OPTIMIZATION OF SUBMERGED MEMBRANE BIOREACTOR (MBR) USING RESPONSE SURFACE METHODOLOGY (RSM)

By

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NUST201362918MSCEE652113F

A thesis submitted in partial fulfilment of the requirements
for the degree of Master of Science

in

Environmental Engineering

Institute of Environmental Sciences & Engineering (IESE)
School of Civil & Environmental Engineering (SCEE)
National University of Sciences & Technology (NUST)
Islamabad, Pakistan
2016

It is certified that the contents and form of thesis entitled

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Has been found satisfactory for the requirements of the degree of Master of Science in

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DEDICATED TO

I dedicate this dissertation work to my parents, wife and daughter Umm-e-Aiman Abbas (the ultimate love and reason to live for), for their prayers and support. I would not forget to mention Mr. Qaisar Abbas, my inspiration, for his moral and financial support wherever and whenever needed.

ACKNOWLEDGEMENTS

All praise and thanks are for Almighty ALLAH, who is the source of all knowledge and wisdom endowed to mankind and to the Holy Prophet MUHAMMAD (PBUH) who showed light of knowledge to humanity as a whole.

I would like to express my sincere gratitude to my supervisor and mentor Dr. Sher Jamal Khan. His wide knowledge and his logical way of thinking have been of great value for me. His understanding, encouraging, and personal guidance have provided a good basis for this study. I am also thankful to Dr. Zeeshan Ali Khan and Prof. Dr. Liaqat Ali Qureshi for their continuous guidance and support.

Thanking the batch of MS-2013, the whole IESE Faculty, admin and Lab staff for providing me the second home at NUST. Engr.Muhammad Bilal Asif, Engr. Rasikh Habib and Fakhar Hassan were always happy to help me, thank you to them too.

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ABBREVATIONS

Abbreviations	**Description**
MBRs	Membrane Bio Reactors
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
CASP	Conventional Activated Sludge Process
CFV	Cross Flow Velocity
CMBR	Conventional Suspended Growth MBR
EPS	Extra Polymeric Substance
SMPs	Soluble Microbial Products
F/M	Food to Microorganism Ratio
HF	Hollow Fiber
HRT	Hydraulic Retention Time
SRT	Solid Retention Time
J	Operational Flux
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
OLR	Organic Loading Rate
S-MBR	Submerged Membrane Bioreactors
S-COD	Soluble Chemical Oxygen Demand
UF	Ultra Filtration
MF	Micro Filtration
NF	Nano Filtration
RSM	Response Surface Methodology
BBDM	Box-Behnken Design Model
ANNOVA	Analysis of Variance

ABSTRACT

Water is a valuable reserve for the endurance of mankind but we are losing it every day. We can conserve or recharge our ground water by using treated wastewater as an alternative water resource or recharging the ground water respectively. The conventional methods to treat the wastewater are not meeting the recent discharge standards. Eliminating the process of sedimentation, the membrane bioreactor (MBR) is the well-organized way of treating wastewater by the combination of biological process and membrane technology. However, there are some limitations which restrict its applicability i.e. membrane fouling and energy consumption etc. current study focuses on investigating the fouling behavior which is mainly due to increasing flux demand and lack of backwashing and proper relaxation modes in an MBR. Therefore, optimization of these parameters was studied; (1) Flux, (2) Backwashing and (3) Relaxation patterns. The job was done by using Box-Behnken Design Model (BBDM) (Response Surface Methodology (RSM)). The bench scale MBR was installed at wastewater Technology Lab of University. Sewage Treatment Plant, Islamabad provided the mixed liquor suspended solids (MLSS) which was acclimatized with real domestic wastewater (UET, Taxila) for a period of 30 days. To get the medium strength raw water, the half an hour's pre-sedimentation was allowed. Chemical oxygen demand (COD) of 390.6 ± 25.3 mg/L was recorded initially. The sludge retention time (SRT) was maintained at 28 days which resulted in MLSS concentration range of 7000 and 8000 mg/L. The influence and interaction of flux, backwashing and relaxation was examined and regression models were recognized. The optimization of these parameters was achieved by BBDM. At the same time membrane fouling and permeate quality was analyzed. As a result, flux backwashing and relaxation were predicted as 18.57 LMH, 9.70 sec and 90 sec respectively. The predicted values of TMP, COD, NH3-N, TN and TP were checked and found close to the predicted ones i.e., 21.1058 (KPa), 86.0786%, 72.2403%, 80.6827 and 62.2122% respectively.

Keywords: Membrane fouling, Backwashing, Relaxation, Flux, Box-Behnken Design Model (BBDM), Response Surface Methodology (RSM), Optimization.

Chapter 1

INTRODUCTION

1.1 Background

Water will remain a critical and limiting resource for sustained economic development of the country (Ahmad, 2004). Pakistan is by now one of the mainly water-stressed states in the world; a position that is going to absolute water paucity (World Bank, 2005). The call for the day is to decrease the persistently rising stress on present water possessions for sustainable development. One potential way out to the trouble is wastewater reclamation and reuse through treatment. It is important to treat wastewater before it finds its way to fresh water bodies. The need for cleaner water is increasing day by day therefore the effluent limits go stringent and increase the call for for an advance wastewater treatment system (Liang *et al*., 2010). Wastewater treatment refers to bring used water in a more suitable state for desired usage. Recharge of the groundwater is one of the key profits of reclamation of wastewater. The treated wastewater may also be utilized for agricultural purposes, some industrial activities and other non potable objectives. Hence we must consider wastewater a resource instead of considering it a waste. Now is the time to fix the mismanagement of the wastewater by applying different treatment techniques and replenishing the water bodies.

1.2 Conventional Wastewater Treatment

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 process (CASP) 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 a substitute to attain elevated quality discharges, compact plants and inexpensive management (Ødegaard, 2000).

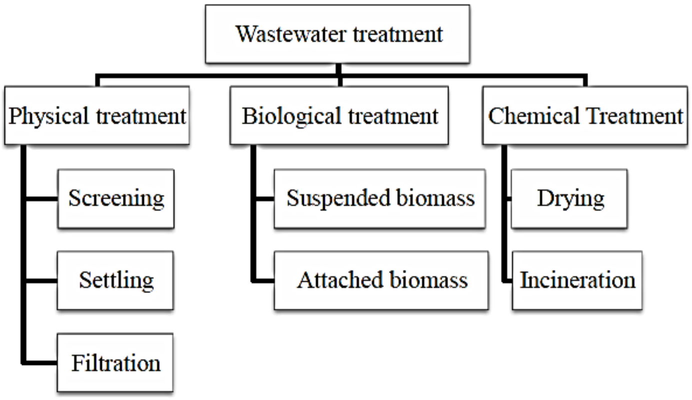


Figure 1.1: Wastewater Treatment (adapted from Henze *et al*., 2008)

1.3 Biological Wastewater Treatment

Treatment system in which natural role of bacteria is utilized for bioconversion; the biological flocs and biofilms are used for degrading or adsorbing dissolved colloidal, settleable and particulate matter (Henze *et al*., 2008). Biological treatment processes include both aerobic and anaerobic systems. Aerobic biological wastewater treatment systems make use of mixed microbial consortia to transform organic and inorganic pollutants to harmless byproducts that can be released easily into the environment (Dias *et al*., 2003). Aerobic technologies are mostly implied for treatment of municipal and industrial wastewaters. But use of anaerobic systems has now increased because of its low construction, operation and maintenance cost. However the biomass production is low and the effluent requires post treatment because of high COD along with nutrients and pathogens (Gašpariková *et al*., 2005).

1.4 Membrane Bioreactors

Membrane bioreactor is state of the art technology capable of treating wastewater successfully. It is progressively being used more as an highly developed technology for biological wastewater treatment. It is considered and experimented to be efficient in removing harmful substances and volatile organic compounds from wastewater (Fallarh, *et al*., 2010). The membrane bioreactor (MBR) systems may be placed as a substitute to accomplish the compact wastewater treatment plants designing.

MBR is a combination of biological process (aerobic biomass) and membrane filtration using either micro or ultra/filtration (Kim *et al*., 2011). This idea was first commercialized in 1970's and since then MBR usage has widely increased. A 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). As the MBR is well capable of separating the organic matter from the feed wastewater, the product water i.e., treated wastewater may be utilized for agricultural purposes, horticulture, cleaning or cooling the water in industries, sanitary uses and other objectives as already stated.

The Membrane Bioreactor utilizes micro or ultra-filtration membranes with pore sizes ranging from 0.01–0.4 µm for solid/liquid segregation removing the secondary clarifiers from the conventional systems. The major advantages are that it enables the independent control of sludge retention time (SRT) which ensures increased nitrification ability of the sludge, low hydraulic retention time (HRT) for compact footprint, 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).

Membrane fouling is the key phenomenon in the repute of MBR technology as it is restricting its widespread use. The membrane fouling can be distinct as the unwanted deposition and buildup of microbes, colloids, solutes, and cell debris within/on the surface of membranes. Fouling mechanisms are macromolecule adsorption, pore blocking and cake deposition. Principle fouling elements include the clogging and sludge cake adherence which reduces the permeate flux or increase the trans-membrane pressure (TMP) relying upon the type of operation (Lee *et al.*, 2001). It is the net result of solute/colloids adsorption on membrane, accumulation of sludge flocs of membrane surface, cake layer formation on the surface of membrane and changes in foulant composition with time and space (Meng *et al.*, 2009).

Normally fouling is of three categories; 1) removable fouling 2) irremovable fouling and 3) irreversible fouling. The first type may easily be removed by applying physical cleaning (e.g., backwashing) whereas the second type requires chemical cleaning to remove it. Type one is occurs due to loosely attached foulants. However, irremovable fouling is due to pore blocking and robustly attached foulants. The type three is also known as permanent fouling which cannot be eliminated by any of the technique.

As an option for the solution of membrane fouling, the addition of biofilm media in MBR is an good-looking option to conventional MBR which may decrease membrane fouling (Leiknes and Ødegaard, 2001). Supporting media helps in membrane surface scouring and the development of biofilm on the media advances the nutrients elimination competence. Basu and Huck (2005) investigated the effect of media in integrated bio-filter submerged membrane bio-reactors. Membrane fouling rate got almost double when the media was not introduced in their study.

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 present experimentation, fouling will be evaluated and discussed in hybrid MBR containing sponge as a moving media operated under different hydrodynamic environments.

1.5 Objectives of Study

The objectives of study were:

- Designing and installation of bench scale aerobic submerged MBR.
- Treatment of domestic wastewater employing hollow fiber membrane to produce high quality effluent.
- Identification of the membrane fouling control by providing concurrent relaxation and backwashing.
- Comparison between TMP of membranes of reference and experimental reactors.
- Performance/ efficiency evaluation of bench scale MBR.

1.6 Scope of the Study

During the research study, two bench scale MBRs (S-MBRs) were operated in the laboratory. MBRs were designed on the basis of mode of operation. The prime focus of the study was to determine the impact of simultaneous backwashing and relaxation on bio-fouling of hollow fiber (HF) membrane treating domestic wastewater. A comparison of fouling rate was determined between a reference reactor with no backwashing and an experimental reactor with permeate backwashing operating at a repeated cycle. The rate of change of trans-membrane pressure (TMP) was observed to ascertain the fouling behavior in both the membranes.

Chapter 2

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.

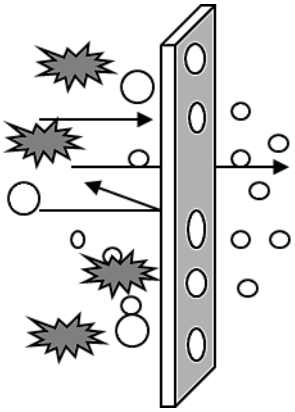


Figure 1: Perm- Selective Membrane

The level of selectivity relies on the openings and material 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. Various genres of membrane that are being used extensively include Micro-filtration, Ultra-filtration, Nano-filtration and reverse osmosis.

Micro-filtration is capable of removing suspended solids, colloidal particles and bacteria, ultra-filtration effectively removes proteins, colorants and natural organics, polyvalent ions are removed by Nano filtration and the rest of the monovalent ions are removed by reverse osmosis.

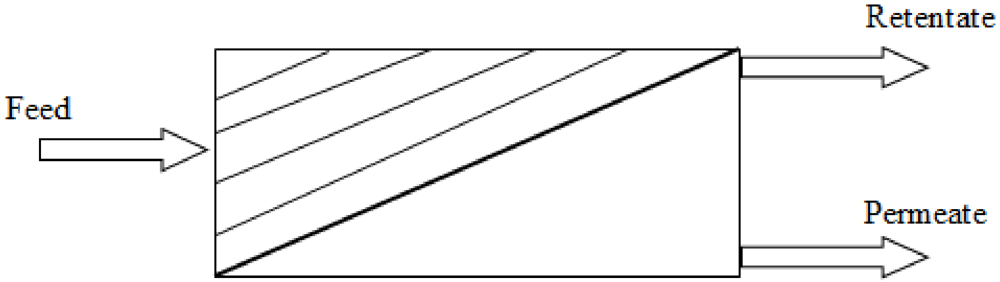


Figure 2.1: Schematic of Membrane

2.2 Membrane Processes

Domestic wastewater reclamation is understood to be a competent method to overcome rising demands of water possessions**.** Although, domestic wastewater due to pollutants may also contain possible health risks, cause of pathogenic infection and poisonous impacts. Therefore, municipal wastewater recovery requires an advance treatment technique to obtain better quality effluents, along with the considerations of financial viability (Chon *et al.*, 2011).

In a variety of wastewater treatment processes, use of membrane has increased to meet environmental regulations. Environmental awareness, laws and improved strength, efficiency and variety of treatment technologies have made the reuse of water more feasible (Hoinkis *et al.*, 2012). Membrane process appears to be well suited to fulfill the water quality requirements for reuse purposes (Jamal and Visvanathan, 2008).

Membrane process involves the separation of most of the suspended and colloidal material. Membrane separation process not only removes the required effluent compound but it can also improve and concentrate it as a product. This product can be recycled and re-used. Thus, pollutant disposed off finally into the environment is condensed leading to a novel and cleaner technology than the previous ones (Eliceche *et al.,* 2002).

2.3 Membrane Operational Modes

Membrane can be operated at various configurations and filtration modes depending upon the extent of impurity and nature of use. Two commonly used modes are dead-end filtration and cross-flow filtration approach.

Dead-end filtration is also known as direct filtration in which the flow of direction is perpendicular to the membrane. The entire feed stream passes through the membrane. The particles retained by the membrane result in cake formation on the surface of membrane. The deposited layer of these particles my damage and clog the pores of the membrane. There is no cross flow and the feed directly moves towards the filter medium. The filterable particles are settled on the filtered surface and with the passage of time fouling develops due to accumulation of solids which can be avoided through backwashing. This type of flow is preferable when feed caries low foulants. Dead-end filtration is advantageous in terms of resource recovery. Figure 4 illustrates dead-end filtration.

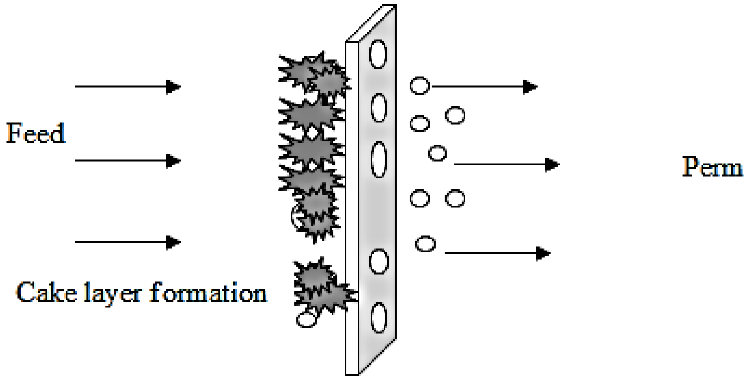


Figure 2.2: Dead-end filtration mode

In cross-flow filtration, the flow is tangential across the surface of the membrane. A fraction of influent passes from the membrane and is known as permeate and the respite is rejected. Cross flow filtration opposes cake formation as it scours the membrane surface along with the flow, until adhesive forces joining the cake layer to the membrane are balanced. Upon this equilibrium a steady state is achieved resulting in higher permeate flow. Figure 5 shows mechanism of cross flow filtration.

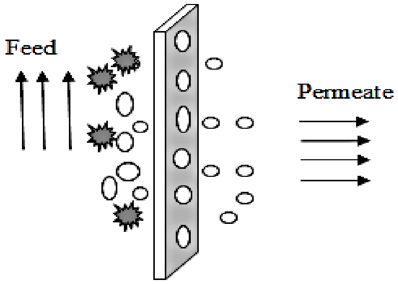


Figure 2.3: Cross flow filtration

2.4 Membrane Modules

MBRs depend on the ability of a membrane unit to pass all the flow coming to membrane so their configuration is very important. The broad range of membrane geometries control the micro or ultra-filtration, representing the membrane fouling tendency is related to the membrane module configuration. Six configurations currently employed for MBR are:

- Plate and frame/ flat sheet (FS)
- Hollow fiber (HF)
- Multi tubular (MT)
- Capillary tube (CT)
- Pleated filter cartridge (FC)
- Spiral wound (SW)

FS, HF and MT are the most suited to MBR because they permit turbulence and regular cleaning (Judd, 2011). For better understanding, their images are provided in Figure 6.

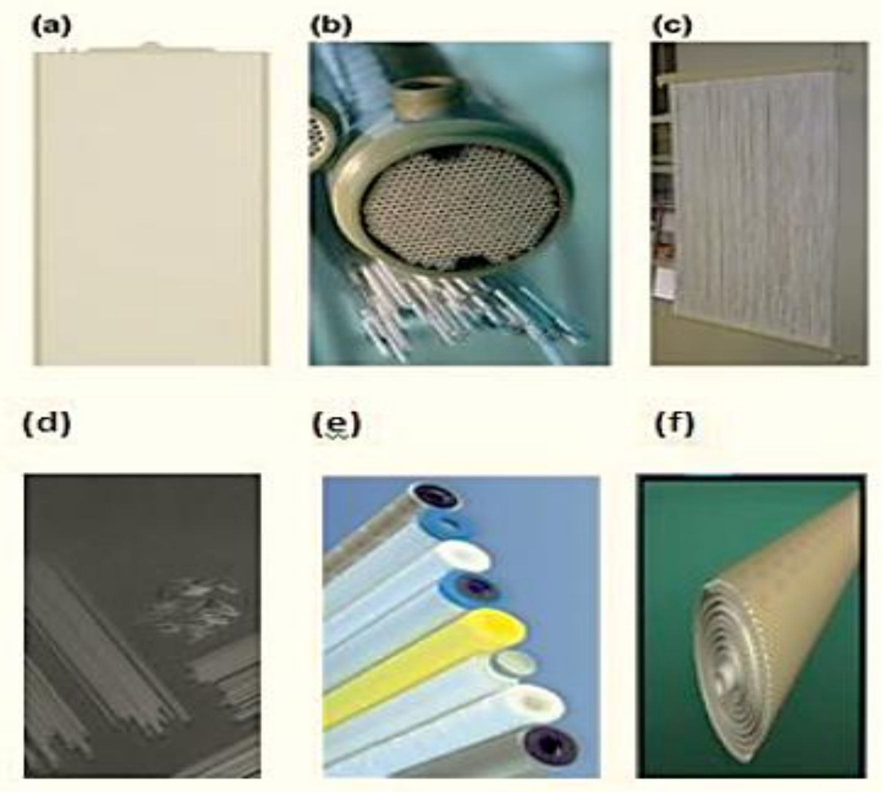


Figure 2.4: Membrane configurations **a)** Flat Sheet **b)** Multi Tubular **c)** Hollow Fiber **d)** Capillary Tube **e)** Pleated Filter Cartridge **f)** Spiral Wound

2.4.1 Hollow Fiber Membrane (HFM)

A hollow fiber scheme has several thin fibers positioned into a sealed unit known as cartridge. The influent wastewater for this system may be either inside of the fiber out or outside in. Effluent is captured from the inside or outside of the fiber at the opening end of the cartridge. Hollow fiber and spiral wound membranes present a huge surface area and permit extra filter through in a little quantity. Microfiltration and ultrafiltration configurations are usually used with simple tubular orientations or with flat sheet cells (EPA 2005).

