following reasons:

- Solute/colloids adsorption on membrane walls
- Accumulation of sludge flocs of membrane surface
- Cake layer formation on membrane surface
- Changes in foulant composition with time and space

2.3.2 Stages in Membrane Fouling

Membrane fouling is complex in nature as it depends on several factors. Cho and Fane, 2002 proposed three stages of membrane fouling as:

Stage 1: an initial short-term rapid rise in TMP;

Stage 2: a long-term weak rise in TMP;

Stage 3: a sharp increase in $dTMP/dt$, also known as TMP jump

Stage 1: An initial short-term rapid rise in TMP

This stage occurs in virgin membranes, when membrane is put in operation a short term rise in TMP is observed. Adsorption of bioflocs and colloids cause pore blocking of the membrane even when the flux is zero.

Stage 2: A long-term weak rise in TMP

A steady but weak rise in TMP is observed in this stage, due to constant deposition of the colloids and Extra Polymeric Substances (EPS), a gel which bounds loose particles aid into the formation of a thin layer on the membrane surface. With the passage of time EPS causes cake formation on the surface.

Stage 3: A rapid rise in $dTMP/dt$, also known as TMP jump

TMP jump is the result of excessive membrane fouling. Cho and Fane. (2002) reported the TMP jump is due to the changes in the local flux due to fouling eventually causing local fluxes to be higher than the critical flux.

It is also considered that the decrease in DO causes cell lyses resulting in excretion of EPS. Changes in sludge characteristics cause production of EPS so the inner layers of the cake do not have sufficient DO and release EPS. (Hwang *et al.*, 2008) reported that rapid increase in the concentration of EPS cause jump of TMP due to death at the inner layer of cake.

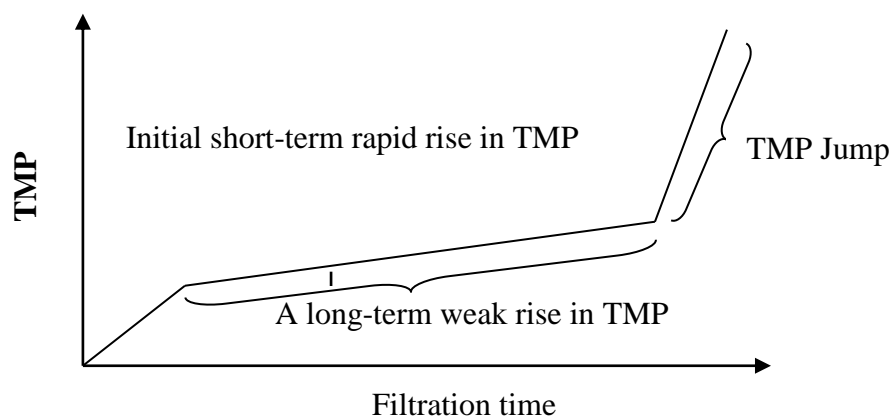


Figure 2.7: Stages of fouling at constant flux operation

A further insight in membrane fouling is shown in the figure 2.8, which describes the role of biological floc and feed as well as the three stages of fouling during the filtration operation in a membrane bioreactor.

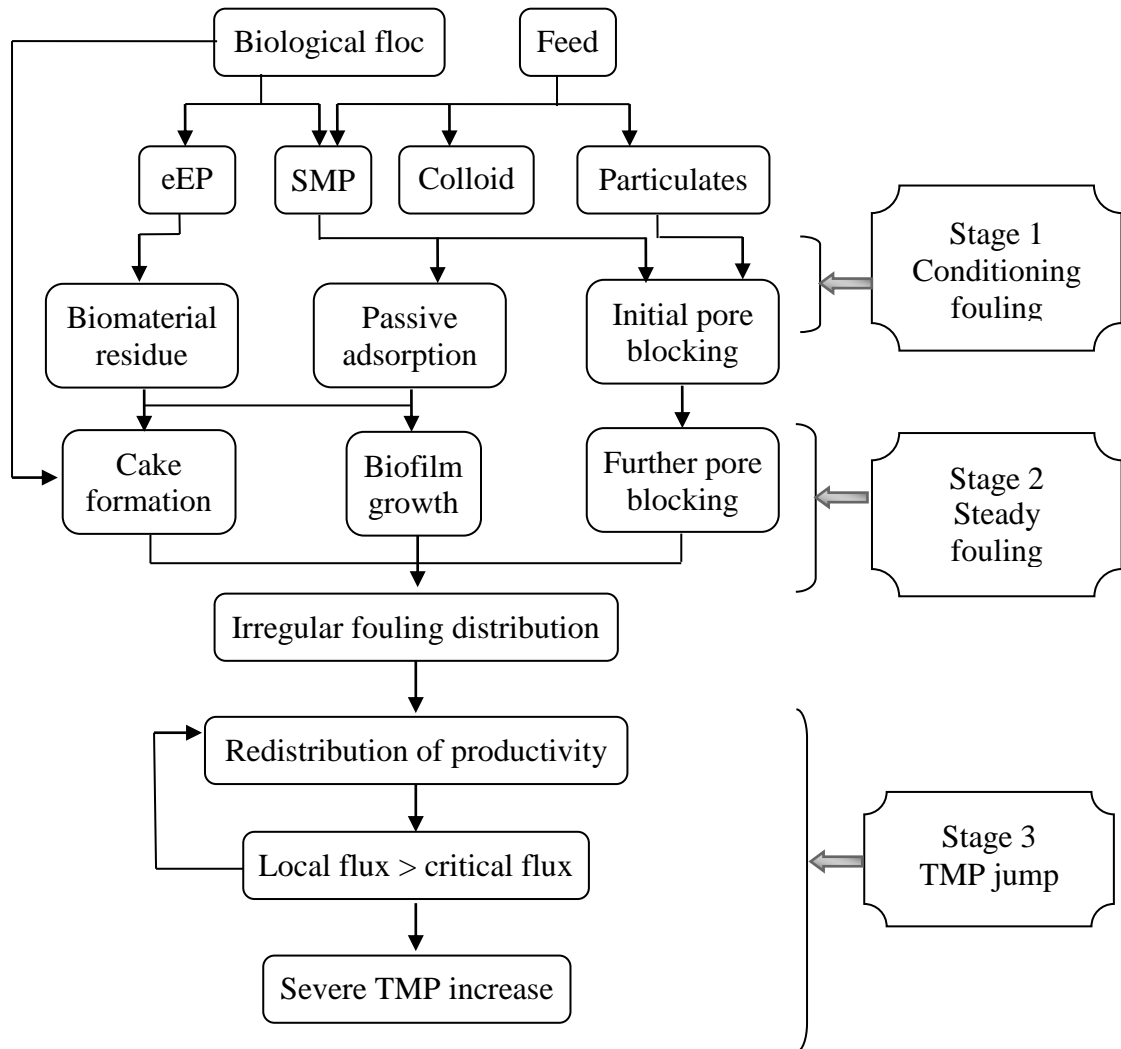


Figure 2.8: Fouling stages for MBR operated at constant flux (adapted from Zhang *et al.*, 2006)

2.4 CLASSIFICATION OF MEMBRANE FOULING

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

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

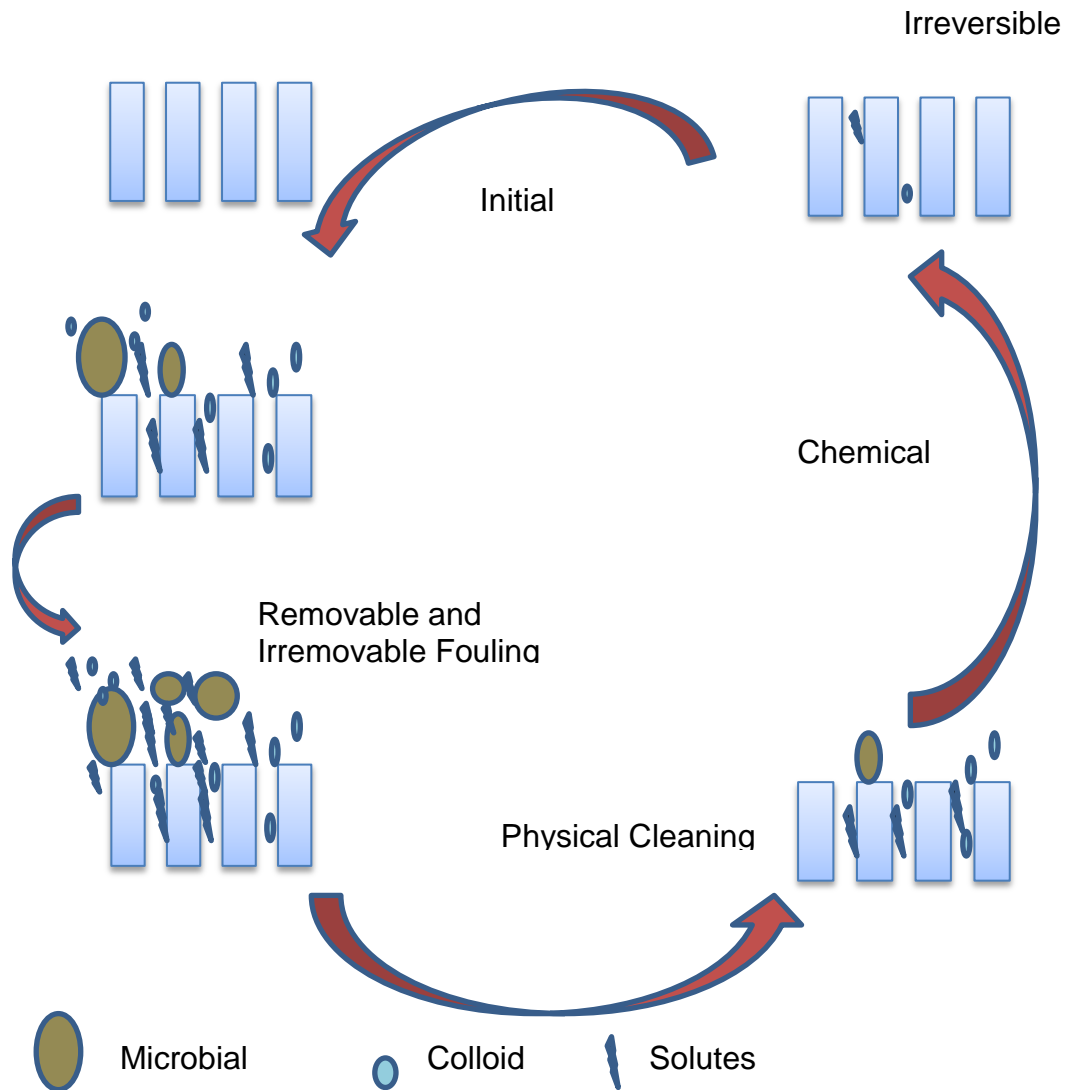


Figure 2.9: Fouling Mechanism in MBR (Adapted from Meng *et al.*, 2009)

2.4.1 Removable Fouling

A cake layer formation occurs when the particle size of the sludge floc is larger than the pore size of the membrane. This leads to the deposition of particles and a layer is formed that hinders the permeate flux. Removable fouling is caused by loosely attached particles. Physically washing the membrane removes the cake layer.

Lee *et al.* (2001) reported that the formation of cake layer is the main source of membrane fouling. Filtration resistances included membrane resistance (12%), cake resistance (80%), blocking and irremovable fouling resistance (8%).

2.4.2 Irremovable fouling

Filtration causes colloids, solutes and microbial cells pass through and precipitate inside the membrane pores. However, extended filtration results in the deposition of the cells on the membrane surface comprising a complex matrix of particles causing irremovable fouling. At the same time, some inorganic substances might progressively precipitate onto the membranes or into the membrane pores. Chemical cleaning is done to remove the deposited foulants with in the pores of the membrane.

2.4.3 Irreversible fouling

Chemical cleaning does not completely remove the particles within the pores of the membrane and this deposition goes on until a point reaches where the pores are clogged and cannot be removed by chemical cleaning. Excessive Irreversible fouling ultimately causes the replacement of the membrane unit.

2.4.3 Factors Affecting Fouling

Parameters such as sludge retention time (SRT), hydraulic retention time (HRT), sludge concentration and organic loading rate (OLR), as well as temperature, dissolved oxygen (DO) and pH all play a role in membrane fouling. Factors affecting the membrane fouling propagation include membrane material characteristics, pore size distribution, characteristics of the sludge, operational mode and hydrodynamics of the reactor.

2.4.3.1 Extra polymeric substances (EPS)

EPS is a mixture of polymeric substances. Generally, the protein and carbohydrate portion is considered. Soluble and colloidal biopolymers including proteins, carbohydrates and polysaccharides (PS) combine together. (Rosenberger *et al.*, 2005). However (Wu *et al.*, 2009) reported soluble PS to cause more fouling than colloidal organics. Lesjean *et al.* (2004) recorded that EPS is a major cause of membrane fouling and a linear relationship between fouling rate and polysaccharide concentration was noticed. EPS has been divided into soluble EPS (sEPS) and bound EPS (bEPS). sEPS is related to membrane fouling by researchers while bEPS being related to microbial floc growth.