The category of membranes for under study investigation was chosen as hollow fiber membrane, which have been effectively engaged in a broad range of industries such as food, juice, pharmaceutical, metal working, dairy, wine and most freshly domestic drinking water. The hollow fiber geometry offers a high membrane surface area to be restricted in a compact unit. This way huge volume can be filtered, while using minimum room, with less energy utilization.

Consequently, the hollow fiber membrane was applied in the whole study due to its attractive features. Additionally, since less experimentation has been carried out to explore the product water augmentation for hollow fiber membrane, it is necessary to study this extensively employed membrane in industries.

The primary intention was to be aware of the properties of membrane such as trans-membrane pressure (TMP) and temperature effects on product water flux, and conventional methods for membrane cleaning. The subsequent goal was to build up a mechanistic study of cleaning of particle-fouled membranes.

There are two diverse modes of filtration in hollow fibre membrane depending on the course of product water flow.

a. *Outside-in filtration*

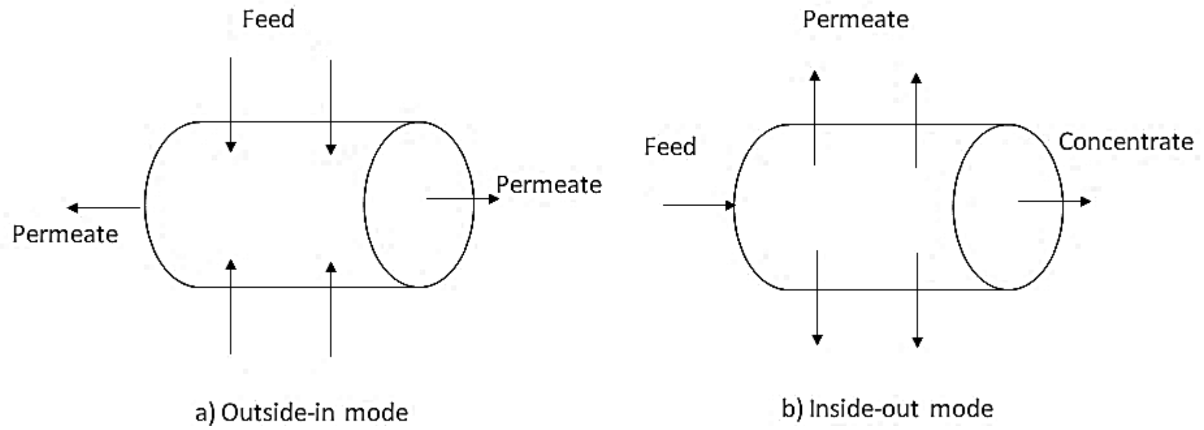
The main benefit of outside-in filtration is the ability of handling very high concentrations of suspended solids. All the commercially accessible hollow fibre modules run at outside-in modes. These modules are directly submerged in mixed liquor without pressure vessel, where influent water (mixed liquor) strikes the shell side of the membrane and effluent is collected by applying the vacuum. Air scouring is provided either constantly or intermittently in the shell side to avoid solids build up on the surface of membrane.

A number of outside-in modules used to treat the water with low suspended solids (<50 mg/L) run under dead-end mode, somewhere all the influent water passes from membranes leaving solids on the surface of membrane. A huge quantity of solids can be stored in the empty spaces between the fibers prior the unit fails to generate design flow rate at the maximum pressure permissible. Back flushing is carried out occasionally to get rid of the accumulated solids whenever pre-determined cycle time is reached or trans-membrane pressure (TMP) crosses the limit. Treated effluent is obtained by vacuum, where hollow fibers are horizontally mounted without pressure vessel. Most other modules for low suspended solids have the hollow fibers enclosed in a pressure vessel, which run under positive pressure at dead-end mode.

b. *Inside-out filtration*

These type of hollow fibers are fine to uphold consistent hydrodynamics in the lumen, but it is almost not achievable to produce the turbulence that is crucial to alleviate cake layer development due to the minute inside diameter and comparatively low water velocity. Additionally, merely the water with low suspended solids like surface water can be filtered by this type of membrane because the fiber lumen can be clogged by the particles present in the influent wastewater.

Fouled fibers can moderately or fully be improved by backwashing. If one fiber is clogged in the center, the concentrate from other unplugged fibers in the same unit can be fed to the clogged fibers from the downstream, which can at least moderately balance the loss of influent flow to the downstream of the plugged area.



a) Outside-in mode

b) Inside-out mode

Figure 2.5: Modes of filtration in Hollow-Fiber membranes

2.5 Membrane Morphology

The membrane performance is directly connected to the membrane morphology, like surface porosity, stuff, molecular weight, pore size, pore distribution and hydrophobicity etc. Thus, understanding of membrane linked with water filtration process is of vital significance for the choice of the most appropriate membrane to optimize its performance and fouling reduction.

2.5.1 Pore Size and Pore Size Distribution

Pore size is a further significant feature in the analysis of fouling pattern as it will directly affect the filtration. The filtration value increases significantly by decreasing the pore size (Koo *et al.*, 2012).

2.6 Membrane Filtration

Filtration can be done at various levels in MBR and those include micro filtration, ultra-filtration, nano-filtration and reverse osmosis. The pore size for micro filtration ranges from 0.1 to 1 micron. Ultrafiltration has a reduced pore size of 0.001 to 0.1 micron. Nano filtration separates salts and sugars from water and is thus used for water softening.

Membrane used in reverse osmosis is highly susceptible to fouling so the feed water requires intensive treatment. Reverse osmosis can remove almost everything from water lending in ultrapure for potable usage. The operating pressure increases for microfiltration and ultrafiltration membranes and the operational cost increases (Naveed *et al*., 2006). Usually the low pressure micro or ultrafiltration is used with membrane being immersed in the aeration tank (Bhatti *et al*., 2009).

Details of membrane filtration, their sizes and pathogen removal are given in Table 1.

Table 2. 1: Membrane Filtration and Pathogen Removal

Membrane Filtration	**Size (µm)**	**Removal**
Micro filtration (MF)	0.1	Removes suspended or colloidal particles and can retain Bacteria.
Ultra filtration (UF)	0.01	Removes organic macro molecules and has the ability to remove viruses.
Nano Filtration (NF)	0.001	Can remove dissolved contaminants and renders water soft.
Reverse Osmosis (RO)	0.0001	Designed to remove dissolved contaminants and remove almost everything from water.

2.7 Membrane Operation

The separation process that involves membrane splits a feed stream into two permeate streams recognized as permeate and retentate. A membrane is known as a fence, that apart two stages and bound carrying of a range of chemical materials. The flow that is separated by membrane is the permeate stream whereas the one retained by the membrane is the retentate. Any of the above streams can be the purpose of membrane separation depending upon the desire (Mulder, 1996). Separation is done by passing fluids on opposite sides of a micro porous membrane. Hollow fiber modules have been widely used in all available membrane module geometries (Gabelman and

Hwang, 1999). A suction force is applied to filter water through the membrane fiber, while the material to be separated is maintained on the membrane surface.

Colloids are tiny particles whose featured rang of size is of 1–1000 nm. In pressure-driven membrane systems, these tiny collides have a strong propensity to clog the membranes, resulting a considerable loss in water permeability and often a deteriorated product water quality (Tang *et al*., 2011). Fouling is resulted by the adherence of particulate, colloidal or soluble substances inside the openings or on the surface of membrane (Bohm *et al*., 2010).

To maintain a proficient process, membranes need regular cleaning in terms of physical or chemical cleaning. Metzger *et al*., in 2007 reported that In situ physical membrane cleaning techniques normally involves aeration, membrane relaxation where filtration is stopped and membrane backwashing where product water is enforced in the reverse route. Frequent chemical cleaning is required to sustain the membrane productivity for long-term operations, which may boost operational cost and eventually cut downs the membrane life. Membrane based separation is key technology for desalination and wastewater reclamation. These technologies have replaced large scale conventional separation processes for wastewater treatment. They are more environmentally consistent and known as a clean technology (Soni *et al*., 2009).

Concerning membrane filtration performance, Extraction processes using membranes with hollow fiber are of particular interest because of their versatility. Due to their robustness and suppleness, membranes are more and more ideal for treatment processes.

2.8 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.

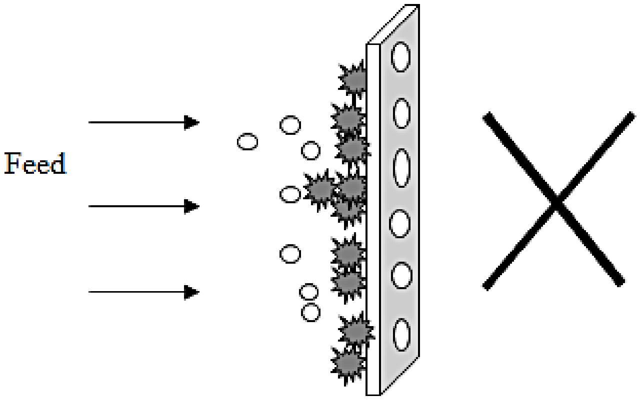


Figure 2.6: Diagram showing a Fouled Membrane

2.8.1 Classification of Membrane Fouling

Activated sludge inside the membrane bioreactor is a composite mixture of soluble and colloidal particles. In MBRs, intensive membrane clogging is repeatedly detected in the preliminary stage of membrane operation where biomass is not wholly acclimated and reinforced with respect to microbial community and biomass characteristics (Li et al., 2012).

Membrane fouling in MBR happens as of the complex relationship among the membrane and the activated sludge constituents. The activated sludge mixed liquor includes activated sludge flocs, microorganisms, organic and inorganic compounds from several lines and it may be separated into three types, i.e. suspended solids (microbes), colloids and solutes (minerals) (Li *et al.*, 2012).

The pore blockage is the obstruction of the membrane pores and this result in the lessening of membrane area for filtration. The filtrate passes only through the unclogged pores. The pore narrowing defines the fouling in internal membrane pores. In the pore contraction model, the membrane is supposed to have uniform pores, which are uniformly compacted in radius due to adhesion of small material that passes through membrane pores. The cake layer is the creation of cake or sludge particles over the membrane surface that can filtrate smaller particles through it due to the suction forces applied (Wu *et al.*, 2011).

In MBRs, membrane fouling may occur because of: (1) adsorption of minerals or colloidal particles on or within the membranes; (2) sludge flocs adherence over the membrane; (3) development of cake-layer on the surface of membrane; (4) detachment of particles due to shear force exerted; (5) foulant composition variations with respect to volume and time (e.g., the variation in microbial and biopolymer constituents in the cake-layer). So, the membrane fouling may be distinct as the contrary deposition and gathering of microorganisms, solutes, colloids, biomass and cell debris on or within the membranes (Meng *et al.*, 2009).

The deposition of larger sludge particles on the surface of membrane (external fouling) and the accumulation of small size collide (e.g., solutes and microbes) inside the membrane pores (i.e., internal fouling) is the main reason for fouling. Quite a few efforts reported that external membrane fouling is the prime cause of membrane fouling in MBRs. While, the internal fouling leads to membrane irreversible fouling, this is damaging for the long duration MBRs operations (Meng *et al.,* 2006). A cake-layer is permeable material has a composite scheme of interrelated particle voids. (Meng *et al.*, 2009)

Membrane fouling in MBRs can be recognized to both membrane pore blockage and sludge cake adherence on membranes which are frequently the principal fouling constituents (Lee *et al.*, 2001). Meng *et al.,* 2009 described that the membrane fouling can happen as a result of:

- 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.

2.8.1.1 Irremovable fouling

Whenever an inorganic matter is deposited on membrane, it can be irremovable because of cohesive characteristics. Most of the researchers had worked and working upon the elementary understanding of the cake deposit, the examination and mechanism of irremovable membrane clogging is very important for long duration and viable operation of MBRs.

Throughout the preliminary filtration by membranes, smaller particles (colloids, solutes and microbes) pass through and swift within the membrane pores. However, when MBRs are operated for a longer span, the set down cells increase and produce Extra Polymeric Substances (EPS) that chokes the pores and forms an intensely attached fouling cover. Simultaneously, some inorganic substances might gradually be placed onto the membrane surfaces or within the membrane openings. The incidence of MBR fouling is a much multilayered course. Therefore, its prediction, understanding and mechanism are significant in MBRs operation.

2.8.1.2 Bio fouling

Bio fouling is deposition of microbial bacteria cells. It denotes to the deposition and growth of microbial communities or flocs on the membranes and their mechanism to develop. This has been a very serious issue in tem of membrane fouling (Pang *et al*., 2005; Wang *et al*., 2005). In microfiltration and ultrafiltration membrane processes for treating wastewater, bio fouling is a key issue as most of the foulants in MBRs are far bigger as compared to the openings of the membrane.

Bio-fouling can twitch with the adherence of discrete cell or cell group over the surface of membrane, and then the number of cells goes on increasing and develops a bio cake. Several investigators proposed that EPS concealed by bacteria plays vital part in the cake layer development due to placement of bio foulants (Flemming *et al*., 1997; Liao *et al*., 2004; Ramesh *et al*., 2007).

2.8.1.3 Organic fouling

Organic fouling is deposition of biopolymers on or within membrane. Adherence of biopolymers results in Organic fouling in MBRs (i.e., proteins and polysaccharides) on the membranes. The biopolymers which have minor sizes may be deposited onto the membranes more willingly as they have lesser back transport velocity because of the lift forces as compared to large particles (e.g., colloids and sludge flocs) (Meng *et al*., 2009).

2.8.1.4 Biopolymers (Extra Polymeric Substances)

Metzger *et al*. (2007) have done a thorough study to describe deposited biopolymers on membranes. Their results show that the outer fouling layer was collection of a permeable, lightly bound cake-layer constructed of sludge flocs. The inner fouling layer consisted of EPS and bacterial aggregates, with high quantity of polysaccharides. The lower one layer was formed below the outer one, represented the irremovable foulants and prevailed by soluble EPS, and exhibited a higher quantity of bound proteins content. Wang *et al.*, (2012) have revealed that biopolymers play vital role in developing sludge accumulation and keeping microbes moving well excluding their involvement in the membrane fouling. The lack of biopolymers (EPS) may cause the deviation of microbial floc morphology and thus membrane fouling may occur.

Soluble EPS is group of organic mixtures come into solution from substrate breakdown. Recent studies delivered that soluble EPS is adsorbed on the membrane; clog the membrane openings and develops a gel layer over the membrane surface, which results in increase in hydraulic resistance to permeate flow. The soluble EPS similarly enhances the adhesiveness of the membrane that allows an easier and quicker union of biomass flocs to the membrane. It was found that half of the total resistance was due to soluble EPS deposition. Also, EPS bind the attached biomass flocs more firmly composed, also rising the hydraulic filtration resistance. Therefore, EPS are tangled in the fouling process in many ways and are accountable for the formation of a weighty barrier to permeate flow (Metzger *et al*., 2007).

2.8.2 Fouling Factors

Membrane fouling tendency can be affected by: 1) membrane morphology parameters like membrane material, membrane hydrophobicity/hydrophobicity, membrane pore size, membrane module; 2) feed wastewater composition (i.e. ionic strength, pH and type); 3) hydrodynamic conditions applied to MBR (*Koo et al.,* 2012).

Le-Clech *et al.* (2006) also described some features relating to membrane fouling i.e. membrane properties, influent biomass composition and operational limits. Yan *et al*., (2012) submitted that particularly the bound EPS and soluble EPS are strictly linked to membrane bio-fouling. While according to Li *et al.,* (2012) smaller particles, higher fractal dimension (DF) of particles and higher EPS, which are closely related to microbial population and growth, are main providers to the severe fouling. He also found that these contributors basically depend upon membrane characteristics, hydrodynamic conditions, and physiological characteristics of the activated sludge.

Various researchers showed that the resistance offered by cake layer developed due to microbial deposition was accountable for the overall resistance increment (Bae and Tak, 21 2005; Van *et al*., 2010), whereas others conveyed that soluble complexes or solutes and colloids can be the foremost reason of membrane fouling (Li *et al*., 2008; Farquharson and Zhou, 2010). Wu *et al*.,

(2011) also claimed the EPS content as the defining aspect for Trans- Membrane Pressure (TMP) sudden increase during membrane fouling progression.

According to him, bound and soluble EPS are the key parameters responsible for effective membrane surface area reduction. According to some other authors (Guo *et al*., 2008; Sun *et al*., 2011; Wang *et al*., 2012), the soluble part of sludge is understood to be accountable for pore narrowing, colloids for pore clogging and suspended solids for increase in cake layer. The preliminary pore narrowing is because of the deposition of soluble solutes within internal pores. This increases the membrane resistance. The pore restriction stops after the pore inlet is choked and flow distracted to unclogged pores. In the actual filtration process, the rapid increase in cake layer thickness may lessen the advance pore narrowing and obstruction. The cake layer formation may be helpful to keep the pore clogging and pore narrowing rate lower, but also can increase the cake resistance. In fouling phenomenon, pore blocking occurs immediately if cake layer deposited on membrane surface consists of larger particles. Fine colloidal particles penetrate through the void spaces of larger particles and cause pore blocking and irremovable fouling.

The void spaces in cake formed by bigger flocs are more than cake formed by small particles of sludge as shown in Figure 9. Less penetration of colloids occurs when dense cake layer is formed. With the progress of cake formation, the particles responsible for irremovable fouling are intercepted and pore constriction phenomenon is under control. But this small particles cake layer formation also reduces the flux rapidly.

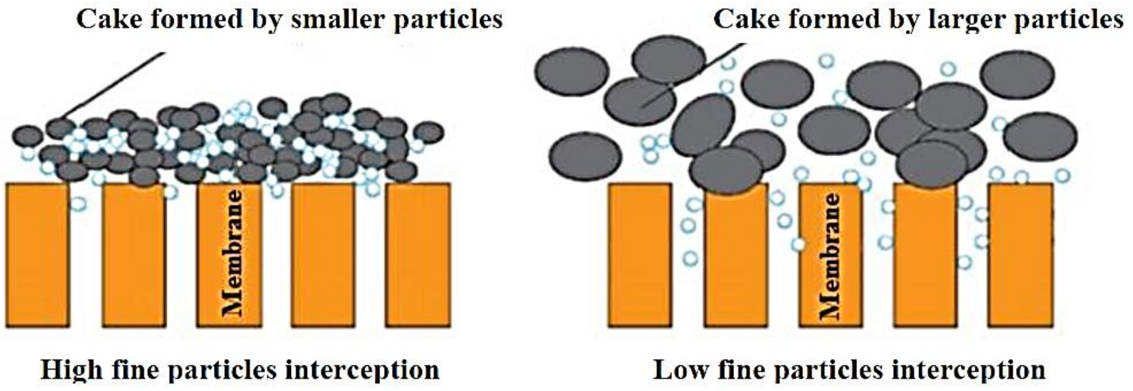


Figure 2.7: Fouling Phenomenon

Bound EPS contain of proteins, carbohydrates in the form of polysaccharides, nucleic acids, lipids, humic acid, etc. which are situated over the cell surface. Substrate breakdown results soluble EPS in the solution (as the biomass grows) and biomass growth and decay phenomenon (Barker and Stuckey, 1999). Therefore, soluble EPS may be split into two classes:

- Substrate-utilization-associated products, formed right through the breakdown, and
- Biomass-associated products, made of biomass, due to cell death (Laspidou and Rittmann, 2002).