2.4.3.2 Pore size distribution and pH

Due to large pore size of microfiltration membranes the internal fouling is more common than a flat sheet membrane where higher amount of polysaccharide can enter and adhere to it. Le –Clech *et al.* (2007) confirmed that polymer sticks inside the pore size of a 0.45 μm membrane while it forms a thick layer gel on the top of a 0.2 μm membrane. In MF membrane cake layer is removed by backwashing in hollow fiber causing internal fouling by the PS as compared to UF flat sheet membrane which exhibits external fouling. pH plays a vital role in fouling propensity. pH or presence of ions might alter the polymers aggregation, fouling and gelling propensity (Bacchin *et al.*, 2006)

2.4.3.3 Role of floc size and air flow rate

Microbial floc size also controls the operation time of filtration in a MBR. If the floc size is smaller than the pore size of the membrane, internal fouling

occurs. Kim *et al.* (2001) reported that membrane filtration interval decreases as microbial floc decreases.

Air flow rate plays a significant role on filtration and fouling of the membrane. A higher flow rate causes less deposition of the cake on the membrane surface thus allowing the MBR to filter for a longer time as compared to the system running under lower flow rates. However if the air flow rate is too high it causes the microbial floc size to reduce due to the mixing intensity and frictional forces and it may lead to internal fouling of the membrane. So an optimum air flow rate will aid into long filtration intervals.

2.4.3.4 Microbial consortium

Filamentous bacteria directly govern membrane fouling and sludge characteristics. (Meng *et al.*, 2006) concluded that sludge floc with negligible filamentous bacteria leads to severe pore blocking while the sludge having filamentous bacteria results in the formation of a non porous cake layer on the membrane surface. Furthermore the excessive growth of filamentous bacteria results in large secretion of EPS and cause hydrophobicity of the sludge floc.

2.4.3.5 Effect of retention time

Sludge retention time (SRT) controls the mixed liquor suspension solid (MLSS) concentration and has an impact on fouling propensity. F:M ratio alters as the SRT increases which in turn increases the MLSS concentration, so the sludge characteristics changes. Increased SRT resulting in higher MLSS concentration causes ore cake layer formation on the membrane surface (Judd, 2006).

Increased MLSS concentration needs higher aeration rate to keep it in suspension thus increasing the operating cost. HRT is another parameter controlling membrane fouling. Long HRT requires low permeate flux, while a short HRT requires higher permeate flux. Huang *et al.* (2011) reported that membrane fouled rapidly in 60 days at an HRT of 8 h as compared to HRT of 12 h, the membrane fouled within around 90 d. The reason of rapid fouling is due to the increase of biomass concentration resulted from an increase in OLR as the HRT was reduced, which greatly enhanced membrane fouling rate.

2.5 ATTACHED GROWTH MEMBRANE BIOREACTOR (AG-MBR)

Conventional wastewater processes can be modified with moving or fixed media for the growth of biofilm. This modification gives the benefit of higher nitrification and denitrification rate and MLSS concentration in the system, longer SRTs resulting in less sludge production, less complexity and high tolerance to organic loading rate and shorter HRTs. However (Odegaard., 2000) summarized some of the drawbacks of other attached growth systems as presented in table 2.1:

Table 2.1: Comparison of Attached growth systems with other systems

Type of attached growth systems	Drawbacks
Tricking filter	<ul style="list-style-type: none"> • Unable to treat large volume
Rotating biological contactor (RBC)	<ul style="list-style-type: none"> • Frequent mechanical failure of the drum • Large surface area for biofilm attachment
Fixed media submerged biofilter	<ul style="list-style-type: none"> • Unequal loading on the media
Granular media biofilter	<ul style="list-style-type: none"> • Higher pore clogging
Fluidized bed reactor	<ul style="list-style-type: none"> • Hydraulic instability

Attached growth systems can be classified into fixed bed and moving bed reactors known as IFAS and MBBR respectively. In moving bed reactors, the suspension of the media and biomass is attained by coarse bubble aeration in the aerobic zones, and by mechanical mixing in the anoxic or anaerobic zones. The suitable specific properties of biofilm carrier selected are: low density close to water (sponge or plastic carriers), high specific surface area and porous enough to hold the biomass.

The access of food and oxygen into the deeper layers of the culture in the biofilm must be assured (Lessel., 1991). Research has been done on different types of media for better removal of nutrients from wastewater. Nguyen *et al.* (2010) tested sponge of different sizes of 1x1x1 cm, 2x2x2 cm, 3x3x3 cm and found that 2x2x2 cm sponge had the best removal efficiency.

Under aerobic condition, the COD, TN and TP removal efficiencies were up to 70%, 45% and 55%, respectively. Ngo *et al.* (2008) studied the effect of high and low density polyester-urethane sponges, with sponge volume fraction of 10% and maintaining MLSS of 10g/L concluded that sponge resulted in increasing the permeate flux, better nutrients removal and lowered the TMP development. Remy *et al.* (2009) studied the effect of powdered activated carbon and concluded that a low dose of PAC i.e., 0.5 g/L and increasing the SRT up to 50 days favor long term filtration interval. Membranes without PAC were severely fouled. Table 2.2 shows a comparison of different media used in MBR study by researchers and the major findings:

Table 2.2: Comparison of different media used in MBR studies

Media	Media Specifications	Major Findings	References
MPE50 TM (Membrane Performance Enhancer)	Modified cationic polymer	<ul style="list-style-type: none"> • Increased overall oxygen transfer rate by 10–20%. • Fouling rates were almost constant at the flux moderately higher than the critical flux. 	Yoon and Collins., 2006
MPE 30 TM (Membrane Performance Enhancer)	Modified cationic polymer	<ul style="list-style-type: none"> • Increase in permeability upto 400% • Reduction of the TMP constantly more than 75% • Significant reduction of the chemical cleaning frequency 	Thomas Wozniak., 2010
KD452	Modified cationic polymer	<ul style="list-style-type: none"> • 51% SMP removal to 74% reduction in fouling rates 	Koseoglu <i>et al.</i> , 2008
Activated carbon coated polyurethane cubes	Surface area = 35,000 m ² /m ³	<ul style="list-style-type: none"> • Lower fouling rate possibly due to collision between the media and the membrane 	Lee <i>et al.</i> , 2006
Polyurethane porous, flexible carriers	Density 30 kg/m ³ , Porosity 90% Size 10*10*10 mm ³	<ul style="list-style-type: none"> • Lower fouling due to suspended carriers • 20% increased critical flux • 86% decrease in cake resistance 	Yang <i>et al.</i> , 2006
Polyester–urethane sponges	High density: S2830/45R, density of 28–30 kg/m ³ with 45 cells per 25 mm Low density: S16–18/80R density of 16–18 kg/m ³ with 80 cells per 25 mm	<ul style="list-style-type: none"> • Flux increase 2 times for S28–30/45R and 1.4 times for S16–18-/80R 	Ngo <i>et al.</i> , 2008

Membrane-coupled moving bed biofilm reactor (M-CMBBR) was compared with MBR in a study by (Lee *et al.*, 2006) and lower bio fouling rate was noticed in M-CMBBR than in a conventional MBR.

M-CMBBR bio fouling was not dependent only on biochemical effects of the mixed liquor but also on the collision and scouring effect of the media with the membrane surface. Two membrane modules were studied, one with membrane module covered with iron net and the other without any covering. Polyurethane cubes (1.3 cm) coated with activated carbon (surface area = 35,000 m²/m³, Samsung Engineering Co., Korea) was mixed in the reactors. TMP increase was about 5 times higher in membrane unit covered with iron net.

Sponge has been considered as the most feasible attached growth media because it acts as a mobile carrier for active biomass, retain microorganisms by incorporating a hybrid growth system (both attached and suspended growth) and reduce fouling of the membrane.(Guo *et al.*, 2009) reported that Sponge not only reduces cake layer formation by scouring and maintain a balance of suspended-attached microorganisms in submerged membrane bioreactor (SMBR), but also can enhance dissolved organic matter and nutrient removal.

(Guo *et al.*, 2010) determined the optimum size and effective volume of the polyurethane foam for aerobic moving and fixed bed bioreactors and concluded that optimum thickness of the sponge cube should be 1 cm. The sponge volume had significant impact on phosphorus removal and 20% volume of sponge could achieve up to 100% T-P removal within 3 h in a sponge batch reactor (SBR).

METHODOLOGY

3.1 EXPERIMENTAL SET-UP

Two Identical laboratory scale acrylic made MBR were set up, each having effective volume of 14 L for the study. Perforated plates divided the reactor into three compartments, membrane being installed in the middle one. Perforated plates helped in mixing of the sludge in the reactor as well as maintaining proper aeration in each compartment of the reactor. Figure 3.1 represents MBR set up in the laboratory.

Hollow fiber membrane (Mitsubishi Rayon, Japan) were immersed in middle compartments of both reactors having a nominal pore size of 0.1 μm and surface area of 0.2 m^2 . Table 3.1 shows detail characteristics of the membrane. Polyurethane sponge was used as moving biofilm carrier media in moving bed membrane bioreactor (MB-MBR). Specific properties of the sponge are given in Table 3.2

Peristaltic Pump (Master Flex, Cole-Parmer, USA) was used to periodically draw permeate at a cycle of 10 min ON, 2 min OFF, maintaining HRT of 8 Hrs. Sludge retention time (SRT) was set to 25 days. Air pumps provided sufficient air to keep the media in suspension, letting it scour the membrane fibers along with maintaining dissolved oxygen (DO) concentration of 5-6 mg/L. Diffused aeration was provided in the reactor by the help of air diffusers. Flow meter was used to monitor the proper suspension of the media by keeping the aeration rate at 7 L/m. (3 L/m in the membrane compartment and 4 L/m in the side compartments.)

Trans-membrane pressure (TMP) was recorded using Data logging manometer (Sper-Scientific 840099, Taiwan) as indicator of membrane fouling tendency. The membranes were operated till the TMP reached to a limit of 50 KPa.

Table 3.1: Hollow-fiber (HF) membrane characteristics

Item	Characteristic
Manufacturer	Mitsubishi Rayon Engineering Co. Ltd., Japan
Membrane material	Polyethylene
Pore size	0.1 μm
Filtration area	0.2 m^2
MLSS	5,000-12,000 mg/L recommended (3,000 - 15,000 mg/L)
Filtration flow rate	Constant
Suction pressure	5-30 kPa
Intermittent suction	Operating time \leq 13 min; relaxing time \geq 2 min
Temperature	15-35 $^{\circ}\text{C}$

Source: Mitsubishi Rayon

The specific properties of the sponge media used during the research study is as listed.

Table 3.2: Specific properties of sponge media

Properties	Description
Manufacturer	United Foam Industries (Pvt) Ltd. Pakistan
Commercial name	Unifoam
Density	30 Kg/m ³
Dimensions*	1 cm × 1 cm × 1 cm
% Fill Volume	20
Material	Polyurethane

* Guo *et al.*, (2010).

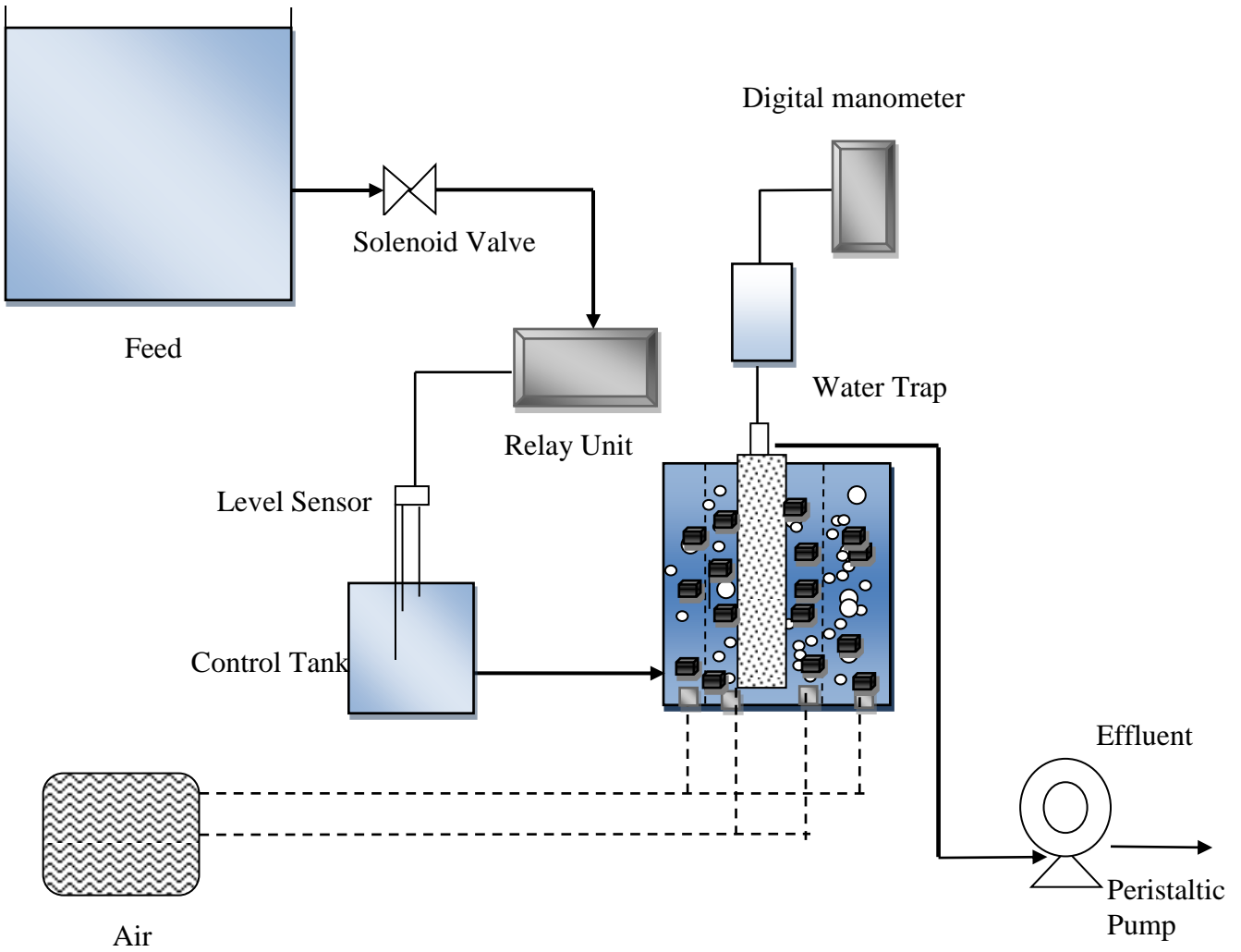


Figure 3.1 Schematic diagram of AG- MBR

3.2 ACCLIMATIZATION OF SLUDGE AND MEDIA WITH SYNTHETIC WASTEWATER

The activated sludge from I-9 Sewage Treatment Plant, Islamabad was acclimatized with synthetic wastewater for a period of 30 days in MBR, along with sponge media acclimatization.