Bound EPS have been recounted as most abundant sludge floc components, which keep the floc in a three-dimensional matrix, Bound EPS is considered to be main foulants of MBRs. Cho et al. (2005) established an association among the bound EPS and specific cake resistance (SCR) and he presented a useful mathematical expression that showed SCR was directly proportional to EPS. As the bound EPS concentration increased in mixed liquor, the SCR amplified, and subsequently caused increase of trans membrane pressure (Meng *et al*., 2009).

EPS usually comprises of high molecular weight complexes with active groups having some charge on them and hold both adhesive and cohesive properties. EPS come from the regular secretions of microbial products, cell lysis and hydrolysis compounds. Furthermore, in MBRs, EPS found both in the mixed liquor and over the membrane would have created a viscous mixed liquor and increase in filtration resistance of the membrane (Bin *et al*., 2008).

Fractal dimension is the term to define the geometric individualities of the multileveled floc configuration, e.g., activated sludge flocs. Euclidean geometry refers to even objects and shapes like points, curves, surfaces, and cubes by means of integer dimensions 0–3, correspondingly. Subsequently sludge floc masses are muddled and irregular in shape, the floc structure is difficult to be labeled by Euclidean geometry as the scale-dependent dealings of length, area and volume. These items are known as fractals, and their dimensions are non-integral in measurements and well-defined as fractal dimensions. A fractal object may be distributed into parts, in which each part is alike the whole object. Fractal dimension is pronounced as more if flocs are bigger and high fractal dimension means more potential to membrane clogging (Meng *et al*., 2006).

Le-Clech *et al.* (2006) also categorized the impacts disturbing membrane fouling into four groups: 1) membrane resources, 2) biomass features, 3) feed wastewater properties and 4)

Operating situations. The complex contacts between these influencing features make the membrane fouling understanding as tough. In MBR course, the fouling behavior is straight away measured by biomass parameters and hydrodynamic limits applied. However, operating conditions like SRT, HRT, F/M and feed wastewater have lesser impact on membrane clogging as they have potential to vary the sludge characteristics. Figure 10 gives the relationship among many fouling parameters and membrane clogging. Key foulants including bound EPS and soluble EPS are actually reliant on wastewater characteristics and hydrodynamic conditions provided. As aggregates formation and EPS release is function of microbial growth and constituents, the aeration intensity, reactor design and operating conditions have direct effect on microbial population, microbial growth and floc size.

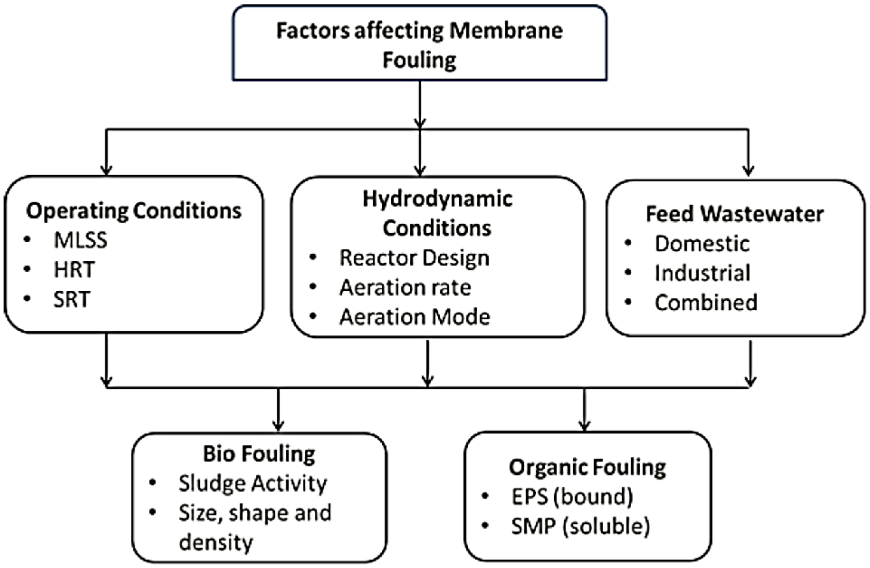


Figure 2.8: Factors Affecting Membrane Fouling

TMP is the variation among inside reactors and permeate side pressure. As the aggregates formed over membrane surface, TMP rises.

Critical flux is the highest flux beyond which TMP increases rapidly. First stage fouling also known as conditioning is caused by initial pore clogging and adsorption of solutes on membrane. Second stage fouling, the steady one occurs because of biofilm development and pore narrowing. In this stage, particles are deposited by haphazard motion and aggregates formation in the form of cake layer. In this stage, the applied flux of membrane is less than critical flux. In third stage, the sudden increase in TMP occurs, due to increase in particles deposition rate and thick cake formation. The void spaces in cake are completely filled with colloidal particles fixation and membrane flux decreases to significant level.

2.8.3 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 quick rise in TMP

It occurs in virgin membranes, when membrane is put in operation an increase in TMP for a while is reported. Adsorption of bio flocs 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 increase in TMP is reported in this phase, due to constant deposition of the colloids and Extra Polymeric Substances (EPS), a gel which bounds loose particles aid into the development of a thin layer on the surface of membrane. As time passes, EPS causes cake formation on the surface.

Stage 3: A quick rise in dTMP/dt, (TMP jump)

It is the result of excessive membrane clogging. According to Cho and Fane (2002) it is due to the variations in the local flux due to fouling ultimately resulting local fluxes to be more as compared to 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.

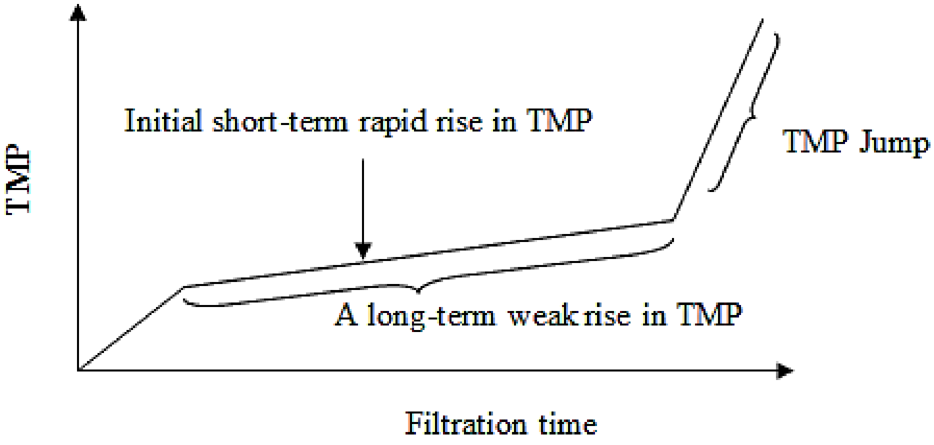


Figure 2.9: Stages of Fouling at Constant Flux Operation

2.8.4 Fouling Control

The financial optimization techniques for limiting the clogging of membrane are in fact critical to reduce the happening of fouling. Membrane fouling may be reduced by having appropriate pretreatment (Koo *et al*., 2012).

In MBR processes, adequate aeration is required to maintain viable flux and to delay membrane fouling (Rahimi *et al*., 2011). Former research by Han *et al*. (2005) exposed that the cake removing proficiency by aeration did not rise proportionately with the rise in the air flow rate. Moreover, air flow rate has an optimized value for cake removal from membrane surface. Favorable hydrodynamic conditions tone down membrane fouling (Meng *et al*., 2009).

2.8.5 Hydrodynamic Conditions

In MBRs, the size and flow rate of air bubbles are very much effective in providing good hydrodynamic conditions and power requirement. Fane *et al*. (2005) related influence of two nozzles of sizes 0.25 & 0.5 mm radius, on producing air bubbles and membrane clogging. The bigger nozzle produced bubbles of larger sizes. However, the fouling mechanism, regarded as dTMP/dt, was prominently enhanced by using smaller nozzle with small bubbles. Prieske *et al*. (2008), though, proposed that the magnitude of minor bubble (1 mm) could encourage a lower circulation velocity as compared to the large bubbles, determined that larger bubbles appear to be extra effective for air scour of the surface of membrane. As higher circulation velocity increased the lift and drag forces over membrane (Ndinisa *et al*., 2006). Recently, air sparging in MBRs has got much attention in efficient control of membrane fouling (Delgado *et al*., 2008; Psoch and Schiewer, 2008).

Air sparging resulted in efficient use of aeration and improved hydrodynamic conditions. Optimization of most of the hydrodynamic parameter is tangled in improving air scour efficiency. Aeration rate and bubble size have sound consequence on cross sectional velocity and shear. Smaller bubbles resulted less membrane fouling (Drews, 2010).

In short, improvement of hydrodynamic conditions is an active approach to diminish membrane fouling in MBRs. But, the hydrodynamic conditions are closely related to aeration amount and bubble volume, MLSS quantity and viscosity, etc. As in the real situation, the scouring of air acts as a mean of fouling control, that appreciates the operation of MBRs on experimental basis rather than analyzing the physical considerations (Böhm *et al*., 2012).

Reversible fouling can be decreased by physical methods like back flushing or relaxation of membrane filtration cycle (Teychene *et al*., 2011). Hence, the maintenance of hydrodynamic conditions in MBRs is very difficult to optimize and improvement of aeration intensities along with Computational Fluid Dynamics (CFD) modeling and simulation can be a useful tool for hydrodynamic conditions optimization. Bio fouling can be controlled by controlling DO conditions and organic loading of EPS and SMP (Meng *et al*., 2010).

2.8.5.1 Membrane Characteristics

Membrane characteristics and properties are much influential for fouling minimization. In MBR process, for hollow fiber membranes, the ideal fiber orientation is vertical rather than horizontal. But it is also fact that influence of fiber direction on purification is lesser than the commotion by backwashing and relaxation (Chang *et al*., 2002).

In hybrid flat sheet membranes, the space size among membranes is also important for limiting the fouling (Ndinisa *et al*., 2006). When the space size was greater than 7mm i.e 14 mm, the clogging appeared to be poorer and the mark of clogging reduction by two-stage flow reduced to 40% created on suction pressure increase (dTMP/dt). Besides, fiber movement and fouling control are affected by fiber tension with considerably better enactment for a little free fiber

(Wicaksana *et al*., 2006). Membrane unit and tank dimensions, membrane spacing and fiber softness are much effective in fouling control in MBRs (Drews, 2010).

2.8.5.2 Process Adjustment

A substitute to the conventional MBR is to integrate the bio reactor with the filtration process of the floating solids, which can decrease the consequence of membrane fouling by large biomass concentrations (Rahimi *et al*., 2011). An acceptable balance between MLSS and biofilm segments is significant to attain high removal proficiency and low fouling propensity in MB-MBRs (Yang *et al*., 2012).

Fouling can also be disallowed before its happening by: (1) refining the anti-fouling characteristics of the membrane, (2) operating the MBR in precise less fouling conditions (3) pre-treating the sludge and substrate in suspension to minimize the fouling (Le-Clech *et al*., 2006). One favorable approach to lessen fouling in MBR is to alter the sludge filtration features by the accumulation of flocculants or adsorbents (Iversen *et al*., 2009). Pulsed operation upgraded solute flux at all cross-flow rates examined by as far as two orders of scale, thus illuminating that negative TMP pulse can be operative in dropping solute flux resistance (Curcio *et al*., 2002). Efforts have been made to limit the fouling or change sludge characteristics through the use of ultrasound, ozone and electric field application in MBRs (Chen *et al*., 2007; Huang and Wu, 2008; Sui *et al*., 2008). Ultrasound can control membrane fouling efficiently while membrane damage can also happen (Wen *et al*., 2008). Another exciting way is the practice of an electric field that can stop the sludge flocs and colloids dumping on the surface of membrane. Furthermore, efforts have also been completed to limit MBR fouling by finding new filtration patterns (Wu *et al*., 2008).

Chapter 3

MATERIALS AND METHODS

3.1 Materials

Municipal wastewater from University of Engineering and Technology, Taxila was used as feed with 350-500 mg/L of COD range. The activated sludge was taken from I-9 Sewage Treatment Plant, Islamabad. It was acclimatized with domestic wastewater for a period of few days in MBR in Environmental Analytical Techniques Laboratory, UET Taxila.

3.2 Wastewater Characteristics

Domestic wastewater was provided continuously to the MBRs throughout the whole period of the study. The domestic wastewater was of medium strength having an average COD value of 400 mg/L.

Table 3. 1: Characteristics of screened raw wastewater inside Reactor

S#	Parameter	Units	Value
1	pH	-	7.5 ± 0.1
2	Total solids (TS)	g/L	850 ± 25
3	Total suspended solids (TSS)	mg/L	160.5 ± 25.4
4	Biological oxygen demand (BOD_5)	mg/L	262 ± 43.7
5	Chemical oxygen demand (COD)	mg/L	390.6 ± 25.3
6	Ammonium nitrogen (NH_4^+-N)	mg/L	30.9 ± 2.2
7	Total nitrogen (TN)	mg/L	55.5 ± 5.1
8	Total phosphorus (TP)	mg/L	9.5 ± 0.8

3.3 Membrane Characteristics

Hollow fiber membranes (HFM) were selected due to their compact size, large filtration area, high packing density, low manufacturing cost and moderate energy requirements. In HF membrane, hollow threads with small pores on the surface form a complete module and due to negative pressure (suction), the permeate flows from outwards to inwards. The fibers are vertically and loosely connected to module on both ends.

Figure 3.1: Hollow Fiber Membrane

Hollow Fiber membrane is a synthetic membrane best known for its separation processes. It is usually intended for use in industry or laboratory purposes. It has small pores on its surface which allow outward to inward flow by providing negative pressure or suction. Peristaltic pump can be used to serve the purpose.

3.4 MBR Installation

A lab scale MBR was installed at Environmental Analytical Techniques Laboratory, UET Taxila. The reactor had a submerged Hollow fiber microfiltration module (Hinada Water Treatment Tech Co., Ltd., Guangdong, China), 0.1µm pore size and 0.7 m^2 surface area was studied for the fouling behavior by varying the operating cycle. The acrylic reactor having membrane modules submerged in the center with feed stream making out to in flow due to suction provided by the peristaltic pump. Reactor was aerated using diffusers and air pumps. A feed tank for feeding the reactor was also attached via control tanks. Three stainless steel rods were immersed in the control tank at various levels i.e., Ground or reference level, High level and Low level. A water level sensor was regulating the flow from the feed tank to the control tank and ultimately to the reactor, through solenoid valve. The water level sensor switched the solenoid valve ON as the level in the control tank dropped beneath low level. The solenoid valve automatically switched OFF as the water level attained its high level.

Table 3. 2: HF Membrane Characteristics

Item	**Characteristics**
Manufacturer	Hinada Water Treatment Tech Co., Ltd., Guangdong, China.
Membrane Material	Polyethylene
Pore Size	0.1μm
Filtration Area	4.2 m^2
Suction Pressure	1-35 KPa
Temperature	15-35 ºC

Peristaltic pump (Baoding Chuang Rui Precision Pump Co., Ltd.), a positive displacement pump, was employed to draw permeate via suction and creating the vacuum. The treated permeate was backwashed at periodic cycles to optimize and determine the fouling behavior of HF membrane with different combinations i.e., 8 min filtration, 1min relaxation, 2 min backwashing and 1 min relaxation.

These combinations, later on were analyzed via Response Surface Methodology (RSM) software to investigate the desired and optimized combination. The whole system was made to run on tap water to find out the initial resistance of membranes as well as to inspect proper working and identification of any leakages within the system. The installation of MBR is shown in figure 13.

Figure 3.2: Installation of Submerged MBR

3.5 Experimental Setup

An automated system comprising of a lab scale setup of membrane bioreactor was operated for about four months. Initially it took approximately 30 days to acclimatize the sludge brought from Sewage Treatment Plant, I-9, Islamabad. The acrylic reactor was having a volume of 26L in total, while the working volume was kept at 21L. HF membrane was erected in the MBR. The HF membrane was connected to a peristaltic pump (Baoding Chuang Rui Precision Pump Co., ltd.), which was used to draw permeate via the discharge line at a speed of 30 RPM. The novelty of the research work is comprised of;

i. the simultaneous backwashing and relaxation by providing a repeated operating cycle of 12 min
ii. Use of real domestic wastewater instead of synthetic one
iii. Optimization of the three basic operating parameters i.e,. Filtration, Relaxation and Backwashing

The peristaltic pump based on alternating compression and relaxation of the Teflon pipe was drawing the contents out. Permeate was drawing the effluent at an outflow of 75 ml/min from both the membranes.

To evaluate the behavior of fouling, Data logging mano-meter (Sper-Scientific 840099, Taiwan) was allied to the membrane and measured the trans-membrane pressure (TMP) constantly. The membrane kept functioned till TMP reached 30 KPa and flux reduced as a result of deposition of cake layer on the membrane which causes membrane fouling. After which the membrane was physically and chemically cleaned.

The whole setup was made automated by using various electrical components which include solenoid valve, liquid level sensor and single knob timers. The timers manipulated the operation by maintaining a cycle of concurrent backwashing and relaxation. Three stainless steel rods were immersed in the control tank at various levels i.e., Ground or reference level, High level and Low level. A water level sensor was regulating the flow from the feed tank to the control tank and ultimately to the reactor, through solenoid valve. The water level sensor switched the solenoid valve ON as the level in the control tank dropped beneath low level. The solenoid valve automatically switched OFF as the water level attained its high level.

A schematic diagram of submerged MBR with all components is shown in Figure 14.

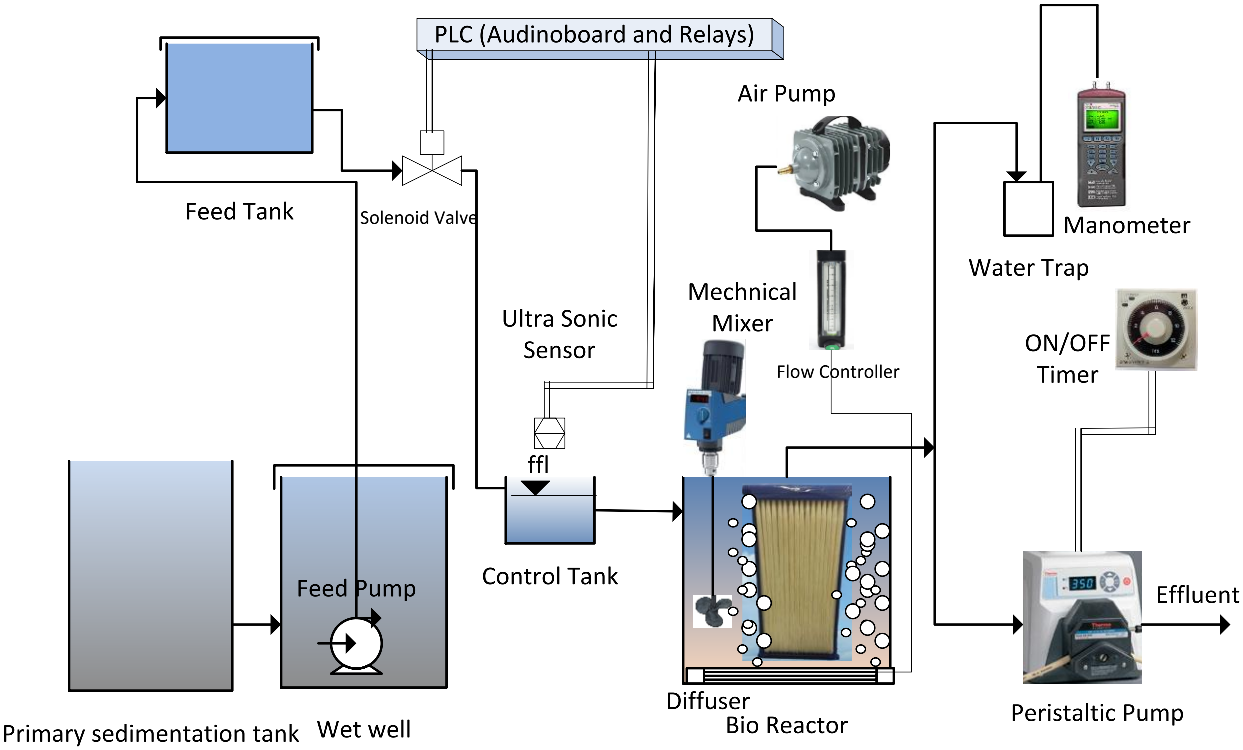


Figure 3.3: Schematic Diagram of Membrane Bioreactor

Figure 3.4: S-MBRs at UET Taxila

3.6 Operating Conditions

MBR was designed to be operated for 4 hours HRT and 30 days SRT. Aeration was maintained adequately. A promising MLSS Organic loading rate (OLR) was maintained. Food-Microorganism ratio for MBR is shown in Table 4 along with other parameters. Operating conditions were kept same for whole research study.

Table 3. 3: Operating conditions of MBR

Parameters	**Condition**
Sludge Retention Time (SRT)	30 days
Hydraulic Retention Time (HRT)	Variable
Organic Loading Rate (OLR)	1.5 Kg/m^3/d
Food to Microorganism Ratio (F/M)	0.2 ± 0.03
Mixed Liquor Suspended Solids (MLSS)	6-8 g/L
pH	7.2-7.8

Parameters	Condition
Trans-Membrane pressure (TMP)	35 kPa
Pumping Cycle	8-1-2-1
Pumped Volume	75 ml/min
Flux	Variable

3.6.1 Impacts of Backwash Sequences

Backwashing is a physical method that helps to limit membrane fouling to some extent in MBRs. While backwashing water from the stored permeate or air flow rearward through the membrane and results in removal of deposit matter on the surface of membrane to some extent. Infect backwashing is useful for the deletion of the integrated deposits on the surface of membrane, which generally constitute the reversible fouling, whereas pore blocking resistance is not completely eliminated and predominantly for high forward filtration fluxes.

As a consequence of the backwashing, membrane recovers its permeability to some extent, and permeation flux or TMP are somewhat regained. Also, a permanent decay in the effluent through membrane might be observed with the passage of filtration time.

Several backwash methods for MBRs are shown in the following Table.

Table 3. 4: Different Backwash Procedures

Backwash duration	Backwash interval	Backward flux or TMP	Forward flux or TMP (L/h.m²)	Membrane Category	References
15 s	15 min	96 L/h.m²	48	HF membrane	Smith *et al.* (2005a)
5 - 10 min	8 s	80 - 90 KPa	18-72	Inside/Outside UF module	Jiang *et al.* (2003)

5 min	1 h	20 KPa	10	Inside/Outside UF module	Katsoufidou *et al*. (2005)
35 s	10 min	Not communicated	18	HF Membrane	Rosenberger *et al*. (2002)
60 s	60 min	100 KPa	10	HF Membrane	Hernandez Rojas *et al.* (2005)

The term "back-pulsing" is often used in literature. It shows a cyclic combination of forward and backward filtration that consists of an exceptionally brisk pulse. During the process back pulsing occurs for few seconds (Ma *et al*., 2001), while the interval of backwash periods and the duration of backwash may remain few dozen of minutes and few minutes correspondingly (Smith *et al*., 2006).

Both backwashing and back pulsing show a positive impact regarding TMP rise or permeation flux conservation for long time filtration, (Yang *et al*. 2006). Smith *et al*. (2006) investigated that reduction in TMP rises and the permeate flux decreases during backwashing, because membrane filtration removes most of the reversible. Thus, backwashing looks to be critical for elongated filtration prior to the physical and/or chemical cleaning.

While, *Ma et al*. (2000; 2001) reported that the cake layer formed on the surface of membrane deprived of backwashing has a positive filtration controlling effect. In fact, it acts as secondary membrane and have a potential to elude the permeation of small particles through the membrane and thus can reduce the inner fouling. Although the backwashing reduces the decline in permeability after some time during filtration, but it helps to regain the flux after long term filtration by limiting the internal membrane fouling. Because regular backwashing reduces the inner fouling as compared to the absence of backwashing.

Generally, to achieve long term filtration, the significant parameters include the backwashing frequency, duration and backward flux. However these parameters are very difficult to be pre-determined accurately in MBR processes, they are associated with some other parameters like the permeate flux, membrane characteristics and concentration of the foulants (Smith *et al.*, 2006).

3.6.1.1 Optimal Backwash Duration

Optimum backwash interval is one which ends after the complete elimination of the reversible coating. Actually, the reversible deposits attached on the surface of membrane cannot be removed properly if the duration of the backwashing is kept too short. Furthermore, Smith *et al*. (2005) described that the deposits removed from the membrane surface are not driven away from the vicinity of the fibers due to the short duration of backwashing. Thus, at the launch of the next filtration cycle these detached deposits are too adjacent to the fibers and the probability of their re-deposition immediately on the membrane surface increases. Which again results in a constant TMP increase.

On the other hand, a too long backwash duration eliminates the entire reversible layer successfully. However, the productivity of the system is affected as the backwashing requires the quantity of permeate. It needs higher energy consumption as well (Smith *et al*., 2006).

3.6.1.2 Optimal Backwash Interval

The difficulty of optimizing the backwash interval is alike to that of the backwash duration. Because, an elongated backwash interval results in an inefficient backwashing and a too short backwash interval causes the loss of productivity in term of permeate production.

Actually, a long filtration period brings the development of a dense cake layer. Moreover, it leads to the firmness of this external layer which gradually becomes an irreversible foulant layer (Chen *et al.,* 2003). While irreversible fouling is incompetent to be controlled on line, continued control of the reversible foulant layer builds up impacts on the degree of irreversible fouling.

Smith *et al*. (2005) investigated the optimum backwash interval for an MBR system occurs when the TMP rise goes to 3% of the maximum pressure limits. This interval was determined for a system having hollow fiber membrane and being operated using synthetic wastewater.

3.6.1.3 Backward Flux or TMP

Backwashing mostly is operated at higher pressure or permeate flux as compared to the forward filtration. Smith *et al.* (2005) used higher flux for backwashing as compared to the permeate flux. Similarly, Katsoufidou *et al*., 2005 used a backwash pressure of 20KPa and the forward pressure of 10 KPa, they reported that if the backwashing is carried out at a pressure which is higher than 34 KPa, the permeate flux may reduce due to the compaction of membrane fibers

In short, backwash orders improve the filtration performance in an MBR system. For long term filtration they induce a better flux or TMP conservation. Key factors for a fruitful backwash process are backwash duration, backwash interval and backwash flux. But, for each MBR system these parameters are changed and must be adjusted to the system. Actually, the foulant tendency of the biological solution, the permeate flux and the shear stress along the membrane determine the working parameters of the backwash process mainly.

3.6.2 Effect of Relaxation Sequences

Applying relaxation orders during filtration in an MBR is another physical method which lessens membrane fouling. Relaxation orders are sequences during which filtration is stopped. Hong *et* *al*. (2002) revealed that the membrane performance was clearly enhanced by such an alternating filtration. However, the membrane permeability is only somewhat recovered, after every relaxation cycle, signifying that irreversible fouling happens (Hong *et al.,* 2002) or that elongated relaxation times would be essential. Consequently, pressure relaxation is only able to eliminate the reversible foulant layer, reversibility being considered at a tolerable time scale.

Gui *et al. (*2002) reported that adherence on the surface of membrane relies on the equilibrium between the velocity towards membrane surface due to membrane flux and the backward transport velocity exerted by shear force. This fact is explained in the figure below, where V_b is the backward transport velocity, V_f is the forward transport velocity and V_s is the cross flow velocity above the membrane surface.

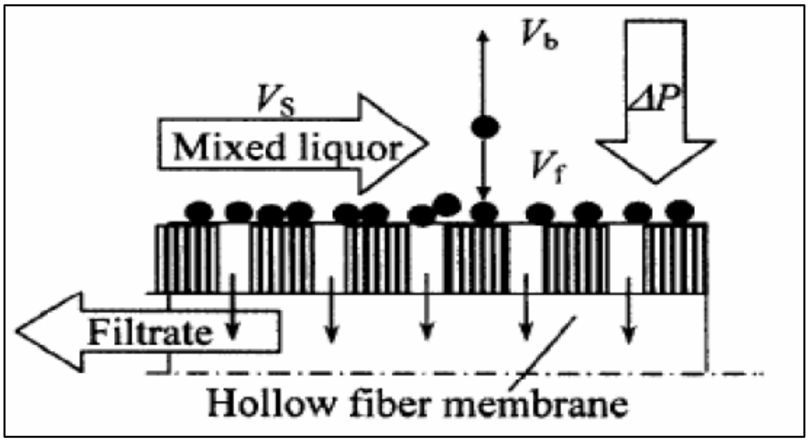


Figure 3.5: Membrane filtration progression, Gui et al. (2002)

The backward transport of influent particles is mostly linked to the cross flow which robustly relies on the aeration rate close to the membrane and the particle concentration (Gui *et al*., 2002).

While filtration is in operation and when the permeation flux is more than the critical flux, V_f is higher than V_b and suspended solids build up onto the membrane surface, thus developing the cake-layer. Therefore, in the relaxation time, V_b is the key factor that makes the particles in progress and thus back transport eliminates reversible foulants from the membrane to the bulk solution. The backward transport normally caused by two key factors given below:

- **Concentration gradient:** If suspended solids between the cake layer and mixed liquor particles not attached irreversibly to the membrane surface due to the presence of already developed cake-layer, they are transferred away of the membrane surface, thanks to the concentration gradient.
- **Air scouring**: In fact Hong *et al*. (2002) investigated that in order to maintain certain balanced membrane permeability, the cake layer is needed to be eliminated by a shear. Frequently in an MBR system, it is implemented by an uplifting flow of bubbling air which is supplied by air diffusers located at the bottom of the membrane; this method is called "air scouring" (Hong *et al*., 2002). Thereby, the back transport of reversible foulant during relaxation sequences is strongly enhanced by the air scouring.

Compared to backwash orders, relaxations orders do not engage permeate use and therefore its use lowers the productivity loss in terms of permeate generation. Furthermore, relaxation sequences do not call for a large amount energy consumption. As a result it appears significant to evaluate productivity and total operational cost for both, MBR systems functioning with either backwashing or relaxation.

3.7 Analytical Parameters

The main objective of this study was to analyze the reduction in the degree of fouling and the efficiency of Membrane Bioreactor.

- Trans-Membrane pressure was monitored after regular intervals by using manometer.

- The parameters used to analyze the removal efficiency of Membrane Bioreactor were Chemical Oxygen Demand (COD), Total Phosphates (TP), Total Nitrogen (TN) and Ammonia Nitrogen (NH_3-H).

Parameters to be determined are listed in figure 16 shown below.

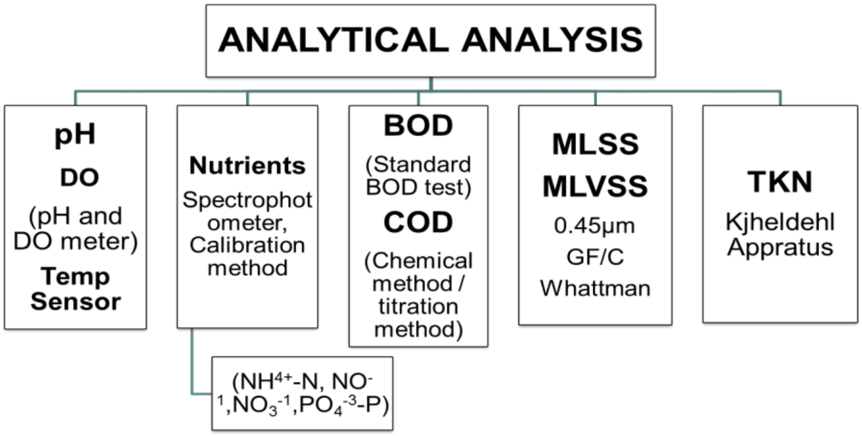


Figure 3.6: MBRs Design of Experiments

The parameters that were investigated, the technique adopted to determine each parameter and the equipment/material used are reported in Table 5.

Table 3. 5: Analysis of Parameters and the equipment/material used

Parameters	Methods	Equipment/ Material Used
MLSS	Filtration- Evaporation	Filtration Assembly, Weighing Machine, 1.2µm Whatman filter paper.
DO	Depletion of DO, Azide modification by Winkler method.	BOD bottles, Titration Assembly, Chemicals (Sodium Thiosulphate, Maganese Sulphate, Sulphuric acid and alkali azide soln.)
BOD	___	BOD bottles, Titration Assembly, Chemicals (Sodium Thiosulphate, Maganese Sulphate, Sulphuric

Parameters	Methods	Equipment/ Material Used
		acid and alkali azide soln.
COD	Titration	COD tube, COD digester, Oven 150^{0}C
Nitrates	Spectrophotometer	Silica used of 1cm light path, Flask, Pipettes, Beaker
pH	pH meter	pH meter.
Temperature	Thermometer	Thermometer
Ammonia	Distillation	Kjeldal apparatus,
Kjeldal Nitrogen	Digestion	Kjeldal apparatus,
Phosphates	Spectrometry	Spectrophotometer

3.8 Response surface methodology

Response surface methodology is a collection of statistical and mathematical methods that are useful for the modeling and analyzing engineering problems. In this technique, the main objective is to optimize the response surface that is influenced by various process parameters. Response surface methodology also quantifies the relationship between the controllable input parameters and the obtained response surfaces (Aslan and Cebeci, 2007).

RSM is mainly advantageous in the less experimental trials needed to evaluate multiple parameters and their interactions. RSM has been successfully applied to the optimization of operational parameters in wastewater treatment (Fu *et al*. 2012).

The design procedure of response surface methodology is as follows (Gunaraj and Murugan 1999):

1. Designing of a series of experiments for adequate and reliable measurement of the response of interest.
2. Developing a mathematical model of the second order response surface with the best fittings.
3. Finding the optimal set of experimental parameters that produce a maximum or minimum value of response.
4. Representing the direct and interactive effects of process parameters through two and three dimensional plots.

3.9 Box–Behnken design

Box–Behnken design is rotatable second-order designs based on three-level incomplete factorial designs. The special arrangement of the Box–Behnken design levels the number of design points to increase at the same rate as the number of polynomial coefficients. For three factors, for example, the design can be constructed as three blocks of four experiments consisting of a full two-factor factorial design with the level of the third factor set at zero (Ghalekhani and Zinatizadeh 2014). Design of experiment (DOE) statistically minimizes the number of experiments and eliminates experimental errors systematically.

In a system involving three significant independent variables X_1, X_2 and X_3, the mathematical relationship of the response, Y, on these variables can be approximated by the second degree polynomial equation.

$$\mathrm{Y} = \mathrm{A}_0 + \mathrm{A}_1\mathrm{X}_1 + \mathrm{A}_2\mathrm{X}_2 + \mathrm{A}_3\mathrm{X}_3 + \mathrm{A}_{12}\mathrm{X}_1\mathrm{X}_2 + \mathrm{A}_{13}\mathrm{X}_1\mathrm{X}_3 + \mathrm{A}_{23}\mathrm{X}_2\mathrm{X}_3 + \mathrm{A}_{11}X_1^2 + \mathrm{A}_{22}X_2^2 + \mathrm{A}_{33}X_3^2$$

Where Y = predicted yield or response,

X_1, X_2 and X_3 = independent variables,

A_0 = constant,

A_1, A_2 and A_3 = linear coefficient,

A_{12}, A_{13} and A_{23} = cross product coefficients,

A_{11}, A_{22} and A_{33} = quadratic coefficients.

3.9.1 DESIGN OF EXPERIMENT:

The Box-Behnken Design Model requires a set of independent variables as input values and provides the output values of dependent variables. Moreover, looking at the prime objective of this study i.e. effects of backwashing and relaxation patterns on membrane fouling, flux, backwashing and relaxation were selected as the input variables. These variables were assigned different values to optimize the operation of the system in a way where minimum membrane fouling occur. Hence the assigned values are shown below in the table:

Table 1: Different patterns assigned to Flux, Backwashing and Relaxation

	Coded Values		
Parameters	**-1**	**0**	**+1**
Flux (LMH) [A]	15	20	25
Backwashing (sec) [B]	0	20	40
Relaxation (sec) [C]	90	120	150

These values were also coded as +1, 0 and -1 because the BBDM works on binomial system. After assigning the values to the above three factors the relevant operational control parameters were examined. These included Trans Membrane Pressure (TMP) in KPa/day, Chemical Oxygen

Demand (COD) in percentage, Ammonia Nitrogen (NH_3-N) in percentage, Total Nitrogen (TN) in percentage and Total Phosphorus (TP) in percentage as well. There values were assessed in all iterations and compared to the effluent discharge standards as well.

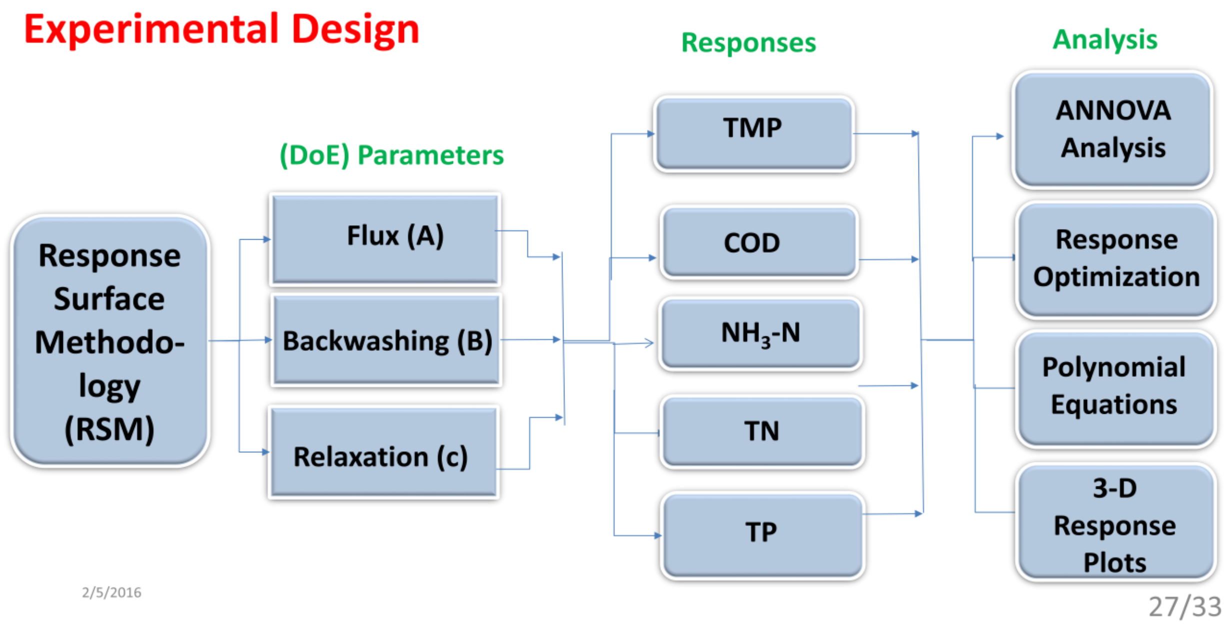


Figure 3.7: Experimental design for Box-Behnken Design Model

The ultimate objective was to reduce the membrane fouling by optimizing the flux, backwashing and relaxation modes. It was also kept in mind that the overall flux must meet the desirability of the system. Thus, different patterns of these three parameters were examined as input to the Box-Behnken design Model and then the model was expected to predict the optimum values. These values must meet the flux requirement as well as reducing the membrane fouling while the removal efficiency was better enough to meet the effluent discharge standards.