High strength wastewater was prepared synthetically in the laboratory having a COD of 1000mg/L and COD:N:P of 100:10:2. To maintain a pH of 7-8, NaHCO₃ was used as pH buffer.

Wastewater composition is listed in Table 3.3

Table 3.3: Chemical Composition of Synthetic Wastewater

Chemicals	Formula	Quantity (mg/L)
		COD/N = 10
Hydrated Glucose	C ₆ H ₁₂ O ₆ .H ₂ O	1031
Ammonium Chloride	NH ₄ Cl	382
Potassium Di-Hydrogen Phosphate	KH ₂ PO ₄	87
Trace elements		
Calcium chloride	CaCl ₂	10
Magnesium Sulphate	MgSO ₄ .7H ₂ O	10
Ferric Chloride	FeCl ₃	3
Manganese chloride	MnCl ₂ .4H ₂ O	2
pH buffer	NaHCO ₃	800

3.3 EXPERIMENTAL CONDITIONS

In the previous study by (Sadaf *et al.*, 2010) and (Shazia *et al.*, 2010), municipal sludge was acclimatized with synthetic wastewater over a period of 60 days in two SBRs run in parallel. This study was conducted under Nitrogen loading rate (NLR) of 0.3 Kg/m³/d. Organic loading rate (OLR) was kept at 3 Kg/m³/d. During this study 20% sponge media was selected and

acclimatized media was introduced in the membrane compartment. Schematic diagram of implementation of this study is illustrated in Fig. 3.2.

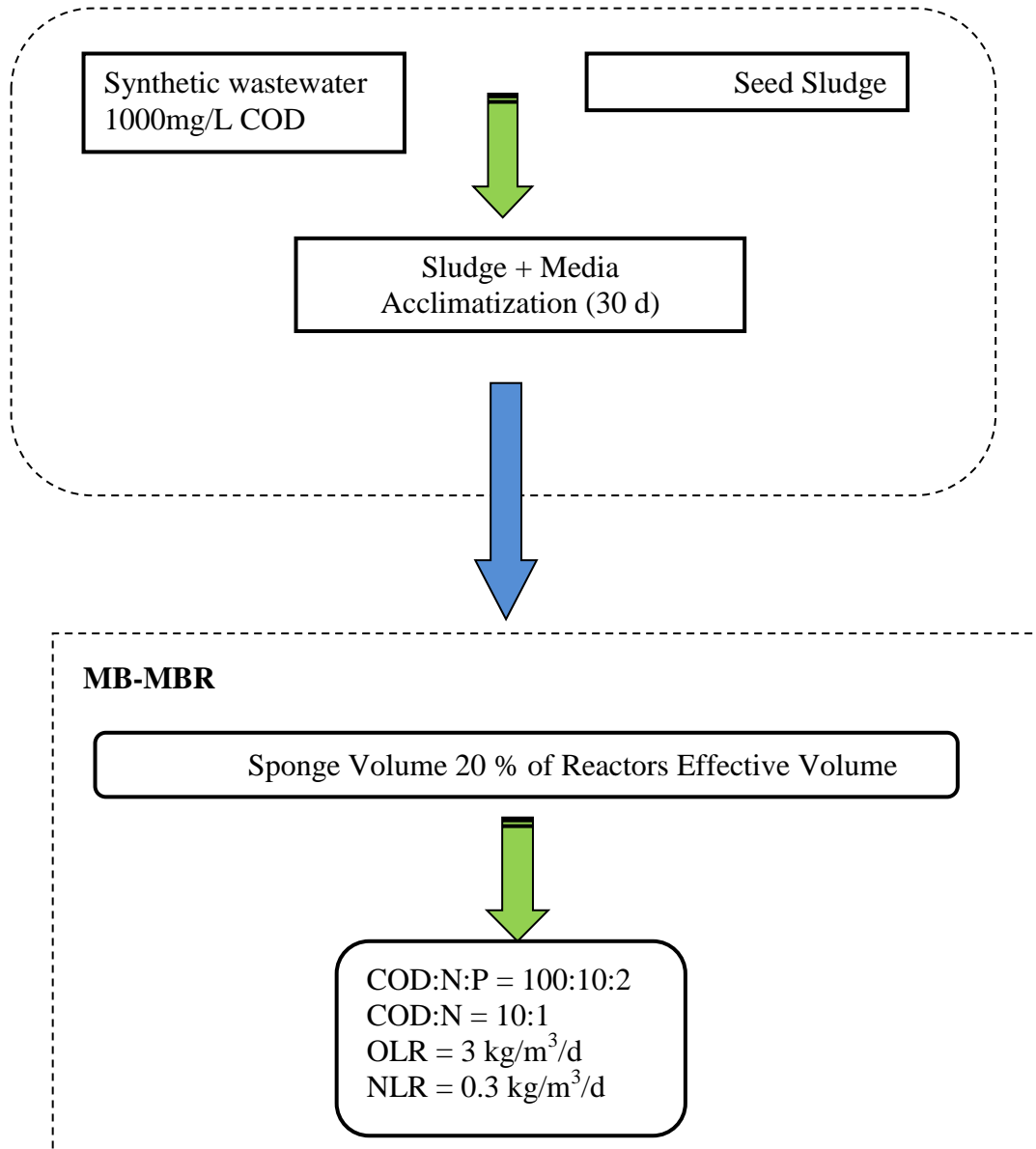


Figure 3.2: Schematic diagram of the experimental study

The influence of biofilm carrier on membrane fouling propensity was studied in MB-MBR. MBR's treatment performance was also monitored. The road-map to investigate the influence of biofilm carrier is outlined in Fig. 3.3.

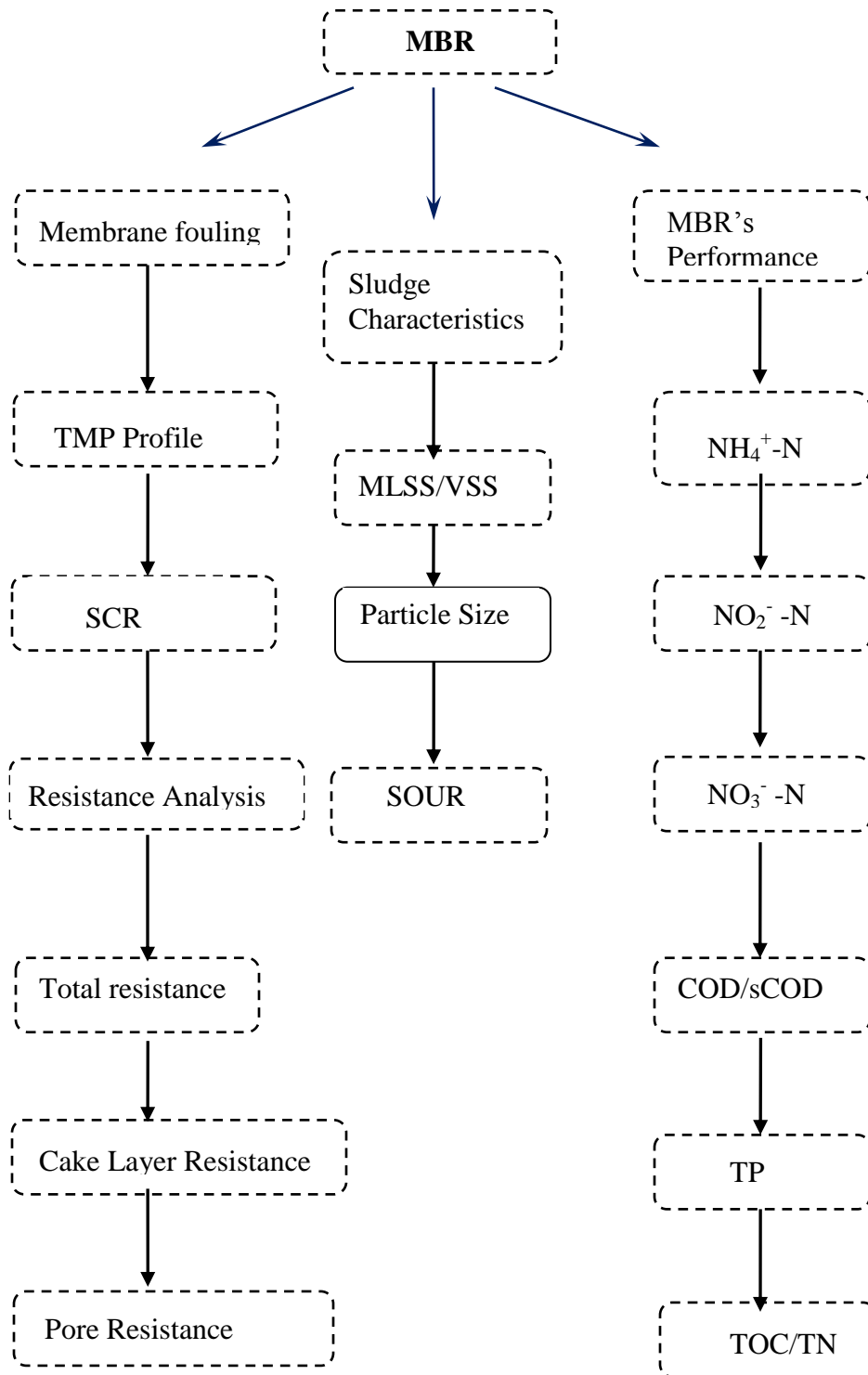


Figure 3.3: Detailed plot of study

3.4 ANALYTICAL METHODS

The parameters that were investigated, the technique adopted to determine each parameter and the equipment/material used are reported in Table 3.4. The detailed protocols for the measurement of the analytical parameters are discussed in the following sections

3.4.1 Specific Oxygen Uptake Rate (SOUR)

Specific Oxygen Uptake Rate (SOUR) was measured to record the respirometric activity of the sludge by using DO meter (YSI 5100, USA) having an built-in SOUR software. Protocol followed for measuring respirometric activity is as follows:

1. Sludge (7000-8000 mg/L) was transferred into 300 mL BOD bottle.
2. Immediately substrate i.e., synthetic wastewater was added at S_0/X_0 of 0.02.
3. DO probe with self stirring device (YSI 5010 BOD probe, USA) was immersed in the BOD bottle.
4. SOUR values were determined directly using MLVSS concentration.
5. Results are reported in $\text{mgO}_2/\text{gVSS/h}$.

Table 3.4: Analytical parameters, methods and equipment

Parameter	Method	Equipment/Material	References
MLSS-MLVSS	Filtration-Evaporation	1.2 μm (GF/C, Whatman); 105°C oven (MLSS); 550°C Muffle Furnance (MLVSS)	APHA., 2005
COD	Close reflux	COD tube; 150°C oven	APHA., 2005
NH_4^+ -N, NO_2^- -N, NO_3^- -N	Hach Reagents	Spectrophotometer (DR 2010, Hach)	APHA., 2005
SOUR	Rate of DO depletion	DO meter (Model YSI 52100, USA)	APHA., 2005
Soluble EPS	Centrifugation, 5,000 rpm	Model 80-2	Zhang <i>et al.</i> , 2006
Bound EPS	Cation exchange resin (CER) extraction method	CER (DOWEX HCR-S/S, Dow Chemical Company, USA)	Frolund <i>et al.</i> , 1996
Carbohydrate concentration	Colorimetric method	Spectrophotometer (DR 2400, HACH, USA)	Dubois <i>et al.</i> , 1956
Protein concentration	Colorimetric method	Spectrophotometer (DR 2400, HACH, USA)	Lowry <i>et al.</i> , 1951
Particle Size Distribution	% Volume vs particle size	LA-300, Horiba, Japan	---
TOC-TN	NDIR	TOC Analyzer	---
Specific cake resistance (α)	Dead-end filtration at constant pressure	Filtration cell (Amicon, Model 8400, USA); 0.22- μm flat-sheet cellulose membrane filter (Millipore, GVWP 09050, USA)	Foley., (2006); Rosenberger <i>et al.</i> , (2006)

3.4.2 Extra Polymeric Substances (EPS)

EPS are present both outside of cells and in the interior of microbial aggregates. Different classes of macromolecules such as polysaccharides, proteins, nucleic acids, lipids and other polymeric compounds were reported by the term EPS by Wingender *et al.* (1999). In this study, the main components of EPS to be considered were protein and carbohydrate, which were measured by the colorimetric methods of Dubois *et al.* (1956) and Lowry *et al.* (1951), respectively, using spectrophotometer (DR 2400, HACH, USA).