Table 3. 6: Different patterns assigned to Flux, Backwashing and Relaxation

Std	NO.	Block	Factor 1 Flux (LMH)	Factor 2 Backwashing (Sec)	Factor 3 Relaxation (Sec)	Response 1 TMP (Kpa/day)	Response 2 COD (%)	Response 3 NH3-N (%)	Response 4 TN(%)	Response 5 TP(%)
9	1	B 1	20	0	90	27	85.672	72.6	82.3	64.1
7	2	B 1	15	20	150	15	84.878	74.4	78.34	62.67

14	3	B 1	20	20	120	16.8	81.032	69.8	76.4	60.76
11	4	B 1	20	0	150	25.6	83.074	71.9	81.89	64.89
2	5	B 1	25	0	120	26.8	80.048	65.98	78.4	62.8
5	6	B 1	15	20	90	16	88.018	73.45	79.15	62.2
16	7	B 1	20	20	120	16.56	81.566	70.11	76.45	60.98
4	8	B 1	25	40	120	16.2	74.092	63.44	74.1	58.13
8	9	B 1	25	20	150	17.4	74.952	64.8	75.4	57.44
12	10	B 1	20	40	150	16.6	77.112	67.89	76.22	58.9
15	11	B 1	20	20	120	17.2	80.766	68.12	77.68	61.23
10	12	B 1	20	40	90	16.5	82.066	69.3	77.67	60.3
1	13	B 1	15	0	120	24.8	91.028	76.4	84.3	66.23
6	14	B 1	25	20	90	17.8	79.054	65.11	77.3	57.88
13	15	B 1	20	20	120	16.36	81.966	69.76	76.97	60.74
3	16	B 1	15	40	120	14.2	83.166	72.6	76.8	63.15

Chapter 4

RESULTS AND DISCUSSIONS

Response Surface methodology (RSM) based on Box–Behnken design (BBD) method was used to investigate the influence of three variables i.e. permeate flux, backwashing duration and relaxation durations on the performance of submerged MBR. Pilot plant experiments were performed at different combination of flux, backwashing and relaxation duration based on the proposed experimental design. The results were completely analyzed using analysis of variance (ANOVA) automatically performed by Design Expert software. Based on experimental results, regression models for effluent quality were generated. ANOVA and R^2 statistic were used to determine whether the developed model was adequate to describe the data. The data from the experimental results were fitted to higher degree polynomial equation i.e quadratic.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. Values greater than 0.1000 indicate the model terms are not significant. Lack of Fit is the variation of the data around the fitted model. If the model does not fit the data well, this will be significant. Lack of fit should not be significant.

How well the estimated model fits the data can be measured by the value of R^2.R^2 is the percentage of variation in the response that is explained by the model. The higher the R^2 value, the better the model fits your data. The R^2 lies in the interval [0,1]. When R^2 is closer to the 1, the better the estimation of regression equation fits the sample data. In general, the R^2 measures percentage of the variation of y around y that is explained by the regression equation. For a good fit model, R^2 should be at least 0.80.

Adequate precision (AP) is a measurement in a certain range to predict response relative to its associated error or, in other words, a signal-to-noise ratio. The values of AP should be 4.00 or more. Conversely, low values of the coefficient of variation (CV) indicates good precision and reliability of the experiments.

Analysis of variance (ANOVA) results for the response surface quadratic model for all responses i.e. TMP after 5 days ,COD, NH_4-N, TN, TP and are given in table 4.1, 4.2, 4.3, 4.4, 4.5 respectively. The very small P-values i.e.< 0.0001 for TP,TMP after 5 days, COD ,0.0002 and 0.0007 for ammonia and TN respectively and a suitable R^2 i.e. >0.97 for all parameters showed that the quadratic model was highly significant and suitable for describing the relationship between the responses and parameters.

Valus of Adequate precision for all responses are greater than 4.Very small values of coefficient of variation i.e. <10% indicate that good precision and reliability of the experiments.

The results obtained as 3D presentations and also as contours are used for visualization to study the effect of system variables on responses. From these three-dimensional plots, the simultaneous interaction of the two factors on the responses was studied. The optimum region was also identified based on the main parameters in the overlay plot.

4.1 Modeling of TMP after 5 days

ANOVA for Response Surface Quadratic Model

Table 4. 1: Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**

Model	293.54	9	32.62	257.80	< 0.0001	significant
A-Flux	8.41	1	8.41	66.43	0.0002	
B-Backwashing	207.06	1	207.06	1636.63	< 0.0001	
C-Relaxation	0.91	1	0.91	7.20	0.0364	
AB	0.000	1	0.000	0.000	1.0000	
AC	0.090	1	0.090	0.71	0.4313	
BC	0.56	1	0.56	4.45	0.0795	
A^2	1.22	1	1.22	9.65	0.0209	
B^2	74.74	1	74.74	590.72	< 0.0001	
C^2	0.56	1	0.56	4.39	0.0811	
Residual	0.76	6	0.13			
Lack of Fit	0.37	3	0.12	0.94	0.5202	not significant
Pure Error	0.39	3	0.13			
Cor Total	294.30	15				

Std. Dev.	0.74	**R-Squared**	0.989
Mean	81.78	**Adj R-Squared**	0.972
C.V. %	0.91	**Pred R-Squared**	0.861
PRESS	40.57	**Adeq Precision**	26.554

4.1.1 Polynomial Equation of models for prediction

The following is second-order polynomial equation in coded form established to explain the TMP after 5 days

$$Y_{TMP} = +16.73 + 1.03A - 5.09B - 0.34C + 0.00AB + 0.15AC + 0.38BC - 0.55A^2 + 4.32B^2 + 0.37C^2$$

Transmembrane pressure (TMP) was monitored as an indicator of membrane fouling at the start and end of each run.The above quadratic equation shows that Permeate flux had negative impact on membrane fouling as TMP is increased with the increase in permeate flux.It means at higher flux there will be more fouling of membrane hence higher flux is not desireable. Relaxation and backwashing had positive impact ,if we increase backwashing and relaxation intervals there will be less rise in TMP and less will be membrane fouling. Interaction between backwashing and relaxation (BC) and interaction between and permeate flux and backwashing(AC) negatively effected the performance of MBR.

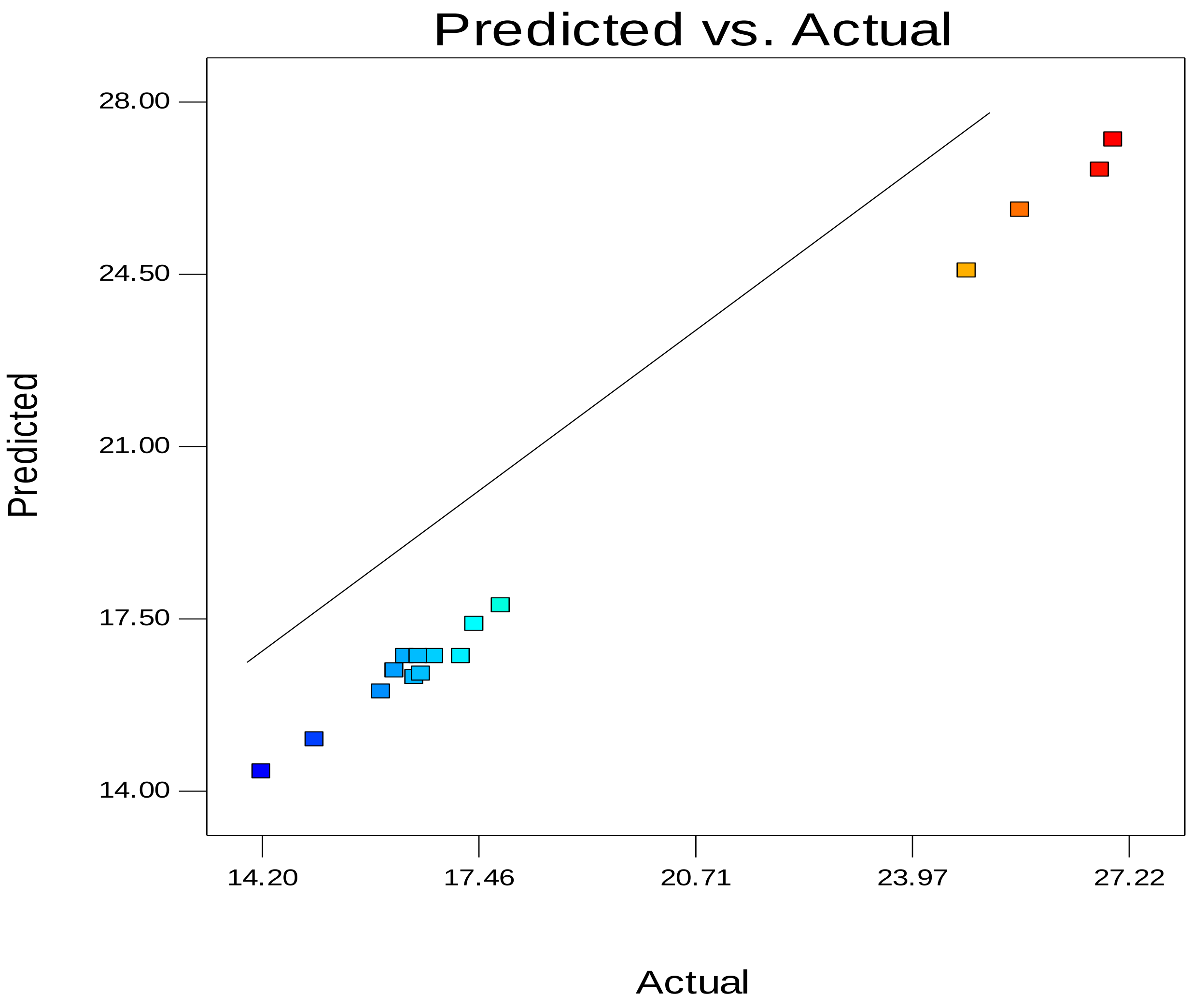


Figure 4.1: Graph showing predicted and actual responses for TMP after 5 days

Three-dimensional response surface plot for the effect of flux rate, backwashing period and relaxation period on TMP after 5 days.

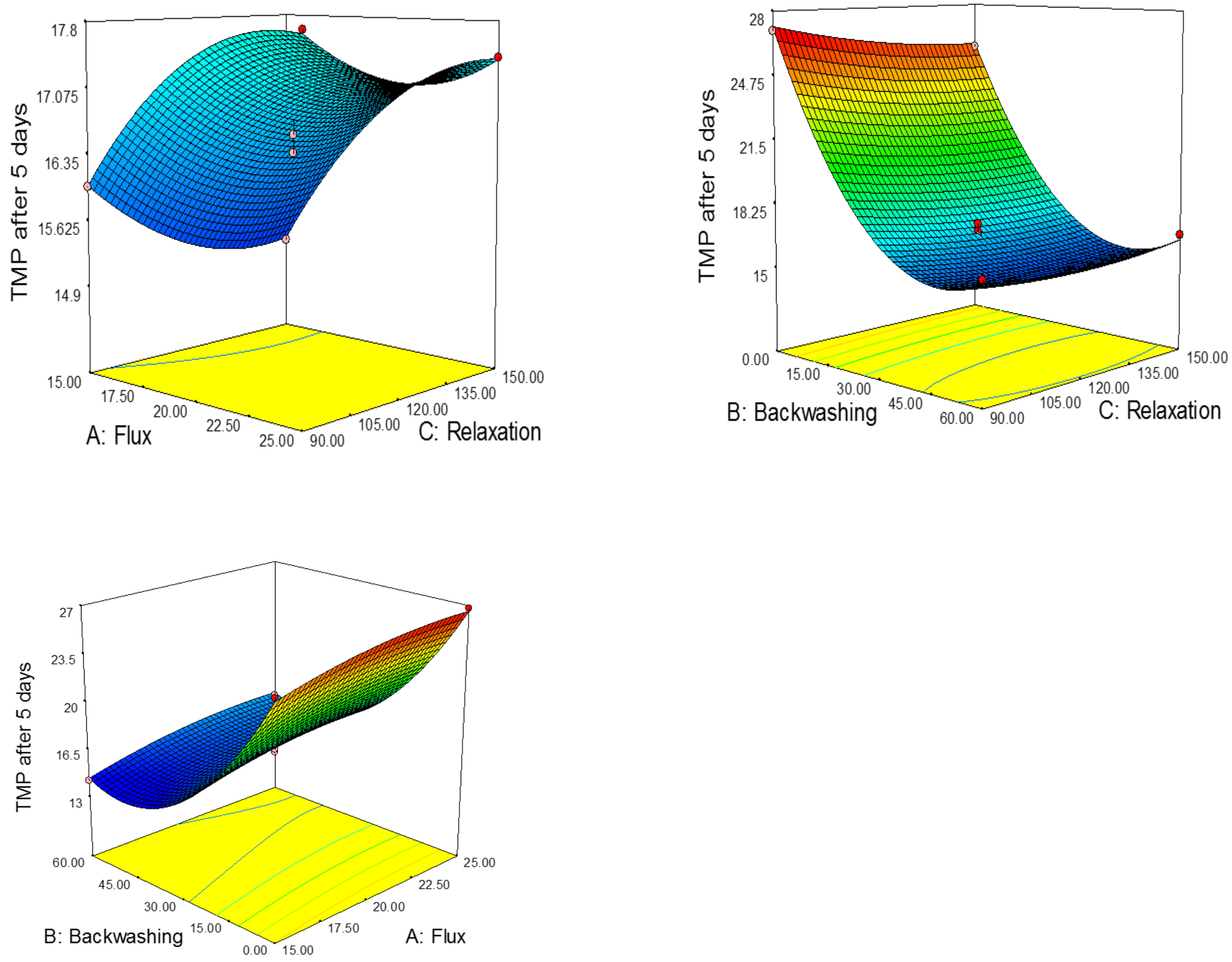


Figure 4.2: 3-D plots showing the interaction and effects of flux rate, backwashing and relaxation on TMP after 5 days.

4.2 Modeling of COD Removal Efficiency

ANOVA for Response Surface Quadratic Model

Table 4. 2: Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	289.17	9	32.13	58.31	< 0.0001	significant
A-Flux	189.58	1	189.58	344.04	< 0.0001	
B-Backwashing	68.36	1	68.36	124.06	< 0.0001	
C-Relaxation	27.36	1	27.36	49.65	0.0004	
AB	0.91	1	0.91	1.65	0.2466	
AC	0.23	1	0.23	0.42	0.5410	
BC	1.39	1	1.39	2.52	0.1636	
A^2	0.25	1	0.25	0.45	0.5293	
B^2	1.01	1	1.01	1.84	0.2239	
C^2	0.084	1	0.084	0.15	0.7091	
Residual	3.31	6	0.55			
Lack of Fit	2.44	3	0.81	2.81	0.2091	not significant
Pure Error	0.87	3	0.29			
Cor Total	292.48	15				

Std. Dev.	0.74	**R-Squared**	0.989
Mean	81.78	**Adj R-Squared**	0.972
C.V. %	0.91	**Pred R-Squared**	0.861
PRESS	40.57	**Adeq Precision**	26.554

4.2.1 Final Equation in Terms of Coded Factors

The following is second-order polynomial equation in coded form established to explain the COD removal efficiency

$$Y_{COD} = +81.33 - 4.87A - 2.92B - 1.85C + 0.48AB - 0.24AC - 0.59BC + 0.25A^2 + 0.50B^2 + 0.15C^2$$

During this study it was found that all three variables negatively influenced the performance of MBR to remove COD but the interaction between permeate flux (A) and backwashing period (B) improved the capacity of MBR to remove COD. Whereas, the interaction of permeate flux (A) with relaxation period (C) and backwashing period (B) with relaxation period (C) had negative impact on treatment efficiency of COD.

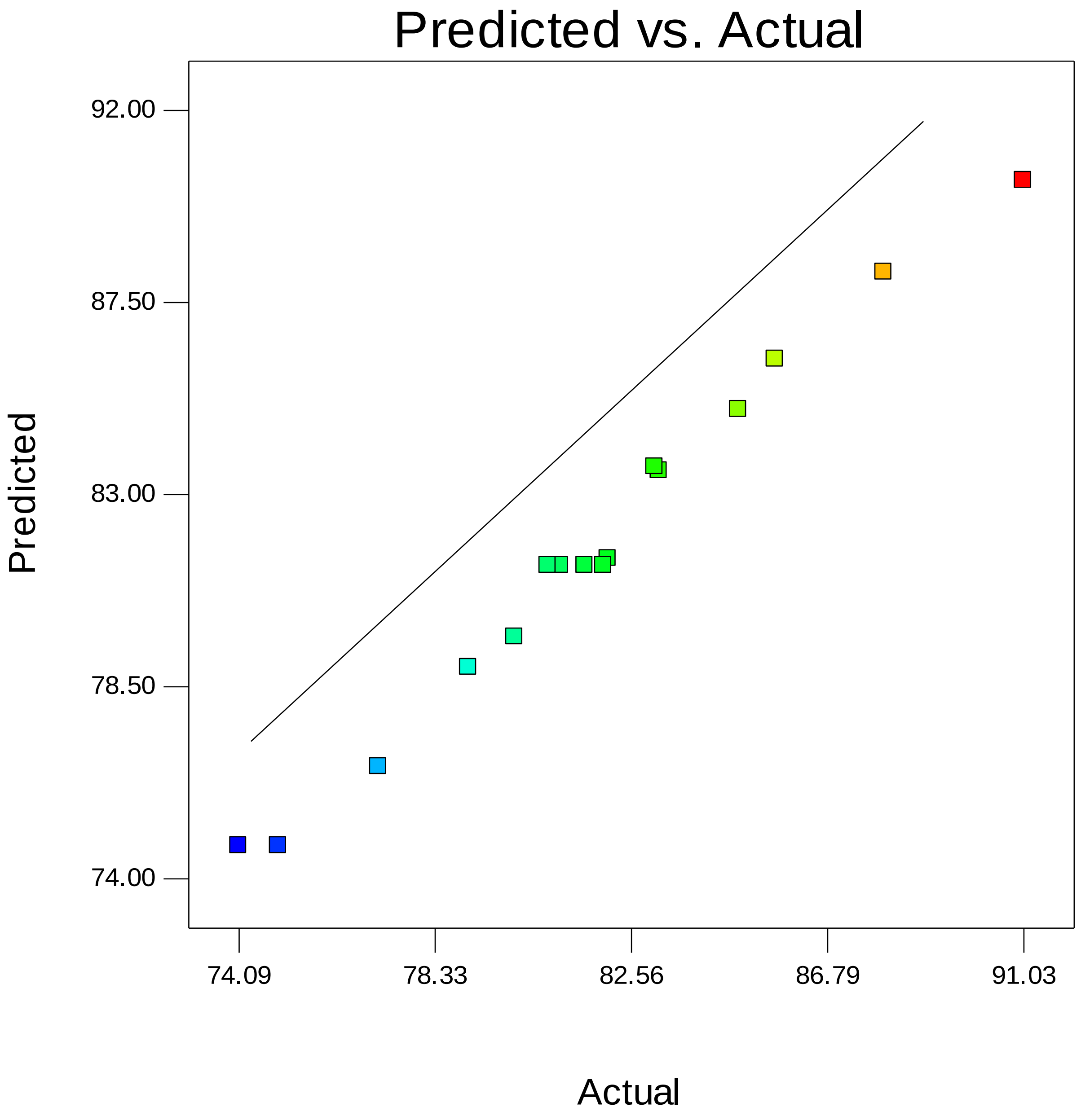


Figure 4.3: Graph showing predicted and actual responses COD removal efficiency

Three-dimensional response surface plot for the effect of flux rate, backwashing period and relaxation period on COD removal efficiency.

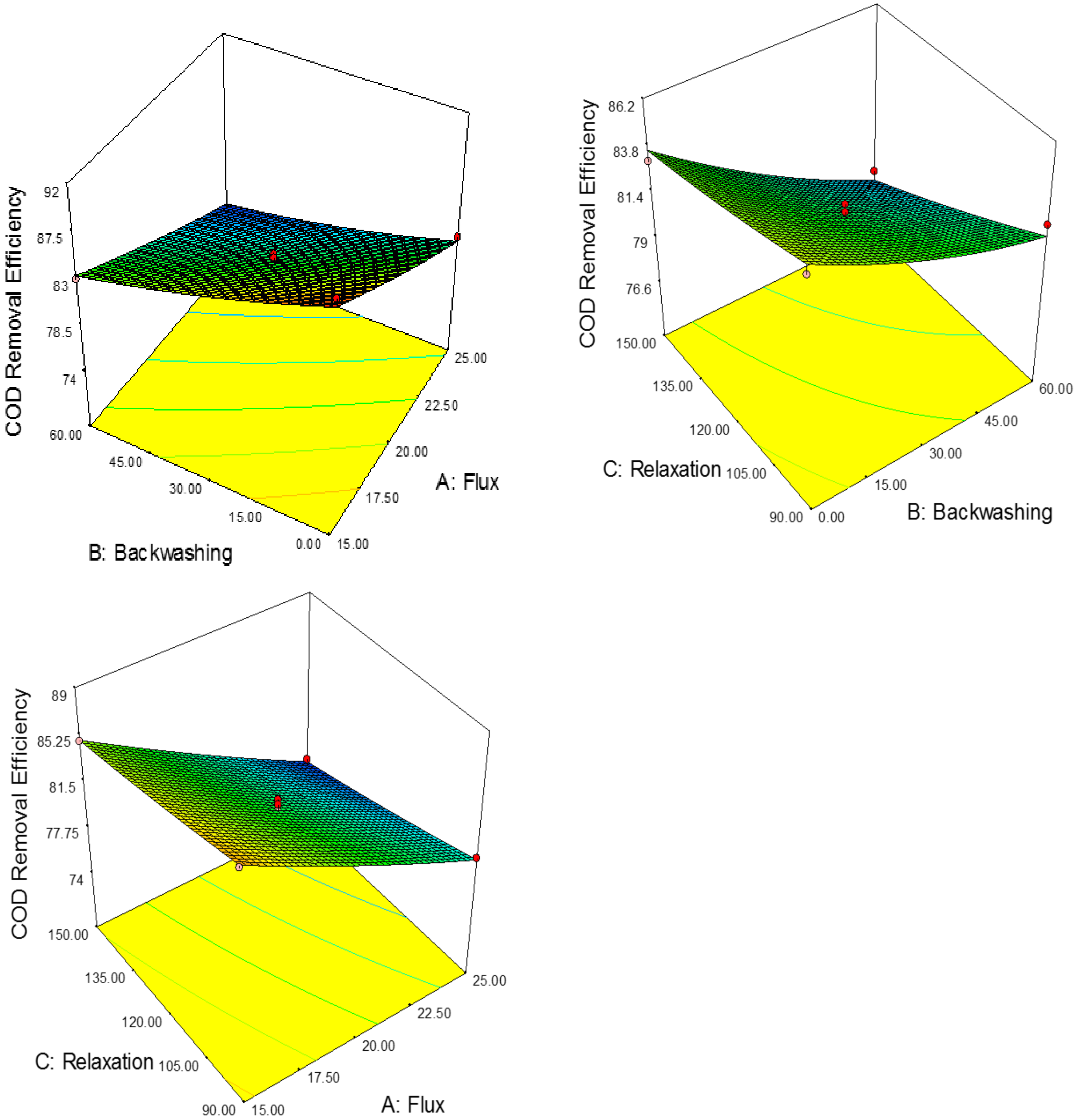


Figure 4.4: 3-D plots showing the interaction and effects of flux rate, backwashing and relaxation on COD Removal after 5 days.

4.3 Modeling of NH_4-N Removal Efficiency

ANOVA for Response Surface Quadratic Model

Table 4. 3: Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	203.09	9	22.57	35.42	0.0002	significant
A-Flux	175.97	1	175.97	276.23	< 0.0001	
B-Backwashing	23.29	1	23.29	36.56	0.0009	
C-Relaxation	0.27	1	0.27	0.42	0.5391	
AB	0.40	1	0.40	0.62	0.4600	
AC	0.40	1	0.40	0.62	0.4600	
BC	0.13	1	0.13	0.20	0.6721	
A^2	0.68	1	0.68	1.07	0.3412	
B^2	1.30	1	1.30	2.04	0.2031	
C^2	0.66	1	0.66	1.03	0.3493	
Residual	3.82	6	0.64			
Lack of Fit	1.40	3	0.47	0.58	0.6685	not significant
Pure Error	2.42	3	0.81			
Cor Total	206.91	15				

Std. Dev.	0.80	**R-Squared**	0.982
Mean	69.73	**Adj R-Squared**	0.954
C.V. %	1.14	**Pred R-Squared**	0.871
PRESS	26.69	**Adeq Precision**	20.274

4.3.1 Final Equation in Terms of Coded Factors

The following is second-order polynomial equation in coded form established to explain the NH_4-N removal efficiency.

$$Y_{NH4-N} = +69.45 - 4.69A - 1.71B - 0.81C + 0.32AB - 0.32AC - 0.18BC - 0.41A^2 + 0.57B^2 + 0.40C^2$$

During this study it was found that all three variables negatively influenced the performance of MBR to remove NH_4-N but the interaction between permeate flux (A) and backwashing period (B) positively affected the NH_4-N removal efficiency. Whereas, the interaction of permeate flux (A) with relaxation period (C) i.e. AC and backwashing period (B) with relaxation period (C) i.e. BC had negative impact on treatment efficiency of COD.

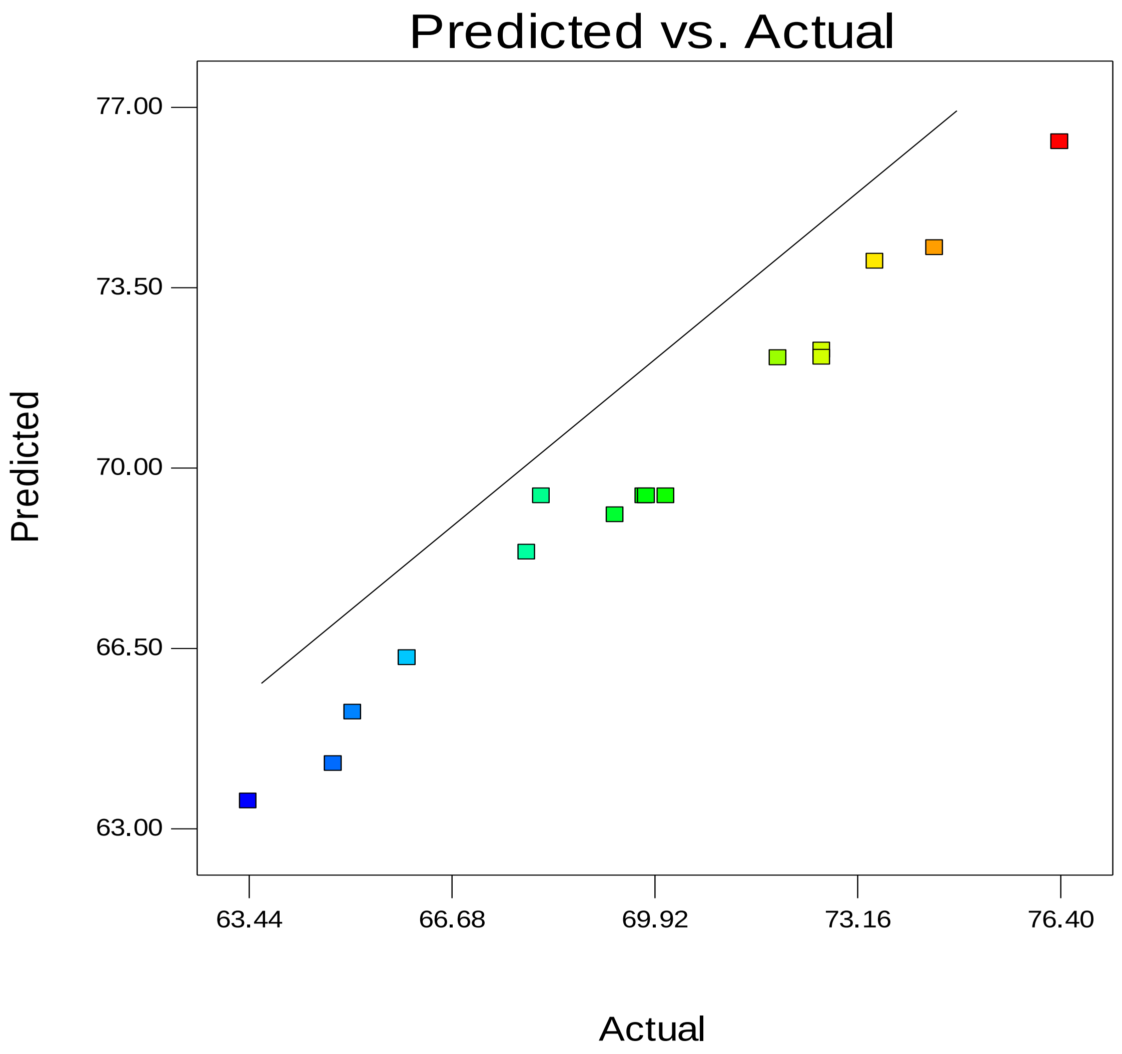


Figure 4.5: Graph showing predicted and actual responses NH_4-N removal efficiency

Three-dimensional response surface plot for the effect of flux rate, backwashing period and relaxation period on NH_4-N removal efficiency.

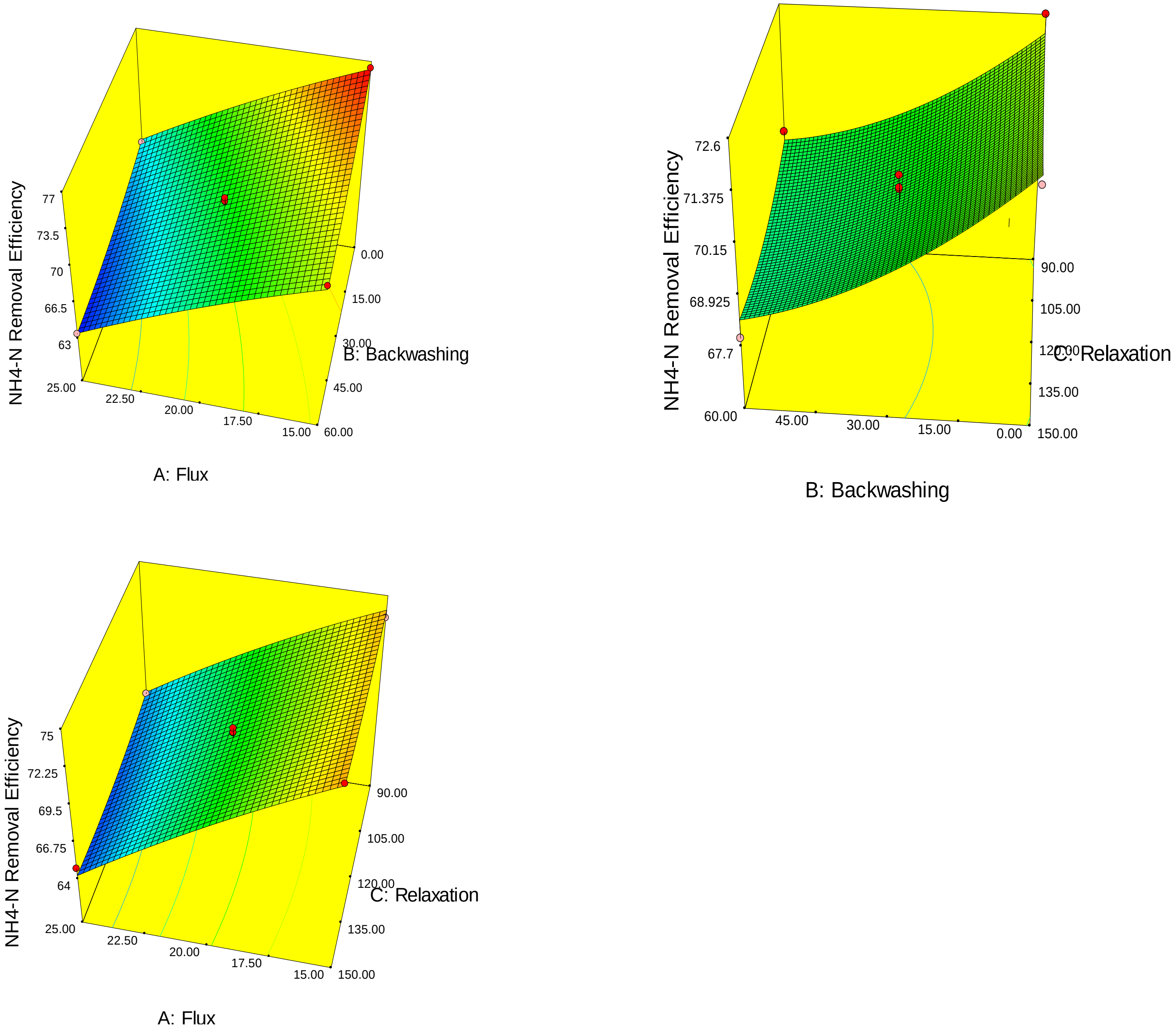


Figure 4.6: 3-D plots showing the interaction and effects of flux rate, backwashing and relaxation on NH_4-N Removal after 5 days.

4.4 Modeling of TN Removal Efficiency

ANOVA for Response Surface Quadratic Model

Table 4. 4: Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	104.85	9	11.65	21.5	0. 0007	significant
A-Flux	22.41	1	22.41	41.38	0.0007	
B-Backwashing	61.05	1	61.05	112.73	< 0.0001	
C-Relaxation	2.61	1	2.61	4.82	0.0705	
AB	2.56	1	2.56	4.73	0.0726	
AC	0.30	1	0.30	0.55	0.4869	
BC	0.27	1	0.27	0.50	0.5063	
A^2	0.20	1	0.20	0.37	0.5654	
B^2	12.23	1	12.23	22.59	0.0032	
C^2	3.21	1	3.21	5.93	0.0508	
Residual	3.25	6	0.54			
Lack of Fit	2.19	3	0.73	2.06	0.2845	not significant
Pure Error	1.06	3	0.35			
Cor Total	108.10	15				

Std. Dev.	0.38	**R-Squared**	0.99
Mean	61.40	**Adj R-Squared**	0.98
C.V. %	0.62	**Pred R-Squared**	0.88
PRESS	11.84	**Adeq Precision**	30.14

4.1.1 Final Equation in Terms of Coded Factors

The following is second-order polynomial equation in coded form established to explain the TN removal efficiency.

$$Y_{TN} = +76.87 - 1.67A - 2.76B - 0.57C + 0.80AB - 0.27AC - 0.26BC - 0.22A^2 + 1.75B^2 + 0.90C^2$$

In conventionally treatment processes, biological nitrogen removal is achieved by nitrification followed by a denitrification process, Due to the usage of high concentrations of MLSS in this study i.e.8000-9000 mg/L the nitrogen concentration was monitored to find out the probability of the biological nutrient nitrogen removal.

Above quadratic equation shows that all three variables negatively influenced the performance of MBR to remove TN but the interaction between permeate flux (A) and backwashing period (B) improved capacity of MBR to remove TN. Whereas, the interaction of permeate flux (A) with relaxation period (C) and backwashing period (B) with relaxation period (C) was not effective COD removal.

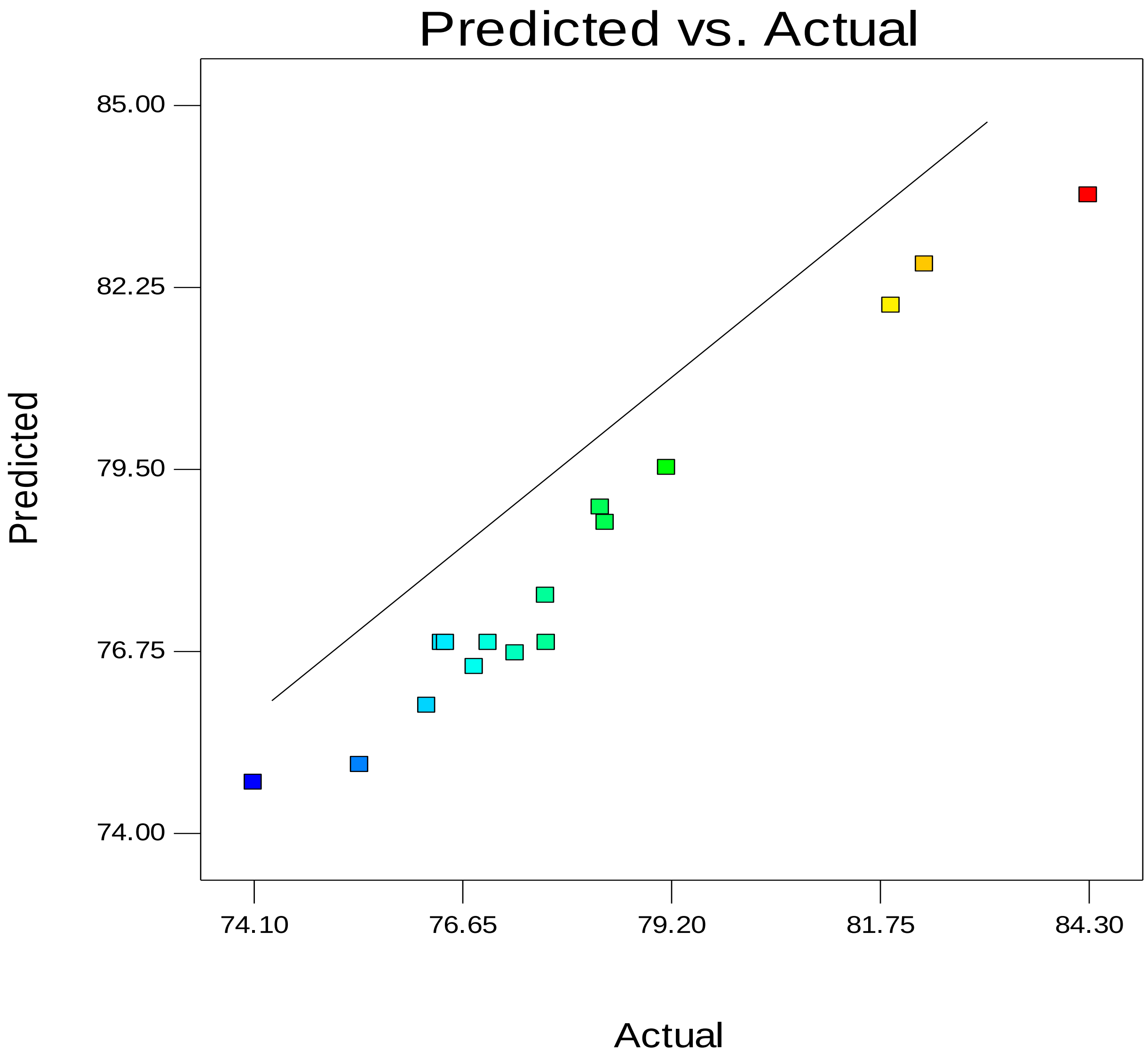


Figure 4.7: Graph showing predicted and actual responses TN removal efficiency

Three-dimensional response surface plot for the effect of flux rate, backwashing period and relaxation period on TN removal efficiency.