The sum of the protein and carbohydrate content represented the total amount of EPS content (Lee *et al.*, 2003). The EPS was measured in the form of soluble and bound EPS. Bound EPS was extracted from the mixed liquor using cation exchange resin (CER) extraction method (Frolund *et al.*, 1996). The CER (DOWEX HCR-S/S, Dow Chemical Company, USA) used was in Na⁺ form with bead size distribution range between 16-50 mesh. The two forms of EPS were extracted at room temperature by the procedure outlined as follows:

1. 50 mL sludge sample was taken
2. Sample was centrifuge without delay at 5,000 rpm for 15 min
3. Supernatant was collected and again centrifuged at 5,000 rpm for 15 min
4. Supernatant was stored at 4 °C for soluble EPS analysis
5. Settled sludge flocs were re-suspend in buffer solution to final volume of 50 mL
6. CER resin was added equal to 70 g/g VSS
7. Sample was stirred at 600 rpm for 1h
8. Sample was then centrifuged at 5,000 rpm for 15 min

9. CER and floc components were removed and supernatant was collected
10. Sample was again centrifuged at 5,000 rpm for 15 min
11. Remaining floc components were removed
12. Supernatant was stored at 4°C for bound EPS analysis

3.4.3 Soluble COD (sCOD)

100 mL of the sludge sample was centrifuged at 5000rpm for 15 minutes and the supernatant was collected for sCOD. COD was determined as per Standard Methods and termed as sCOD.

3.4.4 Specific Cake Resistance (SCR)

The specific cake resistance (α) of the sludge sample was determined through Batch filtration tests. The test was conducted in a 400 mL unstirred filtration cell (Model 8400, Amicon, USA) using a 0.22 μm flat-sheet cellulose membrane filter (GVWP 09050, Millipore, USA) as shown in Figure 3.4

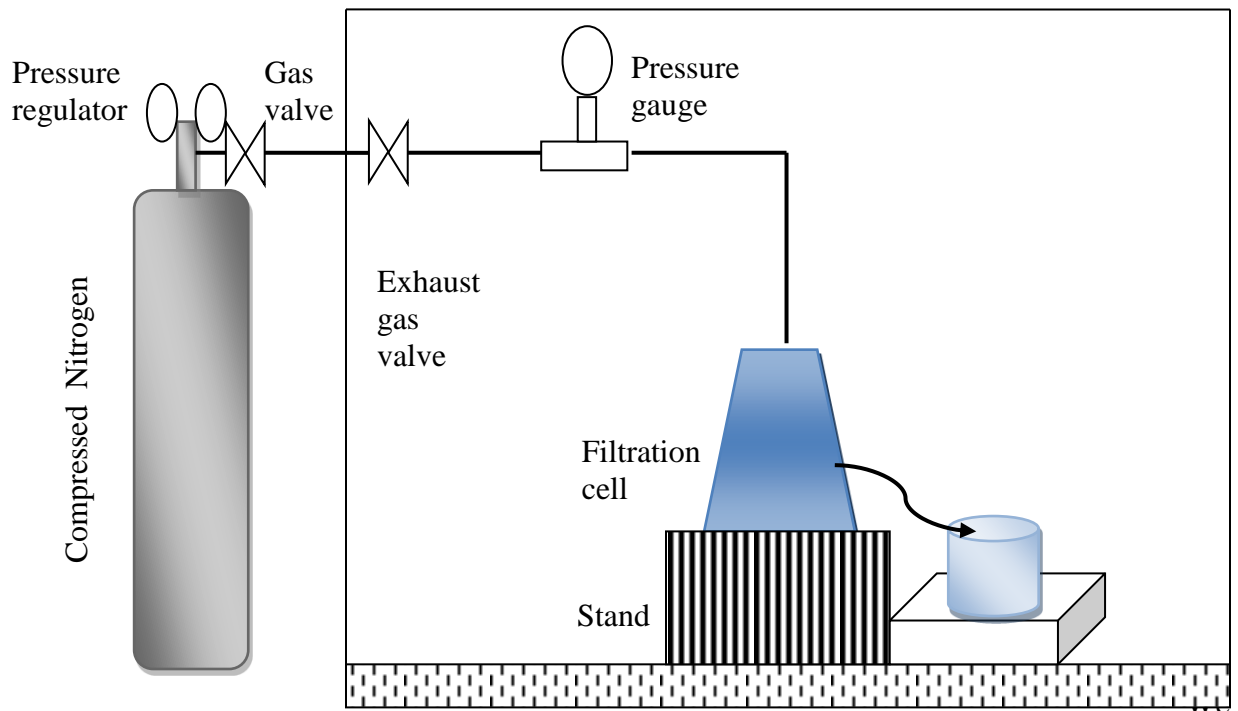


Figure 3.4: Specific Cake Resistance apparatus set up

The Specific cake resistance was calculated as follows:

1. 0.22 μm flat-sheet cellulose membrane filter was cut to circular disc shape.
2. The membrane was placed in cell by removing the O ring at the bottom of the cell.
3. 300 mL sludge was taken in the filtration cell.
4. 30 KPa of Pressurized N_2 gas was applied
5. The filtrate was continuously recorded using electronic balance for SCR.

The specific cake resistance (α) (m/kg) was calculated (Wang *et al.*, 2007)

$$\alpha = \frac{2000 \cdot A_m^2 \cdot \Delta P}{\mu \cdot C_b} \cdot \frac{t}{V} \quad \text{Equation 3.1}$$

Where A represents Filtration area (0.00418m^2), ΔP is the applied pressure in KPa, μ is the viscosity of permeate ($\text{N}\cdot\text{s}/\text{m}^2$) and C is the MLSS concentration (kg/m^3), $[(t/V)/V]$ (s/m^6) is the slope of the straight portion of the curve that is obtained by plotting the time of filtration to volume of filtrate (t/V) versus the filtrate volume (V)

3.4.5 Membrane Cleaning

The Hollow fiber membrane (Mitsubishi Rayon, 2004) module cleaning process termed as ‘out-of-system immersion cleaning’ was applied that involved two main stages. First, membrane unit was physically cleaned to remove all visible cake layer deposited on the membrane fibers and within adjacent fibers. In the second stage, the membrane was chemically cleaned to decompose organic matter deposited on the membrane surface and inside pores restoring the intrinsic TMP. Detailed procedure is as given:

1. Membrane unit was removed from the aeration tank by disconnecting the suction line.
2. Biofilm deposited on membrane fibers were washed with tap water for physical cleaning.
3. Aqueous solution of 4 % wt/vol. aqueous sodium hydroxide and sodium hypochlorite (effective chlorine concentration= 3,000 mg/L) was prepared and membrane unit was completely immersed in a chemical cleaning tank.
4. The membrane was immersed in the solution for about 6–10 hours.
5. After immersion, chemical solution was filtered from the membrane for 30 minutes.
6. The membrane was rinsed thoroughly with tap water to remove chemicals.

7. Distilled water was then filtered through the membrane for next 30 minutes.
8. The membrane was returned to aeration tank.
9. For first 30 minutes, system was operated at a half flux of standard.
10. After that returned to the standard flux and operation was resumed.

3.4.6 Membrane Resistance Analysis

The resistance-in-series model was applied to evaluate the filtration characteristics using following equations (Lee *et al.*, 2001; Rosenberger *et al.*, 2006):

$$J = \Delta P / (\mu \cdot f_t \cdot R_t) \quad \text{Equation 3.2}$$

$$R_t = R_m + R_c + R_p \quad \text{Equation 3.3}$$

Where;

J = Operational flux ($L/m^2 \cdot s$),

ΔP = TMP (kPa),

μ = viscosity of permeate (Pa.s),

f_t = temperature correction to 20°C, $f_t = e^{-0.0239(T-20)}$

R_t = total hydraulic resistance (m^{-1}),

R_m = intrinsic membrane resistance (m^{-1}),

R_c = reversible cake resistance formed by the cake layer (m^{-1}) and

R_p = irreversible fouling or pore resistance caused by adsorption of dissolved and colloidal matter onto the membrane surface and into the pores (m^{-1}).

R_t and R_m+R_p was calculated by filtering tap water through the membrane before and after removing the cake layer, respectively. R_m was measured by filtering de-ionized

(DI) water through a chemically cleaned membrane. Each of the R_t , R_m , R_c and R_p values were obtained using the following equations:

$$R_t = \Delta P_w / (\mu \cdot J) \quad \text{Equation 3.4}$$

$$R_m + R_f = \Delta P'_w / (\mu \cdot J) \quad \text{Equation 3.5}$$

$$R_m = \Delta P''_w / (\mu \cdot J) \quad \text{Equation 3.6}$$

$$R_p = (R_m + R_f) - R_m \quad \text{Equation 3.7}$$

$$R_c = R_t - (R_m + R_p) \quad \text{Equation 3.8}$$

Where J is the constant flux, ΔP_w and $\Delta P'_w$ is the TMP at filtering tap water through the membrane before and after removing the cake layer, respectively and $\Delta P''_w$ is the TMP at filtering DI water through the chemically cleaned membrane

RESULTS AND DISCUSSIONS

4.1 ANALYSIS OF MEMBRANE FOULING

Membrane fouling was evaluated with the help of TMP profile obtained during membrane filtration. In this study TMP was monitored under constant flux of 8.75 L/m².h and the filtration operation was stopped when the TMP reached 50kPa. At this stage the membranes were taken out of operation for physical as well as chemical membrane cleaning meanwhile performing the membrane resistance analysis to determine total resistance (R_t), cake resistance (R_c), pore blocking resistance (R_p), and intrinsic membrane resistance (R_m). Four successive TMP profiles of C-MBR and MB-MBR are shown in Figure. 4.1

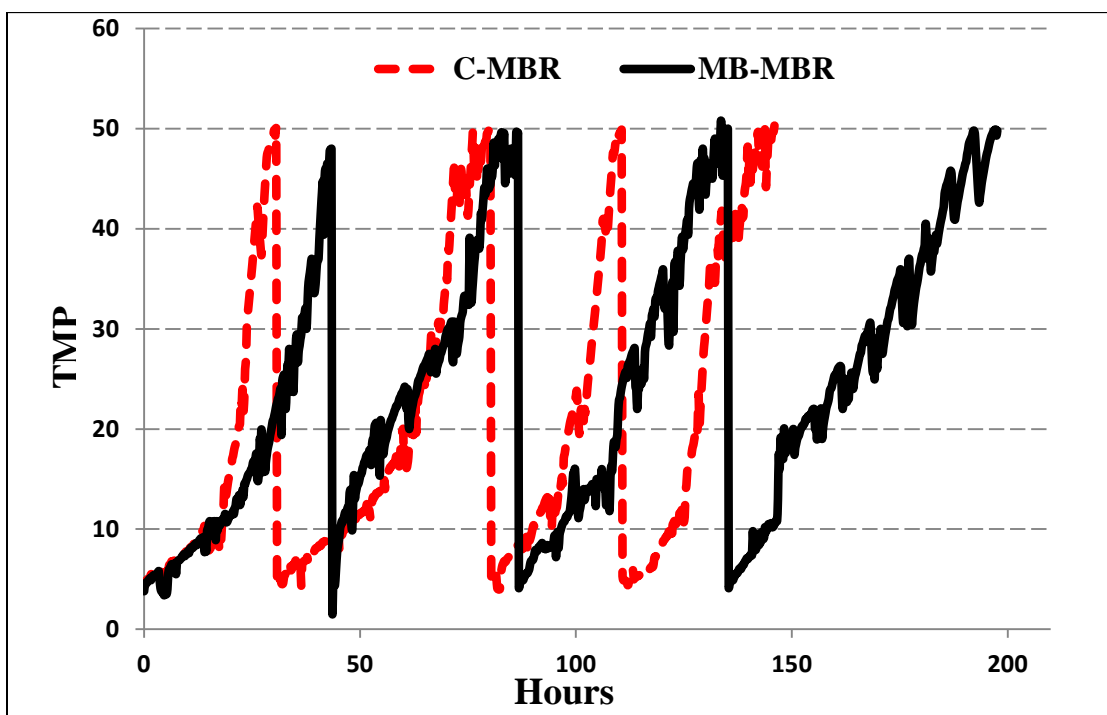


Figure 4.1: Four successive TMP profiles of C-MBR and MB-MBR

The filtration time recorded for C-MBR and MB-MBR after four runs was 150 and 200 hr, respectively corresponding to 37.5 and 50 hr average run time in C-MBR and MB-MBR, respectively. The MB-MBR filtration exhibited 33% increase as compared to that in C-MBR.

Addition of sponge media resulted in the prolonged filtration of MB-MBR which follows similar trends obtained by other researchers (Huang *et al.*, 2008; Lee *et al.*, 2006; Sombatsompop *et al.* (2006). Lee *et al.* (2006) reported that membrane coupled moving bed biofilm reactor (M-CMBBR) showed much lower biofouling rate than conventional MBR. The collision between circulating media and hollow fiber resulted in frictional forces that mitigated cake formation on membrane fibers, thus resulting in prolonged filtration. Both systems were operated under constant flux and same aeration rate, so it can be inferred that addition of media has a vivid effect on filtration performance of the membrane bioreactor.

Figure 4.2 exhibits a two-hour comparison of TMP rise after 24 hours of filtration runs in both the MBRs. There is a remarkable difference in TMP of both MBRs. After 24 hours of filtration, the TMP in MB-MBR was in the range of 15 -21 kPa while TMP in C-MBR was in the range of 35-41 kPa. TMP in C-MBR was almost two folds higher than that of MB-MBR after the same filtration duration

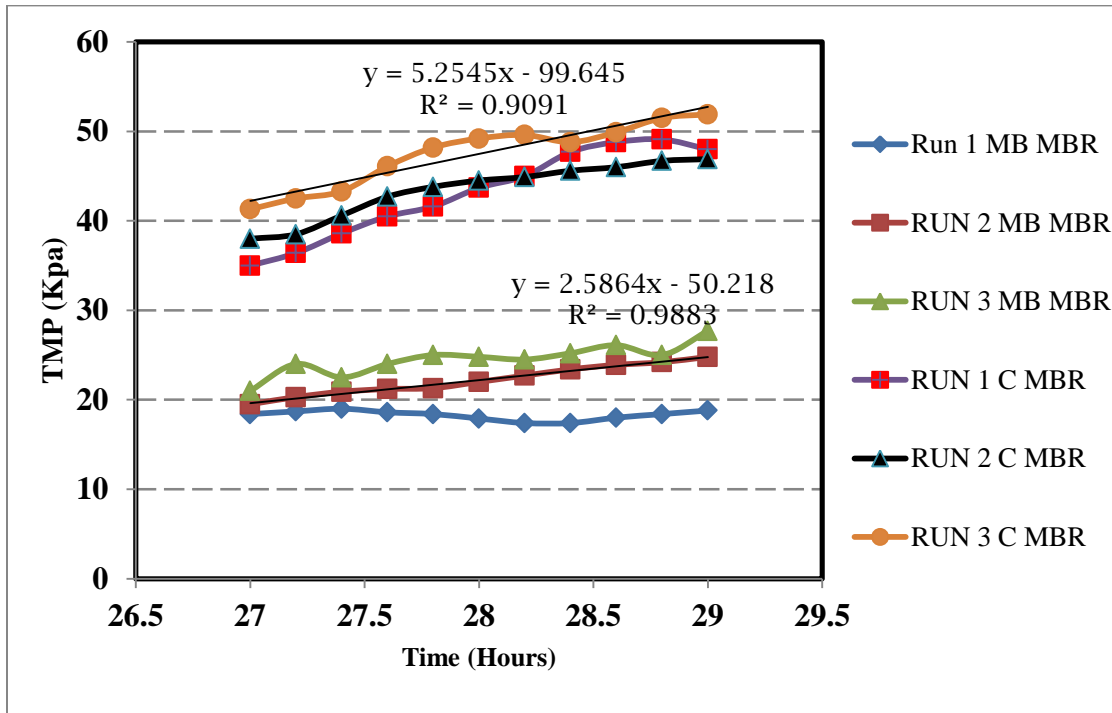


Figure 4.2: Two-hour comparison of TMP rise after 24 hours of filtration

. The filtration profiles in Fig. 4.2 were used to calculate the fouling rates assuming slow TMP rise prior to 24-hour filtration runs. The average fouling rates were found to be 5.75 and 2.84 kPa/hr in C-MBR and MB-MBR, respectively. Again, the difference in magnitude between the fouling rates was almost double. With the help of later results the predominant phenomena resulting in the improved fouling propensity in MB-MBR will be discussed.

4.2 RESISTANCE ANALYSIS

The resistance-in-series model was applied to evaluate the filtration characteristics. The resistance analysis results are summarized in Table 2 which represents the averaged resistance values after replicate experimental measurements.

Total resistance (R_t) as reported in Table 1 was relatively higher in C-MBR despite the fact of shorter filtration runs as compared to that in MB-MBR. The cake resistance (R_c) was found to be the predominant resistance fraction in both the MBR systems contributing 51 and 56% in C-MBR and MB-MBR, respectively.

Table 4.1: Resistance Analysis of both MBR

RESISTANCES	C-MBR	MB-MBR
$R_m(x10^{12}m^{-1})$	1.26E+09	1.46E+09
$R_p(x10^{12}m^{-1})$	4.64E+09	3.95E+09
$R_c(x10^{12}m^{-1})$	7.24E+09	6.74E+09
$R_t(x10^{12}m^{-1})$	1.31E+10	1.21E+10
$R_c/R_t(\%)$	51	56
$R_p/R_t(\%)$	38	32

The R_c as well as the pore blocking resistance (R_p) values were both higher in C-MBR resulting in overall increase in the R_t . The increase in R_c and R_f were found to be 7 and 18 % in C-MBR as compared to MB-MBR. The higher fouling resistances in C-MBR were responsible for the severe fouling propensities in terms of shorter filtration runs and higher fouling rates. It can be suggested that the pore blocking resistance (R_p) had a greater influence on the membrane filtration duration in C-MBR as compared to MB-MBR as shown in Fig. 1. The soft texture of sponge cube carriers apparently caused mild membrane scouring of the membrane fibers in MB-MBR as

depicted by the cake resistances(R_c) in both systems. However, the significant decline in pore blocking resistance (R_p) in MB-MBR can be attributed to the changes in organic foulant concentrations as well as sludge floc morphology which will be discussed later.

4.3 SLUDGE FILTERABILITY CHARACTERISTIC (SCR)

Specific cake resistance (SCR) is a quantitative measure for measuring the fouling potential or filterability of sludge cake. During this batch filtration test, no stirring mechanism was provided so as to observe the effect of sludge cake only on filtration tendencies. Moreover, 300 mL mixed liquor from both MBR systems were taken without sponge carriers for the test. It was found that the average SCR values (α) were 6.2×10^{12} and 5.7×10^{12} m/kg for mixed liquors from C-MBR and MB-MBR, respectively with higher SCR in C-MBR. These results are in agreement with the cake resistances (R_c) from Table 4.1 and R_c values were found having a strong correlation with SCR (α) in C-MBR as compared to those in MB-MBR as shown in Figure 4.3.

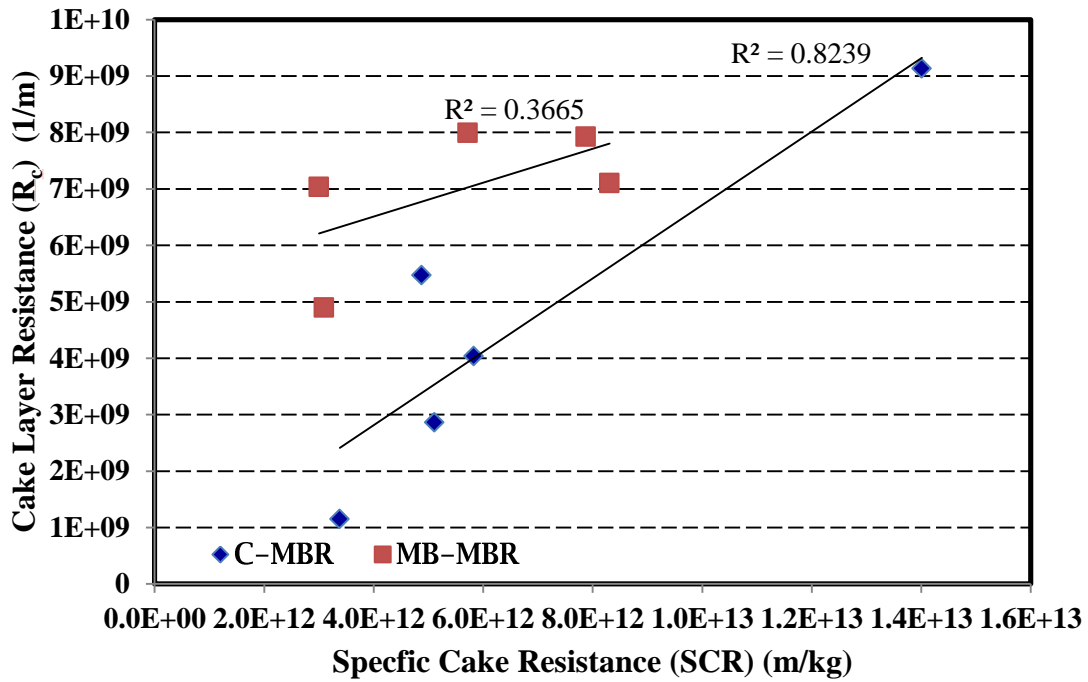


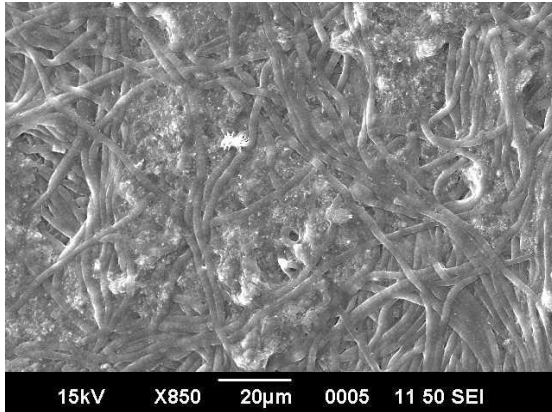
Figure 4.3: Co-Relation of SCR with R_c in MBR

The strong correlation ($R^2 = 0.82$) between SCR and R_c in C-MBR may be due to the fact that no cake layer scouring took place as was the case in MB-MBR where continuously the sponge carriers were having a physical contact with the membrane fibers. Due to this scouring affect a weak correlation ($R^2 = 0.37$) was observed where increase in SCR was not accompanied with similar increase in R_c.

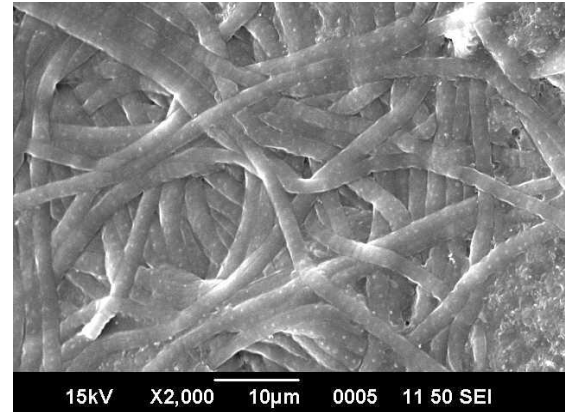
4.4 INFLUENCE OF FLOC MORPHOLOGY ON MEMBRANE FOULING

SEM images of sludge flocs in both MBRs are shown in Fig. 4 a,b,c and d with magnifications at (a) 20 μm, and (b) 5 μm. Rod shaped filamentous bacteria were observed in C-MBR sludge which can lead to floc formation but excessive growth can cause severe fouling of the membrane. Filamentous bacteria form a close fiber

network over the membrane fibers with a thick and non-porous cake layer in appearance allowing very low membrane permeability and over time offer excessive resistance to filtration (Meng *et al.*, 2009).

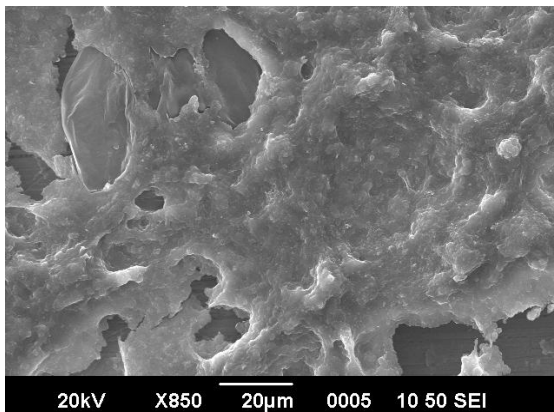


(a) C-MBR Floc magnification at 20 μm

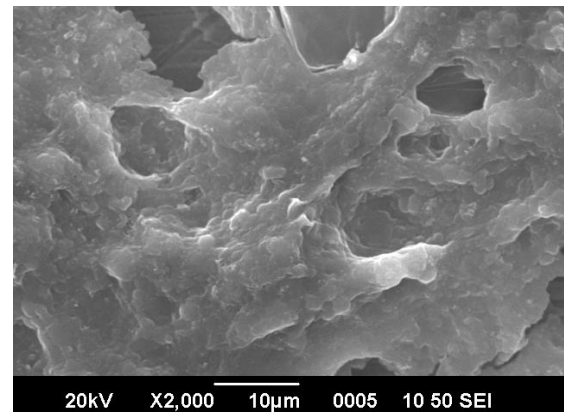


(b) C-MBR floc magnification at 10 μm

On the contrary, coccus shaped bacteria were observed in MB-MBR flocs with moderate filaments which formed slightly porous cake layer over membrane fibers resulting in moderate TMP rise.



(c) MB-MBR Floc magnification at 20 μm



(d) MB-MBR floc magnification at 10 μm

μm

The membrane fouling resistances as presented in Table 2 also increased in C-MBR as compared to MB-MBR due to the abundance deposition of the filamentous bacteria in C-MBR on the membrane surface. These observations are in agreement with the study by Meng *et al.* (2006) where the membrane fouling resistances (R_t , R_c , and R_f) became worse as filamentous index (FI) increased indicating excessive growth of filamentous bacteria has negative effect on membrane fouling.

4.5 INFLUENCE OF PARTICLE SIZE DISTRIBUTION ON MEMBRANE FOULING

The particle size distribution of mixed liquor was evaluated on the basis of particle diameter by its percentage volume in the sludge sample. It was found that the average particle size of C-MBR was higher i.e., 201 μm than that in the MB-MBR i.e., 157 μm . Similar observations were also recorded by Huang *et al.* (2008). Lee *et al.* (2006) observed that the particle size decreased significantly with increased % media volume fraction and Sombatsompop *et al.* (2006) also reported similar observations. Figure 4.4 illustrates below.