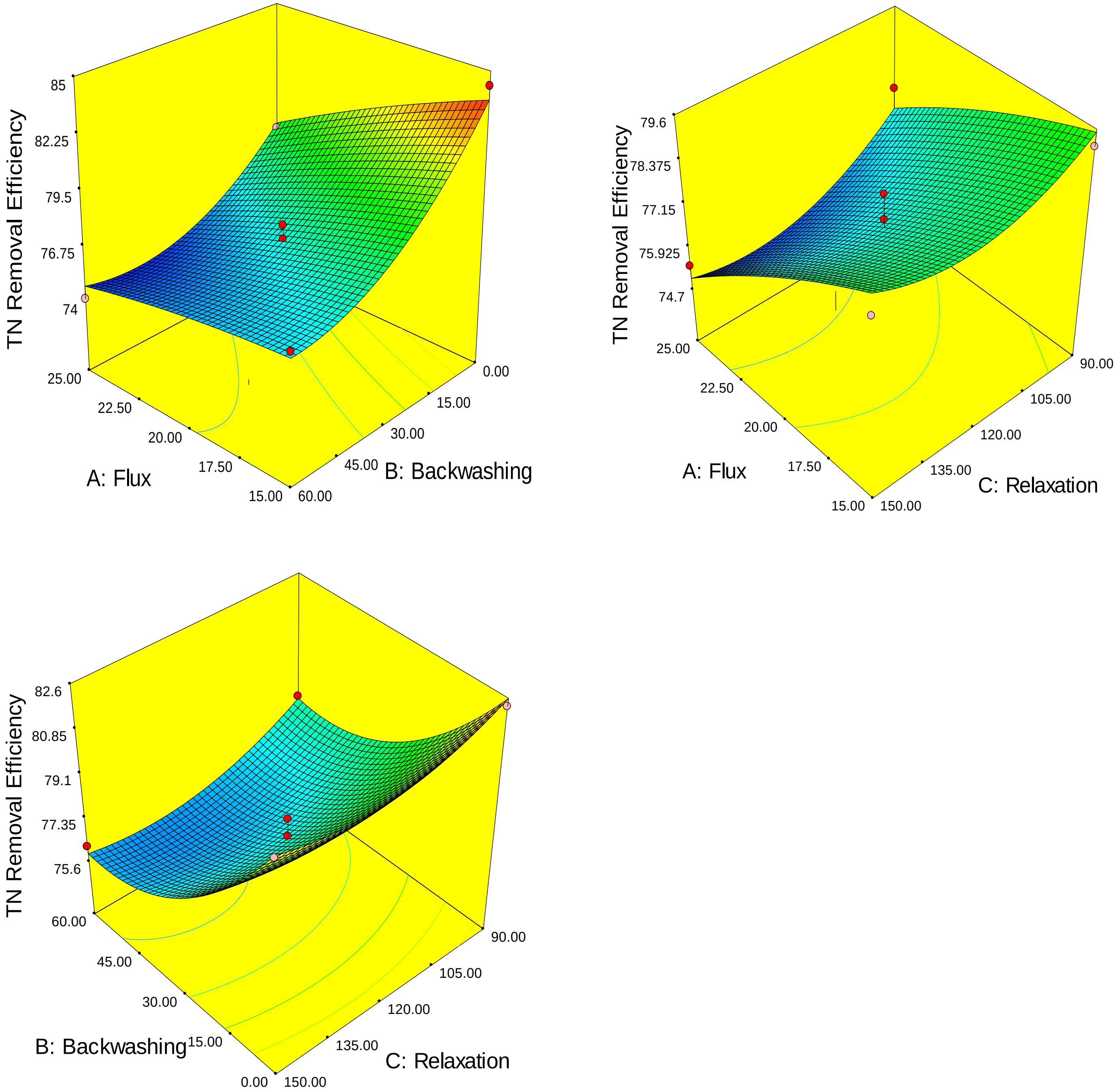


Figure 4.8: 3-D plots showing the interaction and effects of flux rate, backwashing and relaxation on TN Removal after 5 days.

4.5 Modeling of TP Removal Efficiency

ANOVA for Response Surface Quadratic Model

Table 4. 5: Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	96.47	9	10.72	73.07	< 0.0001	significant
A-Flux	40.50	1	40.50	276.10	< 0.0001	
B-Backwashing	38.46	1	38.46	262.17	< 0.0001	
C-Relaxation	0.042	1	0.042	0.29	0.6116	
AB	0.63	1	0.63	4.31	0.0832	
AC	0.21	1	0.21	1.41	0.2797	
BC	1.20	1	1.20	8.17	0.0288	
A^2	0.12	1	0.12	0.84	0.3960	
B^2	13.32	1	13.32	90.82	< 0.0001	
C^2	1.99	1	1.99	13.55	0.0103	
Residual	0.88	6	0.15			
Lack of Fit	0.72	3	0.24	4.59	0.1214	not significant
Pure Error	0.16	3	0.052			
Cor Total	97.35	15				

Std. Dev.	0.74	**R-Squared**	0.970
Mean	78.09	**Adj R-Squared**	0.925
C.V. %	0.94	**Pred R-Squared**	0.659
PRESS	36.87	**Adeq Precision**	15.250

4.5.1 Final Equation in Terms of Coded Factors

The following is second-order polynomial equation in coded form established to explain the TP removal efficiency:

$$Y_{TP} = +60.93 - 2.25A - 2.19B - 0.072C - 0.40AB - 0.23AC - 0.55BC - 0.17A^{2} - 1.83B^{2} - 0.71C^{2}$$

Phosphorus removal in biological treatment process can be done by repeating anaerobic and aerobic steps and this will lead to phosphorus accumulating organisms (PAOs) in the form of polyphosphate. Above quadratic equation shows that all individual parameters and their interaction with other parameters negatively influenced the performance of MBR to remove total phosphorus.

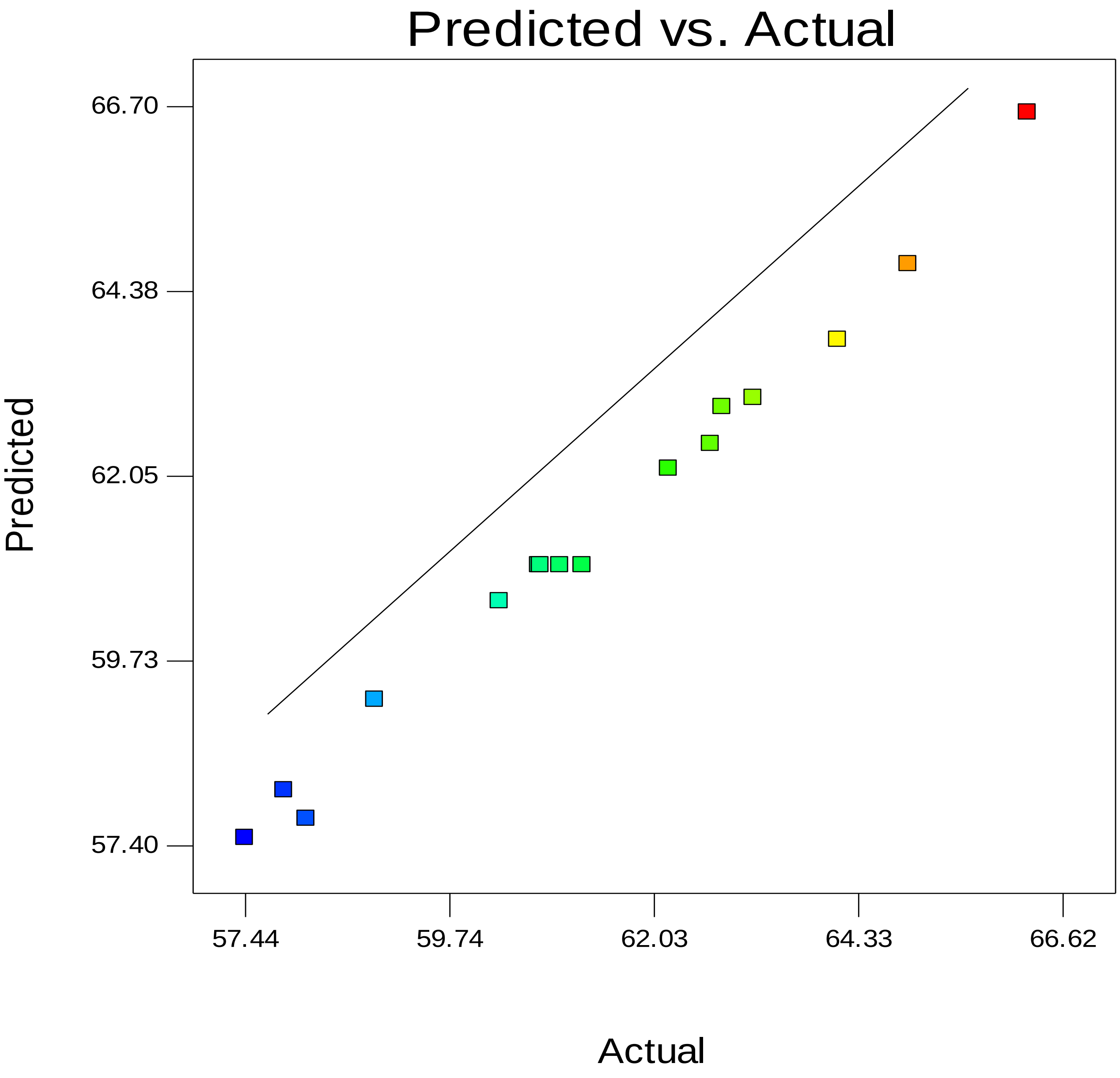


Figure 4.9: Graph showing predicted and actual responses TP removal efficiency

Three-dimensional response surface plot for the effect of flux rate, backwashing period and relaxation period on TP removal efficiency.

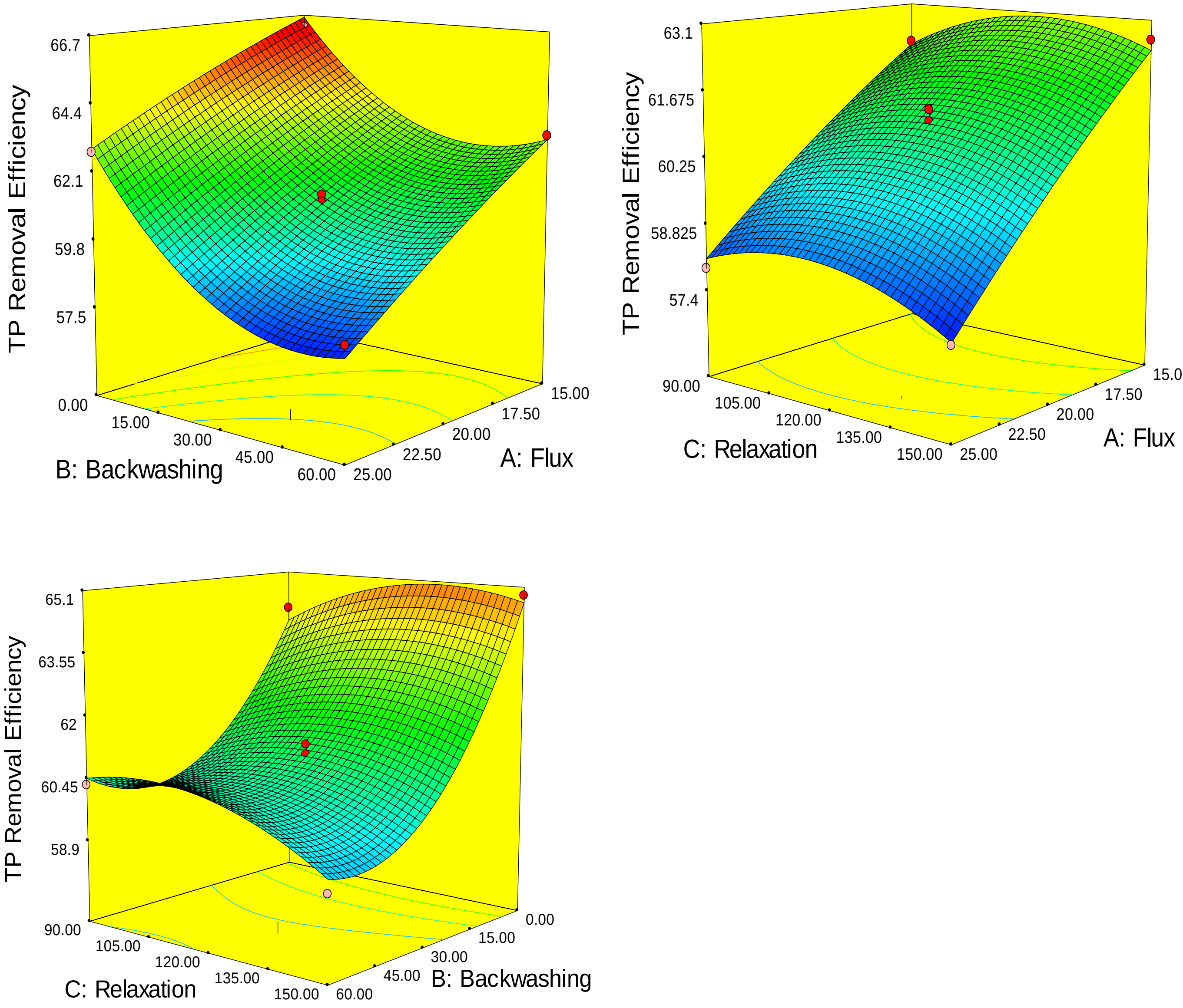


Figure 4.10: 3-D plots showing the interaction and effects of flux rate, backwashing and relaxation on TP Removal after 5 days.

Table 4. 6: Process Optimization by RSM

Number	Flux (LMH)	Backwashing (Sec)	Relaxation (Sec)	TMP (KPa)	COD (%)	NH3-N (%)	TN (%)	TP (%)
1	**18.57**	**9.70**	**90.0**	**21.1058**	**86.0786**	**72.2403**	**80.6827**	**62.2122**
2	**18.52**	**9.65**	**90.0**	**21.1182**	**86.138**	**72.2904**	**80.5968**	**62.133**
3	**18.59**	**9.99**	**90.0**	**20.9665**	**86.0147**	**72.1908**	**80.6255**	**62.1593**
4	**18.40**	**9.56**	**90.0**	**21.1325**	**86.2642**	**72.3965**	**80.5241**	**62.0766**

4.7 Verification of predictive model

In order to check the optimum combination of the key operating parameters i.e. flux rate, backwashing period and relaxation period, confirmation experiments were carried out at the optimal condition. The predicted and confirmation experiments values verified that the optimal conditions were practical.

Chapter 5

CONCLUSIONS

Permeate flux, backwashing and relaxation periods are important process parameter for the operation of an MBR because of their influence on the performance of an MBR and membrane fouling. These process parameters were optimized successfully using Response Surface Methodology (RSM). Box–Behnken design (BBD) was employed to predict responses and to evaluate the influence due to the interaction among permeate flux, backwashing and relaxation periods.

Results have shown that all independent variables negatively affected the performance of MBR. However, backwashing and relaxation periods were found to be effective for membrane fouling control. Since all models were significant and reproducible, so predicted responses were optimized and it was found that optimized values for permeate flux, backwashing and relaxation periods were as given below respectively and were validated experimentally.

The optimal operating conditions resulted from the experimentation are expected to offer important reference values for the continuous flow experiments in the future.

Table 5. 1: Predicted vs experimentally verified results

	Optimized Conditions							
	Flux (LMH)	**Backwashing (Sec)**	**Relaxation (Sec)**	**TMP (KPa)**	**COD (%)**	**NH3-N (%)**	**TN (%)**	**TP (%)**
Predicted	**18.56**	**9.7**	**90**	21.11	86.09	72.25	80.60	62.14
Experimental				20.54	84.75	73.33	79.67	60.8

1. Box-Behnken was found efficient enough to optimize the following process parameters as following:
    - Flux at 18.57 LMH
    - Backwashing Mode at 9.70 sec
    - Relaxation Mode at 90 sec
2. Box-Behnken Design Model predicted the output values of control parameters as below:
    - TMP 21.105 KPa/day
    - COD Removal Efficiency 86.0786 %
    - NH3-N Removal Efficiency 72.2403 %
    - TN Removal Efficiency 80.5968 %
    - TP Removal Efficiency 62.1330 %
3. The results of operational parameters, at these optimized values, were cross examined and found as:
    - TMP 20.54 KPa/day
    - COD Removal Efficiency 84.75 %
    - NH3-N Removal Efficiency 73.33 %
    - TN Removal Efficiency 79.67 %
    - TP Removal Efficiency 60.80 %

At these optimized values the membrane fouling is the lowest among all the patterns, moreover the removal efficiency is also in acceptable range.

Chapter 6

RECOMMENDATIONS

Following recommendations are noteworthy for further study:

1. The backwash frequency and duration of a backwash cycle should also be optimized. This would result to an improved control of irreversible fouling and better overall performance.

2. Looking at the potential benefits, MBR system must be optimized for industrial effluents in future investigations.

3. The energy consumption of the systems should be investigated and optimized.

4. Pilot scale MBR installed at NUST may also be optimized via Box–Behnken (Response Surface Methodology, RSM)

REFERENCES

1. Achilli, A., T. Y. Cath, E. A. Marchand and A. E. Childress (2009). "The forward osmosis membrane bioreactor: a low fouling alternative to MBR processes." Desalination **239**(1): 10-21.

2. Ahmad, S. (2007). "Land and Water Resources of Pakistan—A Critical Assessment." The Pakistan Development Review: 911-937.

3. Ahn, K.-H. and K.-G. Song (2000). "Application of microfiltration with a novel fouling control method for reuse of wastewater from a large-scale resort complex." Desalination **129**(3): 207-216.

4. Al-Amoudi, A. and R. W. Lovitt (2007). "Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency." Journal of Membrane Science **303**(1): 4-28.

5. Aslan, N. and Y. Cebeci (2007). "Application of Box–Behnken design and response surface methodology for modeling of some Turkish coals." Fuel **86**(1): 90-97.

6. Baker, J. and L. Dudley (1998). "Biofouling in membrane systems—a review." Desalination **118**(1): 81-89.

7. Baker, R., A. Fane, C. Fell and B. Yoo (1985). "Factors affecting flux in crossflow filtration." Desalination **53**(1): 81-93.

8. Baş, D. and İ. H. Boyacı (2007). "Modeling and optimization I: Usability of response surface methodology." Journal of Food Engineering **78**(3): 836-845.

9. Belfort, G., R. H. Davis and A. L. Zydney (1994). "The behavior of suspensions and macromolecular solutions in crossflow microfiltration." Journal of Membrane Science **96**(1-2): 1-58.

10. Bouhabila, E. H., R. B. Aïm and H. Buisson (1998). "Microfiltration of activated sludge using submerged membrane with air bubbling (application to wastewater treatment)." Desalination **118**(1): 315-322.

11. Bouhabila, E. H., R. B. Aïm and H. Buisson (2001). "Fouling characterisation in membrane bioreactors." Separation and Purification Technology **22**: 123-132.

12. Brindle, K. and T. Stephenson (1996). "The application of membrane biological reactors for the treatment of wastewaters." Biotechnology and Bioengineering **49**(6): 601-610.

13. Chang, I.-S., K.-H. Choo, C.-H. Lee, U.-H. Pek, U.-C. Koh, S.-W. Kim and J.-H. Koh (1994). "Application of ceramic membrane as a pretreatment in anaerobic digestion of alcohol-distillery wastes." Journal of membrane science **90**(1): 131-139.

14. Chang, I.-S., P. Le Clech, B. Jefferson and S. Judd (2002). "Membrane fouling in membrane bioreactors for wastewater treatment." Journal of environmental engineering **128**(11): 1018-1029.

15. Chang, I., J. Kim and C. Lee (2001). The effects of EPS on membrane fouling in a MBR process. Proceedings of the 3rd International Conference of the MBR (MBR3), Cranfield University.

16. Chang, I., C. Lee and K. Ahn (1999). "Membrane filtration characteristics in membrane-coupled activated sludge system: The effect of floc structure on membrane fouling." Separation science and technology **34**(9): 1743-1758.

17. Charfi, A., Y. Yang, J. Harmand, N. B. Amar, M. Heran and A. Grasmick (2015). "Soluble Microbial Products and Suspended Solids influence in membrane fouling dynamics and interest of punctual relaxation and/or backwashing." Journal of Membrane Science **475**: 156-166.

18. Chen, D., L. K. Weavers and H. W. Walker (2006). "Ultrasonic control of ceramic membrane fouling: effect of particle characteristics." Water research **40**(4): 840-850.

19. Chen, V., A. Fane, S. Madaeni and I. Wenten (1997). "Particle deposition during membrane filtration of colloids: transition between concentration polarization and cake formation." Journal of Membrane Science **125**(1): 109-122.

20. Chiemchaisri, C., Y. Wong, T. Urase and Yamamoto (1992). "Organic stabilization and nitrogen removal in membrane separation bioreactor for domestic wastewater treatment." Water Science and Technology **25**(10): 231-240.

21. Cornel, P. and S. Krause (2008). "Membrane bioreactors for wastewater treatment." Advanced Membrane Technology and Applications: 217-238.

22. Cosgrove, B. and F. Rijsberman (2000). "World water vision." J HYDRAUL RES **38**(4): 57.

23. Crook, J., D. K. Ammerman, D. A. Okun and R. L. Matthews (1992). "Guidelines for water reuse."

24. Defrance, L. and M. Jaffrin (1999). "Comparison between filtrations at fixed transmembrane pressure and fixed permeate flux: application to a membrane bioreactor used for wastewater treatment." Journal of Membrane Science **152**(2): 203-210.

25. Ebrahim, S. (1994). "Cleaning and regeneration of membranes in desalination and wastewater applications: state-of-the-art." Desalination **96**(1): 225-238.

26. FENTON-MAY, R. I., C. G. HILL and C. H. AMUNDSON (1971). "Use of ultrafiltration/reverse osmosis systems for the concentration and fractionation of whey." Journal of Food Science **36**(1): 14-21.

27. Fritsch, J. and C. Moraru (2008). "Development and optimization of a carbon dioxide-aided cold microfiltration process for the physical removal of microorganisms and somatic cells from skim milk." Journal of dairy science **91**(10): 3744-3760.

28. Fu, H.-Y., P.-C. Xu, G.-H. Huang, T. Chai, M. Hou and P.-F. Gao (2012). "Effects of aeration parameters on effluent quality and membrane fouling in a submerged membrane bioreactor using Box–Behnken response surface methodology." Desalination **302**: 33-42.

29. Gao, D., Y. Fu, Y. Tao, W. Wu, R. An and X. Li (2009). "Current research and development of controlling membrane fouling of MBR." African journal of biotechnology **8**(13).

30. Ghalekhani, G. and A. Zinatizadeh (2014). "Process Analysis and Optimization of Industrial Estate Wastewater Treatment Using Conventional and Compartmentalized Membrane Bioreactor: A Comparative Study." Iranica Journal of Energy and Environment **5**(2): 101-112.

31. Gkotsis, P. K., D. C. Banti, E. N. Peleka, A. I. Zouboulis and P. E. Samaras (2014). "Fouling issues in membrane bioreactors (MBRs) for wastewater treatment: Major mechanisms, prevention and control strategies." Processes **2**(4): 795-866.

32. Gunaraj, V. and N. Murugan (1999). "Application of response surface methodology for predicting weld bead quality in submerged arc welding of pipes." Journal of Materials Processing Technology **88**(1): 266-275.

33. Hoinkis, J., S. A. Deowan, V. Panten, A. Figoli, R. R. Huang and E. Drioli (2012). "Membrane bioreactor (MBR) technology–a promising approach for industrial water reuse." Procedia Engineering **33**: 234-241.

34. Hong, S., T. Bae, T. Tak, S. Hong and A. Randall (2002). "Fouling control in activated sludge submerged hollow fiber membrane bioreactors." Desalination **143**(3): 219-228.

35. Huang, X., R. Liu and Y. Qian (2000). "Behaviour of soluble microbial products in a membrane bioreactor." Process Biochemistry **36**(5): 401-406.

36. Ivanovic, I. (2011). Application of biofilm membrane bioreactor (BF-MBR) for municipal wastewater treatment, Norwegian University of Science and Technology.

37. Jiang, T., M. Kennedy, B. Guinzbourg, P. A. Vanrolleghem and J. Schippers (2005). "Optimising the operation of a MBR pilot plant by quantitative analysis of the membrane fouling mechanism." Water Science & Technology **51**(6-7): 19-25.

38. Jorand, F., F. Zartarian, F. Thomas, J. Block, J. Bottero, G. Villemin, V. Urbain and J. Manem (1995). "Chemical and structural (2D) linkage between bacteria within activated sludge flocs." Water research **29**(7): 1639-1647.

39. Kim, J.-S., C.-H. Lee and I.-S. Chang (2001). "Effect of pump shear on the performance of a crossflow membrane bioreactor." Water research **35**(9): 2137-2144.

40. Le-Clech, P., V. Chen and T. A. Fane (2006). "Fouling in membrane bioreactors used in wastewater treatment." Journal of Membrane Science **284**(1): 17-53.

41. Le-Clech, P., B. Jefferson and S. Judd (2003). "Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor." Journal of Membrane Science **218**(1): 117-129.

42. Lee, E. K., V. Chen and A. Fane (2008). "Natural organic matter (NOM) fouling in low pressure membrane filtration—effect of membranes and operation modes." Desalination **218**(1): 257-270.

43. Longgenburg, T., D. Herold and C. Kullman (2010). Membrane Bioreactors (MBR) for Landfill Leachate Treatment. Water Institute of South Africa Conference.

44. Lu, J.-y., X. Du and G. Lipscomb (2009). Cleaning membranes with focused ultrasound beams for drinking water treatment. Ultrasonics Symposium (IUS), 2009 IEEE International, IEEE.

45. Metzger, U., P. Le-Clech, R. M. Stuetz, F. H. Frimmel and V. Chen (2007). "Characterisation of polymeric fouling in membrane bioreactors and the effect of different filtration modes." Journal of Membrane Science **301**(1): 180-189.

46. Ng, A. N. and A. S. Kim (2007). "A mini-review of modeling studies on membrane bioreactor (MBR) treatment for municipal wastewaters." Desalination **212**(1): 261-281.

47. Ohkuma, N., M. Ohnishi and Y. Okuno (1994). "Waste water recycling technology using a rotary disk module." Desalination **98**(1): 49-58.

48. Peng, W., I. C. Escobar and D. B. White (2004). "Effects of water chemistries and properties of membrane on the performance and fouling—a model development study." Journal of membrane science **238**(1): 33-46.

49. Ping Chu, H. and X. y. Li (2005). "Membrane fouling in a membrane bioreactor (MBR): sludge cake formation and fouling characteristics." Biotechnology and bioengineering **90**(3): 323-331.

50. Poorasgari, E., T. Vistisen Bugge, M. Lykkegaard Christensen and M. Koustrup Jørgensen (2015). "Compressibility of fouling layers in membrane bioreactors." Journal of Membrane Science **475**: 65-70.

51. Porcelli, N., P. Hillis and S. Judd (2009). "Microfiltration membrane plant start up: a case study with autopsy and permeability recovery analysis." Environmental technology **30**(6): 629-639.

52. Postel, S. L. (2000). "Entering an era of water scarcity: the challenges ahead." Ecological applications **10**(4): 941-948.

53. Psoch, C. and S. Schiewer (2006). "Direct filtration of natural and simulated river water with air sparging and sponge ball application for fouling control." Desalination **197**(1): 190-204.

54. Radjenović, J., M. Matošić, I. Mijatović, M. Petrović and D. Barceló (2008). Membrane bioreactor (MBR) as an advanced wastewater treatment technology. Emerging Contaminants from Industrial and Municipal Waste, Springer**:** 37-101.

55. Sabia, G., M. Ferraris and A. Spagni (2014). "Online monitoring of MBR fouling by transmembrane pressure and permeability over a long-term experiment." Separation and Purification Technology **122**: 297-305.

56. Shi, X., G. Tal, N. P. Hankins and V. Gitis (2014). "Fouling and cleaning of ultrafiltration membranes: a review." Journal of Water Process Engineering **1**: 121-138.

57. Shimizu, Y., M. Rokudai, S. Tohya, E. Kayawake, T. Yazawa, H. Tanaka and K. Eguchi (1990). "Effect of membrane resistance on filtration characteristics for methanogenic waste." Kagaku Kogaku Ronbunshu **16**(1): 145-151.

58. Sonune, A. and R. Ghate (2004). "Developments in wastewater treatment methods." Desalination **167**: 55-63.

59. Stephen Chapman, C. M., I. Law and I. Solutions "Membrane Bioreactors (MBR) for Municipal Wastewater Treatment–An Australian Perspective."

60. Sun, D. D., C. T. Hay, S. L. Khor and J. O. Leckie (2012). Water reclamation without biosludge reproduction, Google Patents.

61. Sun, W., J. Liu, H. Chu and B. Dong (2013). "Pretreatment and membrane hydrophilic modification to reduce membrane fouling." Membranes **3**(3): 226-241.

62. Tansel, B., J. Regula and R. Shalewitz (2001). "Evaluation of ultrafiltration process performance for treatment of petroleum contaminated waters." Water, Air, and Soil Pollution **126**(3-4): 291-305.

63. Tardieu, E., A. Grasmick, V. Geaugey and J. Manem (1998). "Hydrodynamic control of bioparticle deposition in a MBR applied to wastewater treatment." Journal of membrane science **147**(1): 1-12.

64. Urbain, V., B. Mobarry, V. De Silva, D. Stahl, B. Rittmann and J. Manem (1998). "Integration of performance, molecular biology and modeling to describe the activated sludge process." Water Science and Technology **37**(4): 223-229.

65. Vera, L., E. González, O. Díaz, R. Sánchez, R. Bohorque and J. Rodríguez-Sevilla (2015). "Fouling analysis of a tertiary submerged membrane bioreactor operated in dead-end mode at high-fluxes." Journal of Membrane Science **493**: 8-18.

66. Xing, C.-H., E. Tardieu, Y. Qian and X.-H. Wen (2000). "Ultrafiltration membrane bioreactor for urban wastewater reclamation." Journal of Membrane Science **177**(1): 73-82.

67. Yamamoto, K., M. Hiasa, T. Mahmood and T. Matsuo (1989). "Direct solid-liquid separation using hollow fiber membrane in an activated sludge aeration tank." Water Science and Technology **21**(4-5): 43-54.

68. Yao-po, F., W. Ju-si and J. Zhao-chun (1998). "Test of membrane bioreactor for waste water treatment in a petrochemical complex." Journal of Environmental Sciences **10**(3).

69. Zularisam, A., A. Ismail, M. Salim, M. Sakinah and T. Matsuura (2009). "Application of coagulation–ultrafiltration hybrid process for drinking water treatment: Optimization of operating conditions using experimental design." Separation and Purification Technology **65**(2): 193-210.

ANNEXURE

Determination of NH_4-N

Method: 4500-NH_3 B. Preliminary Distillation Step

Apparatus:

70. Distillation apparatus, pH meter

Reagents:

1. Borate buffer solution
2. Sodium hydroxide 6N
3. Dechlorinating reagent
4. Neutralization agent (NaOH 1N or H_2SO_4, 1N)
5. boric acid, Indicating boric acid solution,
6. Sulfuric acid, 0.04N

Procedure:

1. Add 500 mL water and 20 mL borate buffer, adjust pH to 9.5 with 6N NaOH solution, and add to a distillation flask. Add a few glass beads or boiling chips and use this mixture to steam out the distillation apparatus until distillate shows no traces of ammonia.
2. Use 500 mL dechlorinated sample or a known portion diluted to 500 mL with water. When NH_3-N concentration is less than 100 μg/Neutralized to approximately pH 7 with dilute acid or base, using a pH meter.
3. Distilled at a rate of 6 to 10 mL/min with the tip of the delivery tube below the surface of acid receiving solution.
4. Collected distillate in a 500-mL Erlenmeyer flask containing 50 mL indicating boric acid solution for titrimetric method. Determined the ammonia by the titrimetric method
5. .

Determination of Total Phosphate (TP)

Method: 4500-P C. Vanado-molybdo-phosphoric Acid Colorimetric Method

Apparatus:

1. Colorimetric equipment: One of the following is required. Spectrophotometer, for use at 400 to 490 nm or Filter photometer, provided with a blue or violet filter exhibiting maximum transmittance Between 400 and 470 nm.

1. Acid-washed glassware: Used acid-washed glassware for determining low concentrations of phosphorus. Phosphate contamination is common because of its absorption on glass surfaces.

Reagents:

1. Phenolphthalein indicator,
2. Hydrochloric acid,
3. Activated carbon,
4. Vanadate-molydate reagent,
5. Standard phosphate solution,
6. Ammonium metvanadate solution.

Procedure:

1. Adjusted the sample PH If sample pH is greater than 10, add 0.05 mL (1 drop) Phenolphthalein indicator to 50.0 mL sample and discharge the red color with 1 + 1 HCl before Diluting to 100 ml.
2. Removed excessive color in sample by shaking about 50 mL with 200 mg activated carbon in an Erlenmeyer flask for 5 min and filter to remove carbon.
3. Placed 35 mL or less of sample, containing 0.05 to 1.0 mg P in a 50-mL volumetric flask. Add 10 mL vanadate-molydate reagent and dilute to the mark with distilled water.

4. Prepared a blank in which 35 mL distilled water for the sample. After 10 min or more, measured absorbance of sample versus a blank at a wavelength of 400 to 490 nm,

1. Prepare a calibration curve by using suitable volumes of Standard phosphate solution.
2. Calculated the phosphorus by a given formula.

$$\text{mg P/L} = \frac{\text{mg P(in 50 mL final volume)} \times 1000}{\text{mL sample}}$$

Determination of chemical oxygen demand (COD)

Method: 5220 B. Open Reflux Method for COD

Apparatus

1. Reflux apparatus,
2. Blender. Pipets,
3. wide-bore

Reagents:

1. Standard potassium dichromate solution 0.04167M,
2. Sulfuric acid reagent, Ferron indicator solution,
3. Standard ferrous ammonium sulfate (FAS) titrant 0.05M,
4. Mercuric sulfate,
5. Potassium hydrogen phthalate (KHP) standard,

Procedure:

1. Blended sample if necessary and pipet 50.00 mL into a 500-mL refluxing flask. For samples with a COD of >900 mg/l Diluted to 50.00 ml.

2. Added 1 g HgSO4, several glass beads, and very slowly add 5.0 mL sulfuric acid reagent, with mixing to dissolve HgSO4. Cool while mixing to avoid possible loss of volatile materials.
3. Added 25.00 mL 0.04167M K2Cr2O7 solution and mix. Attach flask to condenser and turn on cooling water. Add remaining sulfuric acid reagent (70 mL) through open end of condenser. Continue swirling and mixing while adding sulfuric acid reagent.
4. Covered open end of condenser and refluxing mixture and reflux for 2 hr.
5. Cooled at room temperature and titrate excess K2Cr2O7 with FAS, using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator
6. Examined the change in color of the titration the first sharp color change from blue-green to reddish brown that persists for 1 min Till the blue green color may reappear.
7. Similar manner titrated the blank. Calculation is given below:

$$\text{COD as mg } O_2/\text{L} = \frac{(A - B) \times M \times 8000}{\text{mL sample}}$$

Where:

A = mL FAS used for blank ,

B = mL FAS used for sample,

M = molarity of FAS, and

8000 = milli equivalent weight of oxygen × 1000 mL/L.

Determination of Mixed liquor suspended solids (MLSS)

Method: 2540 D. Total Suspended Solids Dried at 103–105°C

Apparatus:

1. Evaporating dishes,

2. Muffle furnace,
3. Desiccator,
4. Drying oven for operation at 103 to 105°C.
5. Analytical balance, Magnetic stirrer, Graduated cylinder.

Procedure:

1. Heated the clean dish to 103 to 105°C for 1 h. cool dish in desiccator until needed. Weigh immediately before use.
2. Pipet a measured volume of well-mixed sample, during mixing, to a pre weighed dish. Stirer sample with a magnetic stirrer during transfer.
3. Dry evaporated sample for at least 1 h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh.
4. weighing dried sample, and calculated the MLSS as given below:

Where:

A = weight of dried residue + dish, mg,

B = weight of dish, mg.

Determination of Total nitrogen (TN)

Method: 4500-N C. Persulfate Method

Apparatus:

1. Autoclave to develop 100 to 110°C for 30min,
2. Glass culture tubes Automated analytical equipment.

Reagents:

1. Ammonia-free and nitrate-free water,
2. Stock nitrate solution, Intermediate nitrate solution,

3. Stock glutamic acid solution, Intermediate glutamic acid solution,
4. Digestion reagent,
5. Borate buffer solution,
6. Copper sulfate solution,
7. Ammonium chloride solution,
8. Color reagent.

Procedure:

1. Prepared NO3 calibration standards in the range 0 to 2.9 mg NO3 N/L by diluting to 100 mL the following volumes of intermediate nitrate solution: 0, 1.00, 2.00, and 4.00.......29.0 ml. Treat standards in the same manner as samples.
2. Prepare glutamic acid digestion check standard of 2.9 mg N/L by diluting, to 100 mL, a 29.0-mL volume of intermediate glutamic acid solution. Treat digestion check standard in the same manner as samples.
3. To a culture tube, added 10.0 mL sample or standard or a portion diluted to 10.0 mL. Added 5.0 mL digestion reagent.
4. Cap tightly. Mix by inverting twice. Heat for 30 min in an autoclave or pressure cooker at 100 to 110°C. Slowly cool to room temperature. Add 1.0 mL borate buffer solution. And Mixed by inverting at least twice.
5. Carried a reagent blank through all steps of the procedure and apply necessary corrections to the results.
6. Determine nitrate by cadmium reduction.

Run	Block	Factor 1 A:Flux LMH	Factor 2 B:backwashing Sec	Factor 3 C:Relaxation Sec	Response 1 TMP After 5 days (KPa)	Response 2 COD Removal Efficiency (%)	Response 3 NH4-N Removal Efficiency (%)	Response 4 TN Removal Efficiency (%)	Response 5 TP Removal Efficiency (%)
1	{ 1 }	20	0	90	27	85.672	72.6	82.3	64.1
2	{ 1 }	15	30	150	15	84.878	74.4	78.34	62.67

3	{ 1 }	20	30	120	16.8	81.032	69.8	76.4	60.76
4	{ 1 }	20	0	150	25.6	83.074	71.9	81.89	64.89
5	{ 1 }	25	0	120	26.8	80.048	65.98	78.4	62.8
6	{ 1 }	15	30	90	16	88.018	73.45	79.15	62.2
7	{ 1 }	20	30	120	16.56	81.566	70.11	76.45	60.98
8	{ 1 }	25	60	120	16.2	74.092	63.44	74.1	58.13
9	{ 1 }	25	30	150	17.4	74.952	64.8	75.4	57.44
10	{ 1 }	20	60	150	16.6	77.112	67.89	76.22	58.9
11	{ 1 }	20	30	120	17.2	80.766	68.12	77.68	61.23
12	{ 1 }	20	60	90	16.5	82.066	69.3	77.67	60.3
13	{ 1 }	15	0	120	24.8	91.028	76.4	84.3	66.23
14	{ 1 }	25	30	90	17.8	79.054	65.11	77.3	57.88
15	{ 1 }	20	30	120	16.36	81.966	69.76	76.97	60.74
16	{ 1 }	15	60	120	14.2	83.166	72.6	76.8	63.15