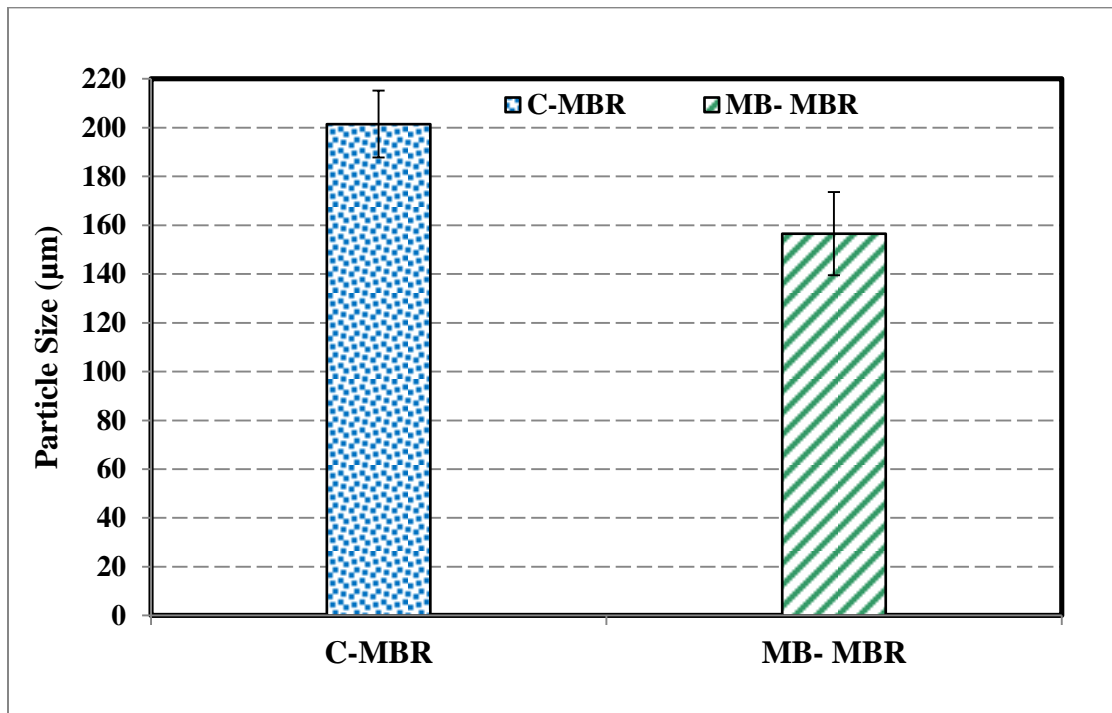


Figure 4.4: Mean Particle size in MBR

Fig. 4.5 shows the particle sizes in the MBRs sludge distributed into four ranges. The floc sizes in C-MBR were slightly smaller by % volume as compared to MB-MBR except in the range of 153-200 µm. The average particle size and particle distribution patterns suggest that constant collision of sponge carriers were responsible for break-up of sludge flocs in MB-MBR.

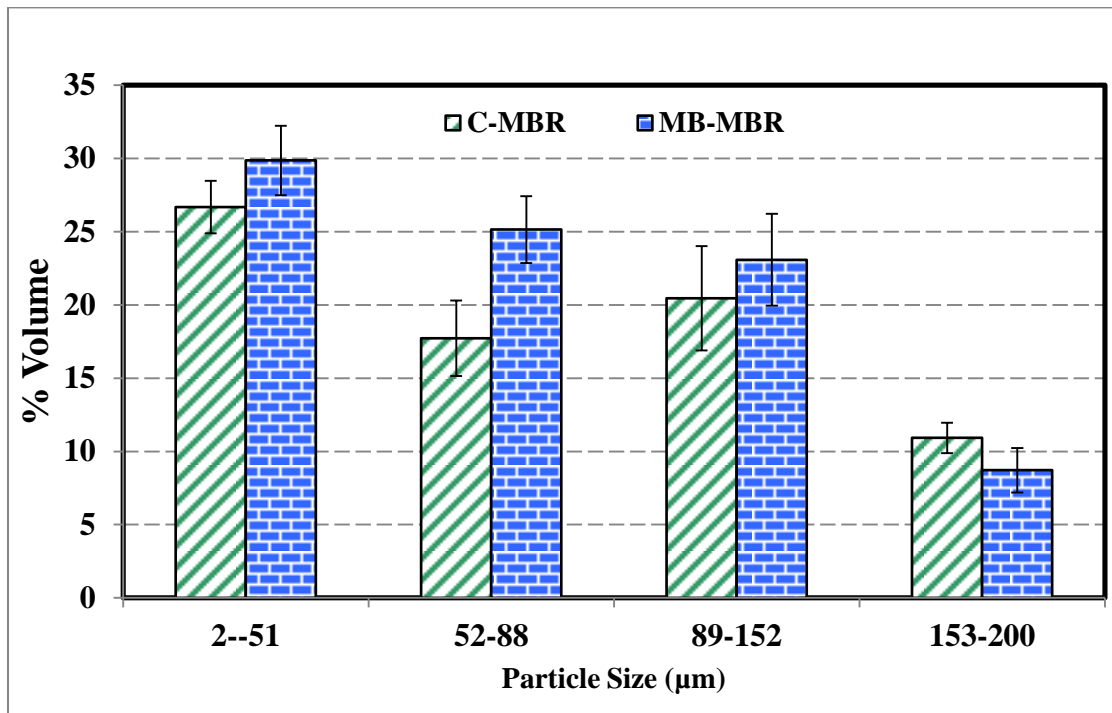


Figure 4.5: Particle sizes in the MBRs sludge distributed into four ranges

However, this floc break-up phenomenon was not serious keeping in view a decrease of 30 % in average particle size in MB-MBR due to the optimized percentage of carriers added to the MB-MBR (20% of effective volume). In a situation where this percentage is very low, there will be no significant improvement in membrane fouling retardation. In case, this percentage is very high, the negative influence of floc-breakage on membrane fouling behavior will surpass the positive effect of mechanical membrane scouring by colliding media (Huang *et al.*, 2008).

Therefore, the size, shape and % fill volume of the carriers in the MB-MBR controls the synergetic effect on bio-particle size distribution and membrane filtration. However, floc size tends to be influenced by various other factors including sludge

age, aeration intensity and reactor configuration (Galil *et al.*, 1991; Jamal Khan and Visvanathan., 2008).

4.6 INFLUENCE OF EXTRACELLULAR POLYMERIC SUBSTANCE (EPS) ON MEMBRANE FOULING

Membrane fouling is significantly influenced by EPS concentration, which is considered to be an important foulant (Drews *et al.*, 2006; Meng *et al.*, 2009; Sheng *et al.*, 2010). EPS is a heterogeneous matrix containing variety of polymeric materials such as: carbohydrates, proteins, lipids, and nucleic acids, etc originating from cell lysis, microbial metabolites or un-metabolized wastewater components. These constituents are either embedded in the floc matrix (bound EPS) or freely suspended/dissolved in the supernatant (soluble EPS) (Drews *et al.*, 2006). Generally, the sum of protein and carbohydrate is considered to represent the total amount of EPS as these are the dominant components in soluble EPS and bound (extracted) EPS (Frølund *et al.*, 1996).

EPS also accelerate the formation of microbial aggregates through binding cells closely (Liu *et al.*, 2004). Li and Yang. (2007) reported that sludge fed with glucose had more EPS production than that feed with acetate which highlights the fact that EPS generation depends on the substrate composition and concentration. Nutrient levels also have significant effect on EPS production and composition as well. Jang *et al.* (2007) investigated that increase in food to microorganism ratio increases the EPS content in sludge. Moreover, Meng *et al.* (2006) found that filamentous bacteria produced more bound EPS as compared to floc forming bacteria, thus the presence of

excess filamentous bacteria can be responsible for rapid fouling rate due to high EPS content.

As shown in Fig. 4.6, the averaged soluble EPS (sEPS) concentration was found to be 170 and 94 mg/L in C-MBR and MB-MBR, respectively. sEPS concentration in C-MBR was much higher as compared to MB-MBR. Since higher sEPS excretion is related to greater fouling tendency, the C-MBR fouling rate was higher than that of MB-MBR as depicted by the TMP profiles (Fig. 4.1).

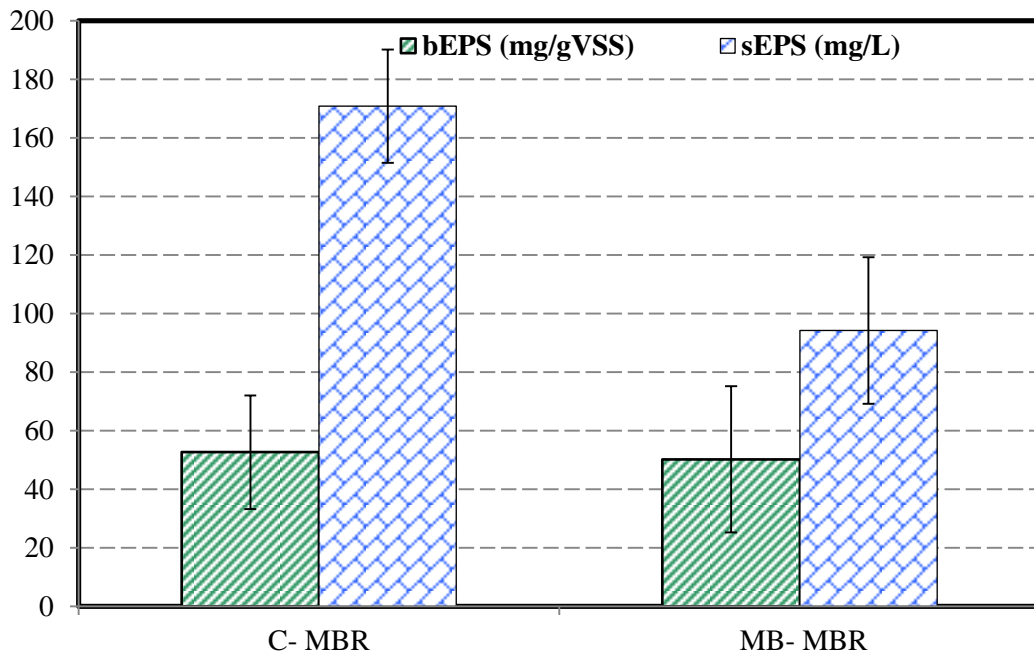


Figure 4.6: Averaged EPS concentration in both MBR

Bound EPS (bEPS) in both MBRs was in close range to each other i.e., 50.2 and 52.6 mg/g VSS in C-MBR and MB-MBR, respectively. It can be inferred that higher secretion of sEPS can also be a major contributing factor to higher fouling in C-MBR.

Figure. 4.7 exhibits protein and carbohydrate fractions of sEPS in both MBRs and carbohydrate fraction was the predominant one of the total sEPS. C-MBR carbohydrate concentration was 158 mg/L as compared to 79 mg/L in MB-MBR. Protein fraction was comparatively minimal and can be considered as having no significant impact on membrane fouling. Protein values of 10.7 and 12.9 mg/L were recorded in C-MBR and MB-MBR, respectively. It can be inferred that carbohydrate concentration contributed more towards membrane fouling of the MBR system as previously reported by Drew *et al.* (2006).

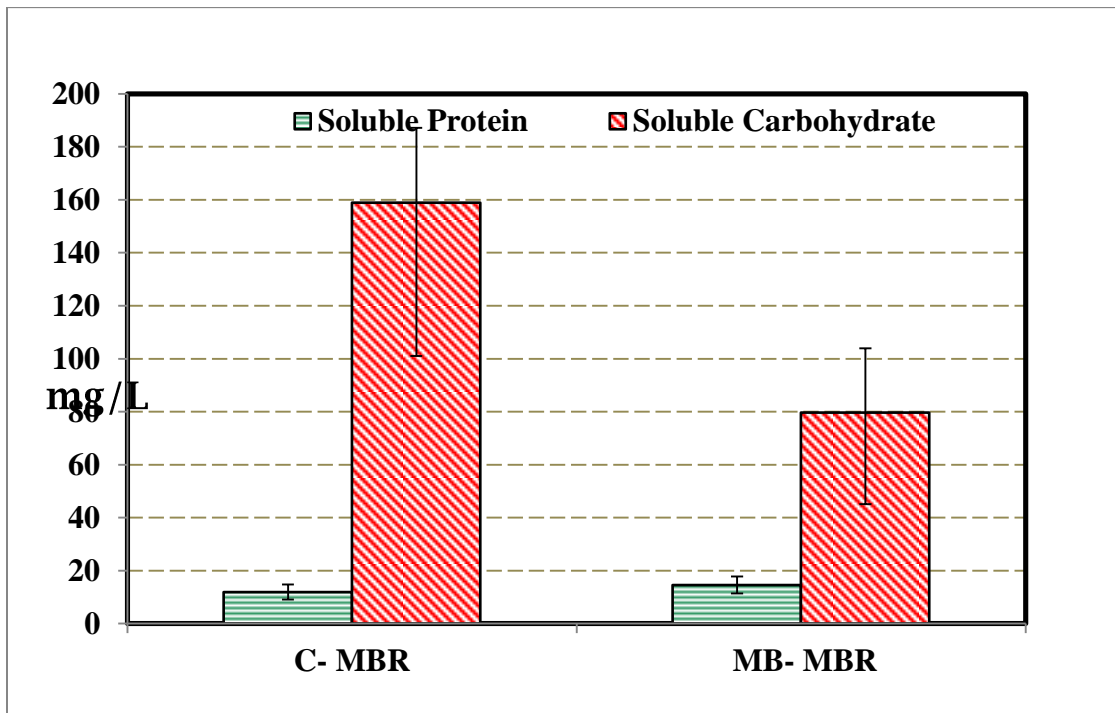


Figure 4.7: Protein and carbohydrate fractions of soluble EPS in MBR systems

Meng *et al.* (2009) reported that bound EPS (bEPS) is a major sludge floc component keeping the floc in a three-dimensional matrix. Fig. 4.8 shows that the protein fraction of bEPS concentration in both MBR systems was higher as compared to bound carbohydrate EPS. Bound EPS is growth-related and is produced in direct proportion to substrate utilization (Laspidou and Rittmann., 2002).

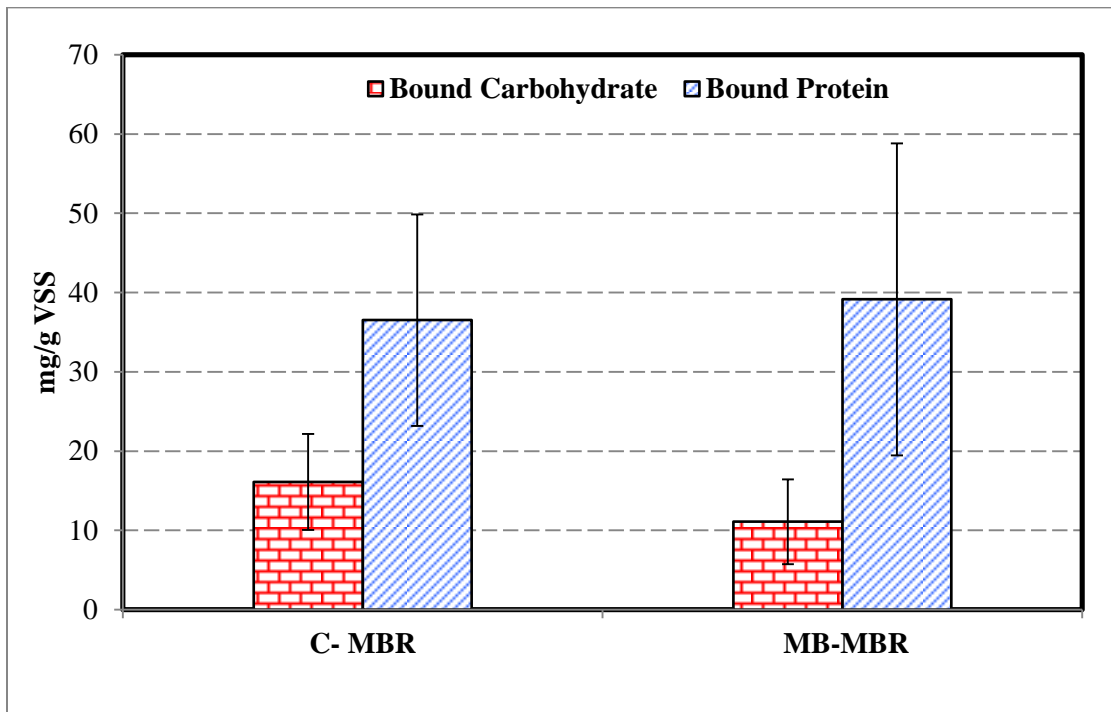


Figure 4. 8: Carbohydrate and protein fractions of bound EPS in MBR systems

The predominance of protein in bEPS (Protein/Carbohydrate > 2) could be due to the fact that cellular structures and enzymes are mostly protein in nature (Meng *et al.*, 2006). Yamato *et al.* (2006) and Geng and Hall. (2007) found that there was no clear relation between bound EPS and membrane fouling. In this study as well, as shown in Fig. 4.8, bEPS fractions were almost similar and no direct relation with membrane fouling could be established.

4.7 BIOLOGICAL ENVIRONMENT

4.7.1 General Appearance and MLSS/MLVSS

Color of the sludge throughout the experimental stage was yellowish-brown instead of dark-brown or khaki. However the color of C-MBR turned pale yellow during winter season and the concentration of MLSS dropped as well. Sludge was slimy with temperature drop resulting in rapid fouling of C-MBR. No cake layer on SG MBR was observed and intense internal fouling was noticed during this period.

Yang *et al.* (2009) reported that the specific color was due to addition of sponge which had an effect on the microbial community resulting in different color. The addition of sponge media aided biomass to grow within the pores resulting in growth of different microorganisms. Due to porous media and collision with the walls of the reactor the membrane pores exhibited no visible film on the sponge cubes and the biomass was entrapped within the sponge cubes.

Initially SRT of 30 days was maintained in both reactors having an equal MLSS of approximately 9.05 g/L. But with seasonal variation as temperature dropped the MLSS also decreased in C-MBR to 6.39 g/L and sludge wastage was stopped. However, with rise of temperature the steady state was achieved and excessive growth of MLSS was recorded after which SRT of 25 days was set and the MLVSS of 9.0 g/L and 9.5 g/L was present in mixed liquor in C-MBR and MB-MBR respectively. MLVSS/MLSS fraction representing active biomass in sludge was in the range of 0.7-0.85 in both conditions. The figure 4.9 below shows the detail.

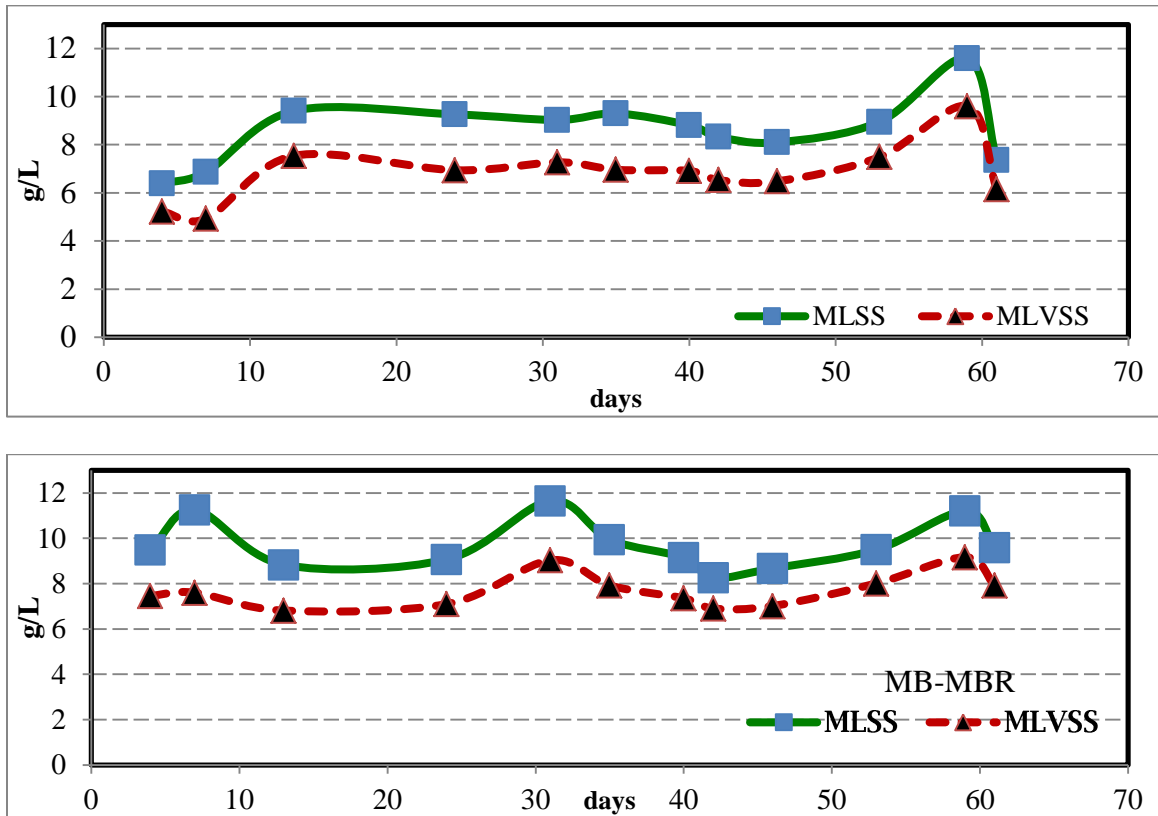


Figure 4.9: MLSS & MLVSS concentration in both MBR systems

4.7.2 Performance Evaluation:

Membranes treatment performance was measured in terms of nutrients removal, TOC/TN removal and Specific oxygen up take rate (SOUR).

Table 3 below shows the overall treatment performance of both bioreactors. C-MBR $\text{NH}_4\text{-N}$ removal was higher than MB-MBR. This can be related to the growth of nitrifiers in the system. TN removal was almost same in both reactors. Phosphorus removal was also in close range to each other. 59.8 and 57.65 % removal in C-MBR and MB-MBR was achieved. C-MBR showed better TOC removal as compared to MB-MBR having a removal efficiency of 53.1 and 43.7 % respectively.

Table 4.2: Treatment Performance of both MBRs

Parameter/ System	Effluent Concentration				Removal Efficiency	
	C-MBR	S.D	MB-MBR	S.D	C-MBR	MB-MBR
NH ₄ -N	17.40	±10.76	23.82	±8.24	86.11	77.24
NO ₂ -N	18.25	±12.20	8.32	±9.24	-	-
NO ₃ -N	9.00	±14.00	19.69	±7.10	-	-
TN	36.4	±1.40	34.4	±8.12	67.93	69.68
PO ₃ -P	7.74	±1.47	8.11	±1.14	59.80	57.65
TOC	11.2	±3.72	13.6	±3.14	53.15	43.74
COD	-	-	-	-	95±2.69	90.3 ± 6.81

Average influent TOC recorded was 642.6 mg/L and TN 104.7 mg/L respectively and average effluent TOC values in C-MBR and MB-MBR were recorded as 11.2 and 13.6 mg/L respectively. (Chu *et al.*, 2011) reported that up to 90% of TOC removal efficiency was achieved in reactor filled with Polyurethane foam at a hydraulic retention time of 14 h. The bioreactor filled with polyurethane carriers showed better performance in TOC and ammonium removal because of the entrapment of various microorganisms on the pores of the PU carriers which enhance nitrifies to inhabit.

CONCLUSIONS AND RECOMMENDATIONS

This study investigated the fouling behavior under the affect of sponge carrier fed MBR (MB-MBR) in comparison to conventional submerged MBR (C-MBR). It was demonstrated that MB-MBR exhibited longer filtration runs due to low membrane fouling resistances both reversible (R_c) and irreversible (R_f) as compared to that in C-MBR. The higher cake layer resistance (R_c) in C-MBR was influenced by the non-porous cake layer structure comprising of predominant filamentous bacteria having serious negative effect on membrane permeability. The pore blocking resistance (R_p) was influenced by the high soluble EPS deposition and adsorption on the membrane wall sand within pores accelerating the fouling rate in C-MBR.

The conclusions drawn from this study and recommendations for future studies are given as under.

5.1 CONCLUSIONS

Following conclusions were drawn from this study:

1. The addition of media has a vivid effect on filtration performance of the MB-MBR. Scouring effect of the media discourages excessive cake layer formation of the membrane surface.

2. Rod shaped filamentous bacteria were observed in C-MBR sludge which can lead to floc formation but excessive growth can cause severe fouling of the membrane.
3. The irreversible fouling was predominant in C-MBR due to high soluble EPS content.
4. Particle size did not decrease significantly with increase % media volume fraction.

5.2 RECOMMENDATIONS

Following recommendations are noteworthy for further study.

1. The microbial community should be explored for further understanding of the fouling behavior of MBR.
2. The energy consumption of the systems should be investigated and optimized.
3. Other media types should be introduced into the system to investigate fouling and treatment performance.

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APPENDIX - A

EPS MEASUREMENT

Cation Exchange Resin (CER)

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

Table A- 1: CER buffer solution constituents

Chemical name	Concentration	Amount in 1 L DI water
Na ₃ PO ₄ .12H ₂ O	2 mM	$380 \times 2 / 1000 = 0.76$ g
NaH ₂ PO ₄ .2H ₂ 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

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 % Phenol solution
- Sulfuric acid (H₂SO₄)
- D-Glucose for standard solution

Procedure

Standardization:

1. Make all measurements in duplicate

- 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.
- 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.
- Allow the tubes to stand 10 min.
- Thoroughly mix the solutions using vortex machine.
- Place in water bath for 15 min to cool the solutions
- Measure absorbance at 490 nm.
- Prepare a calibration curve of concentration of sugar (Glucose-D) versus absorbance (Figure A-1).

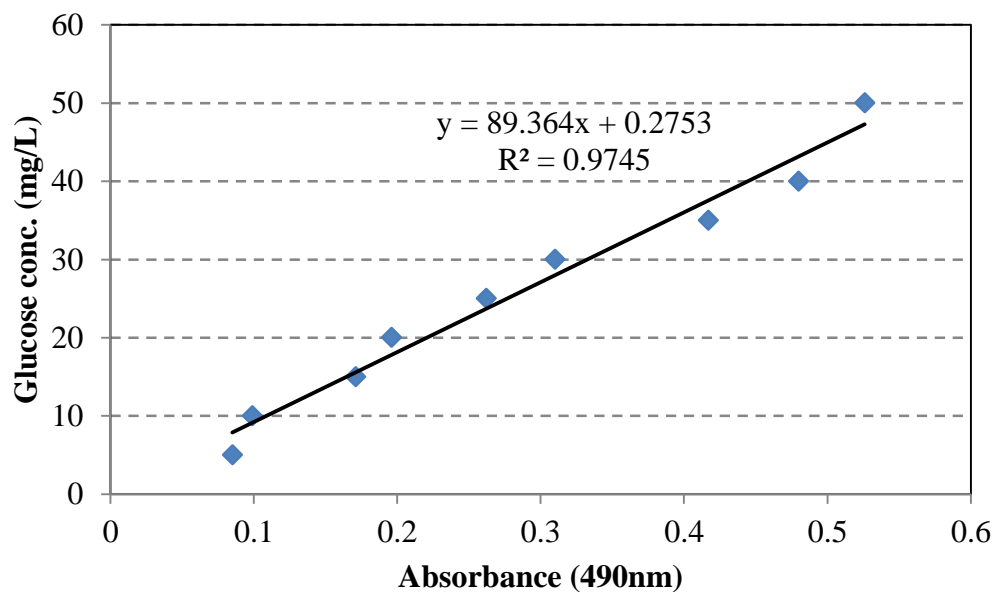


Figure A- 1: Standard curve of carbohydrate

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/g VSS for bound EPS.

Calculations

Soluble EPS

According to the carbohydrate standard curve and with the dilution factor (2):

$$\text{Carbohydrate (mg/L)} = 2 \times (89.36 \times \text{ABS} + 0.275) \quad \text{Equation A-1}$$

Bound EPS

According to the carbohydrate standard curve and with the dilution factor (2):

Carbohydrate mg gVSS

$$= \frac{2 \times 89.36 \times \text{ABS} + 0.275 \text{ mg/L} \times \text{Final Volume(mL)}}{\text{VSS g L} \times \text{Original Volume(mL)}}$$

Equation A-2

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
- Na_2CO_3
- 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;

- 20 g Na_2CO_3
- 4 g 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 10 min
5. Add 0.25 mL Solution D and thoroughly mix again.
6. After 20 min, measure absorbance at 750 nm.
7. Prepare a calibration curve of protein (BSA) concentration (mg/L) versus absorbance.

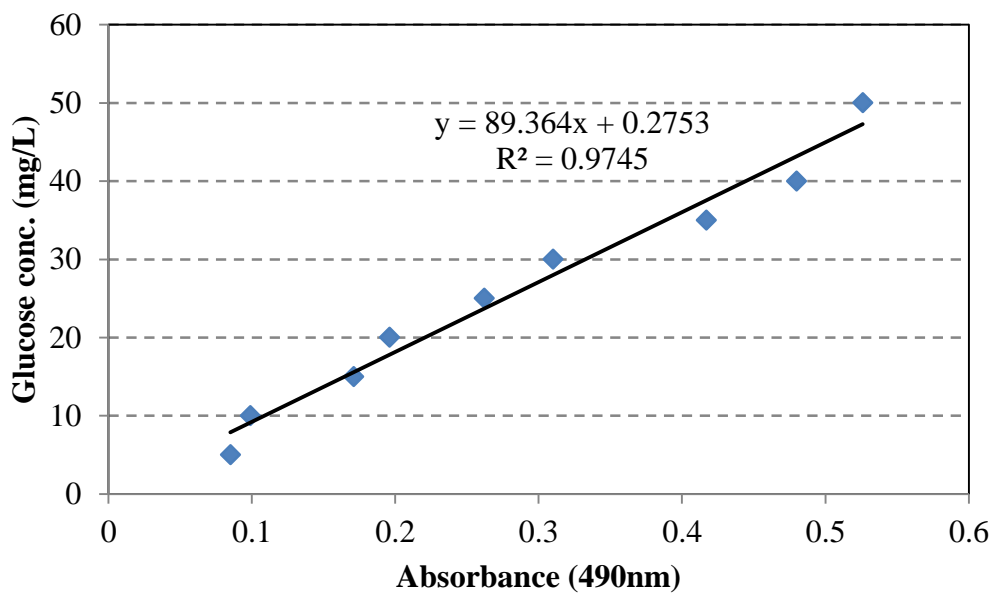


Figure A- 2: Standard curve of protein (BSA)

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.

Calculations

Soluble EPS

According to the protein standard curve:

$$\text{Protein (mg/L)} = 287.63 \times \text{ABS} - 0.2823 \quad \text{Equation A-3}$$

Bound EPS

According to the protein standard curve and with the dilution factor (2):

$$\text{Protein mg gVSS} = \frac{2 \times 287.63 \times \text{ABS} - 0.2823 \text{ mg/L} \times \text{Final Volume(mL)}}{\text{VSS g L} \times \text{Original Volume(mL)}}$$

Equation A-4

APPENDIX B

SLUDGE CHARACTERISTICS

Table B- 1: MLSS and MLVSS concentrations in C-MBR and MB-MBR.

Day	MB-MBR			C-MBR		
	MLSS	MLVSS	MLVSS/MLSS	MLSS	MLVSS	MLVSS/MLSS
4	9.49	7.46	0.79	6.39	5.22	0.82
7	11.25	7.6	0.68	6.87	4.93	0.72
13	8.83	6.81	0.77	9.41	7.54	0.80
24	9.07	7.1	0.78	9.26	6.94	0.75
31	11.65	9.03	0.78	9.03	7.27	0.81
35	9.94	7.92	0.80	9.3	6.96	0.75
40	9.15	7.35	0.80	8.81	6.91	0.78
42	8.26	6.9	0.84	8.33	6.53	0.78
46	8.67	7.01	0.81	8.1	6.48	0.80
53	9.5	8.01	0.84	8.95	7.49	0.84
59	11.21	9.16	0.82	11.59	9.6	0.83
61	9.59	7.92	0.83	7.36	6.15	0.84
65	10.21	8.16	0.80	12.26	9.59	0.78
69	8.12	6.03	0.74	13.96	10.42	0.75
Average	9.5	7.6	--	9.0	7.3	--
S.D	1.11	0.85	0.04	2.09	1.60	0.04

Table B- 2: sEPS and bEPS concentrations in the MB-MBR.

MB-MBR						
Serial No.	Bound		Total	Soluble		Total
	Carbohydrate	Protein		Carbohydrate	Protein	
1	9.8	18.5	-	BDL	BDL	-
2	5.3	18.2	-	99.0	18.8	-
3	16.0	66.7	-	73.5	12.9	-
4	4.5	52.9	-	24.7	15.5	-
5	18.2	20.8	-	58.3	15.5	-
6	14.64	47.3	-	104.21	9.2	-
7	9.14	49.6	-	118.15	15.2	-
Average	11.1	39.1	50.2	79.6	14.6	94.2
S.D. ±	5.3	19.7	25.0	34.6	3.2	37.8

Table B- 3: bEPS concentrations in the C-MBR.

Serial No.	Bound		Total	Soluble		Total
	Carbohydrate	Protein		Carbohydrate	Protein	
1	12.4	23.3	-	BDL	BDL	-
2	10.2	17.8	-	BDL	BDL	-
3	12.7	37.7	-	252.9	7.8	-
4	14.7	38.5	-	111.5	13.2	-
5	28.2	35.2	-	163.19	10.6	-
6	19.49	58.0	-	156.40	12.7	-
7	15.17	45.0	-	110.6	15.2	-
Average	16.1	36.5	52.6	158.9	11.9	170.9
S.D. ±	6.1	13.3	19.4	58.0	2.8	60.8

Table B- 4: Particle size distribution of MBR systems

Dated	C MBR				MB-MBR			
	Range				Range			
	2--51	52-88	89-152	153-200	2--51	52-88	89-152	153-200
25-Jan	10.5	8.747	19.982	16.355	13.19	10.38	21.35	12.697
1-Feb	9.72	12.078	26.055	16.785	10.84	16.29	30.59	15.304
7-Feb	6.642	5.196	18.224	17.461	9.38	12.64	30.85	17.295
11-Feb	7.24	4.213	16.315	17.235	15.98	17.75	32.89	14.13
23-Feb	7.68	6.202	21.941	19.568	11.69	12.135	30.574	17.625
28-Feb	7.39	8.245	24.232	18.724	12.5	12.766	30.885	16.881
3-Mar	6.65	4.427	18.222	18.945	16.56	16.331	30.895	14.67
7-Mar	11.87	7.491	19.804	16.981	14.74	13.586	28.246	16.005
10-Mar	7.565	4.42	15.938	17.635	13.6	13.831	28.515	16.038
15-Mar	9.36	4.464	15.445	17.332	15.76	15.524	29.182	14.983
average	26.68	17.72	20.46	10.93	29.87	25.15	23.08	8.72
SD	1.79	2.58	3.56	1.04	2.37	2.29	3.14	1.52

APPENDIX C

MBR'S PERFORMANCE PARAMETERS

Table C- 1: Influent, sCOD, effluent COD concentrations and corresponding removal efficiencies in MBR

day	Influent	Q	MB-MBR				C-MBR			
			sCOD	% Removal	COD	%Removal	sCOD	% Removal	COD	%Removal
21	982	28	41.6	95.8		100.0	96	90.2		100.0
25	990	32	45	95.5	29.0	97.1	88.0	91.1	39.0	96.1
33	1005	33	52	94.8	24.0	97.6	65.0	93.5	29.0	97.1
36	1010	28	64	93.7	44	95.6	71.0	93.0	40.0	96.0
39	990	31	72.5	92.68	56.00	94.34	100	89.90	65	93.43
41	991	26	85.6	91.36	69	93.04	81	91.83	42.0	95.76
47	989	35	46.1	95.34	33	96.66	77	92.21	49.0	95.05
52	1005	28	45	95.52	29	97.11	62	93.83	44	95.62
59	989	33	51	94.84	37	96.26	59	94.03	40	95.96
61	1024	33	224	78.13	67.2	93.44	249	75.68	BDL	100.00
68	1120	32	105.6	90.57	67.2	94.00	147	86.88	57.6	94.86
70	1015	26	227	77.64	70.4	93.06	265.6	73.83	99.2	90.23
74	1116	33	233.6	79.07	102.4	90.82	256	77.06	86.4	92.26
77	944	33	96	89.83	83.2	91.19	195.2	79.32	BDL	BDL
81	1020	31	294	71.18	99	90.29	243.2	76.16	BDL	BDL
84	1006	34	284.8	71.69	102	89.86	240	76.14	BDL	BDL

Table C- 2: Nitrogen balance in MBR's.

Influent	MB-MBR						C-MBR					
	NH ₄ +-N	%NH ₄ -N Removal	NO ₂ -N	NO ₃ -N	TN	% TN Removal	NH ₄ -N	%Removal	NO ₂ -N	NO ₃ - N	TN	% TN Removal
94	16	77.0	1	23.7	40.7	56.70	5	94.68	25	28	58	38.30
98	8.8	89.0	9	12.5	30.3	69.08	13	86.73	3.5	10	26.5	72.96
91	13	76.7	5.6	11.6	30.2	66.8	9.1	90.0	11.0	4.7	24.8	72.8
96	11	84.5	2.0	8.7	21.7	77.4	16.2	83.1	6.8	26.0	49.0	49.0
88	16	69.8	4.2	8.9	29.1	66.9	10.6	88.0	8.9	15.0	34.5	60.8
92	7.9	83.4	10.7	3.6	22.2	75.9	20.0	78.3	1.3	45.0	66.3	27.9
92	15.5	75.2	5.0	16.5	37.0	59.8	7.7	91.6	34.3	40.0	82.0	BDL
91	27	61.3	8.0	0.7	35.7	60.8	22.0	75.8	23.0	4.7	49.7	45.4
115	42.3	78.2	1.0	0.4	43.7	62.0	15.2	86.8	24.0	24.4	63.6	44.7
95.22	23.8	77.24	8.32	9.00	32.2	66.15	17.40	86.11	18.2	19.69	55.3	51.47
8.0	17.2	8.2	9.2	7.1	7.6	7.1	10.8	6.1	12.2	14.0	20.5	16.1

Table C- 3: Phosphorous balance in MBR's

DAY	PO ₄ -P influent	PO ₄ -P effluent MB-MBR	% Removal	PO ₄ -P influent	PO ₄ -P effluent C-MBR	% Removal
0 7	20.5	6.4	68.78	20.5	4	80.49
1 5	20.00	7.50	62.50	20	8.5	57.50
2 4	21.00	6.30	70.00	21	7.1	66.19
3 6	18.5	9.6	48.11	18.5	9.8	47.03
3 9	20.5	8.9	56.59	18.5	8.9	51.89
4 2	19	10	47.37	21.5	7.6	64.65
4 7	17.5	9.2	47.43	19	8	57.89
55	17	8.5	50.00	17	8.3	51.18
59	18	8.3	53.89	18	9	50.00
61	21.5	7.4	65.58	21.5	6.1	71.63
63	18	7.7	57.22	18	7.7	57.22
65	18.5	8.3	55.14	18.5	8.5	54.05
69	22	7.3	66.82	22	7.1	67.73
AVERAGE	19.38	8.11	57.65	19.54	7.74	59.80
SD	1.62	1.14	8.31	1.63	1.48	9.75

APPENDIX D

MBR'S FOULING PROPOENSITY

Table D- 1: Specific Cake resistances of MBR systems

C-MBR		MB-MBR		
MLSS(Cb)(kg/m3)	Alpha	MLSS(Cb)(kg/m3)	Alpha	
9.26	1.40103E+13	9.07	3.00E+12	
8.81	5.10656E+12	9.15	5.71722E+12	
8.93	1.5231E+12	7.32	3.14447E+12	
8.93	6.32672E+12	7.32	1.27208E+13	
7.3	5.87621E+12	9.5	6.49777E+12	
12.63	3.23071E+12	10.2	7.69303E+12	
13.9	1.88175E+12	8.12	6.31359E+12	
12.2	3.60185E+12	9.8	3.09605E+12	
10.4	3.62164E+12	8.1	8.00834E+12	
10.24	1.37934E+13	8.35	1.47854E+13	
Average	10.26	5.89722E+12	8.693	7.09758E+12