TREATABILITY STUDIES OF DIFFERENT INDUSTRIAL WASTEWATERS AND TECHNICAL AUDITS OF EXISTING TREATEMENT PLANTS

A Project Report

submitted in partial fulfilment of the requirement for the award of degree of

Masters in Technology

in

Environmental Science and Technology

Submitted by

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This is to certify that **Richa Kapila,** was with us as a trainee in the **WWS Division** from August 2nd, 2021 to July 1st, 2022. During this period she has successfully completed her Project on "**Treatability Studies of Different Industrial Wastewaters and Technical Audits of Existing Treatment Plants",** under guidance of **Nandan Prabhune.**

During this tenure, we found **Richa Kapila** to be sincere and hardworking.

We wish **Richa Kapila** success for his future endeavors.

For Thermax Limited.

Pallavi Prasanna Rege
Group Head- EBU & IBG

DECLARATION

I hereby declare that the project work entitled **"Treatability Studies of Different Industrial Wastewaters and Technical Audits of Existing Treatment Plants"** is an authentic record of my own work carried out at **Thermax Limited, Pune**, as a requirement of one year project internship for the award of degree of M.Tech Environmental Science and Technology, Thapar Institute of Engineering and Technology, Patiala under the guidance of **Mr. Nandan Prabhune,** during August 2nd 2021 to July 1st 2021.

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Certified that the above statement made by the student is correct to the best of my knowledge and belief. I have checked all the requirements, formatting and other essential components of this report and it is as per the guidelines and standards.

Date : 24 July 2022

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ABSTRACT

Water scarcity is deemed as one of the largest threats to humankind. Just a small percentage of the world's water is considered fit for human consumption. Being a natural resource, water is indispensable for human life and critical for the sustainability of the environment. Over the years, countries all over the world have taken up initiatives to develop new technologies and practices to mitigate the effect of water pollution. Water treatment is the process of removing harmful constituents from the water in order to make it safe for consumption.

Despite the availability of state-of-the-art treatment technologies, industries may face challenges in achieving desired performance during operations. These challenges can be caused due to multiple reasons, like ageing infrastructure, changes in wastewater quality and quantity, presence of emerging constituents, uncertainties associated with operations and other factors. In order to overcome these challenges, certain customized services maybe required. These customized services include technical audits, treatability studies and membrane autopsy, and pilot-scale testing. Such customized services play a crucial role in identification of wastewater characteristics, design challenges and providing innovative as well as cost-effective solutions to various challenges associated with pre-existing treatment schemes. Application of these techniques helps in determination of treatment schemes for wastewaters.

LIST OF ABBREVIATIONS

ABBREVIATION	MEANING
RO	Reverse Osmosis
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive x-ray Spectroscopy
FRP	Fibre-reinforced Plastic
ATD	Anti-Telescopic Device
AAS	Atomic Absorption Spectroscopy
PAC	Poly Aluminium Chloride
FAB	Fluidised Aerobic Bioreactor
DMF	Dual Media Filter
ACF	Activated Carbon Filter
UF	Ultrafiltration
MF	Microfiltration
NF	Nanofiltration
CEB	Chemically Enhanced Backwash
STP	Sewage Treatment Plant
CIP	Clean In Place
COD	Chemical Oxygen Demand

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

In the recent years, under the impact of global warming and deteriorating environmental conditions, preserving environment has taken precedence. Environmental crisis is a major issue of concern for every nation. Water pollution is one environmental issue that has a drastic impact on the environment, which is also emphasized in UN sustainable development goal no. 6. Water scarcity is deemed as one of the largest threats to humankind. Just a small percentage of the world's water is considered fit for human consumption. Being a natural resource, water is indispensable for human life and critical for the sustainability of the environment. Over the years, states all over the world have taken up initiatives to develop new technologies and practices to mitigate the effect of water pollution. Some of these initiatives include desalination, rainwater harvesting and wastewater treatment. (1) (2)

Water treatment is the process of removal of harmful constituents and nutrients from the water making it fit for consumption. The objective of water treatment is to eliminate the various constituents from the wastewater in order to produce an effluent that can be discharged into the environment without causing health hazards. The process of water treatment is broadly classified into three categories, namely, physical unit operations, chemical unit operations and biological unit processes. The physical unit operations are those operations where the change is brought about due to the application of physical forces, whereas chemical and biological unit processes are those processes where change is brought about due to the chemical and biological activities. Commonly used unit operations in the wastewater treatment include screening, flocculation, floatation, filtration, and comminution. Chemical precipitation, adsorption, disinfection, and dechlorination are some of the chemical unit processes employed in wastewater treatment. Biological unit processes maybe aerobic, anaerobic or facultative.

Depending upon the unit operations and unit processes employed, sewage treatments are classified as :

- Preliminary Treatment

- Primary Treatment
- Secondary Treatment
- Tertiary Treatment

Preliminary treatment consists of removal of floating materials, heavy settleable inorganic solids like grit, sand, and fats, oils and grease from the wastewater. Preliminary treatment is done to prevent the adverse effect of these substances on the treatment system. Primary treatment consists of removal of large suspended solids. Removal of suspended solids is usually accomplished through gravity sedimentation. After sedimentation, the organic solids that are separated out are stabilised through anaerobic decomposition or incinerated.

In secondary treatment, the effluent is further treated through the removal of organic matter and residual suspended particulate matter. The secondary treatment is accomplished through biological unit processes. The effluent from secondary treatment usually has little biological oxygen demand, it may, however, contain certain amount of dissolved oxygen.

Tertiary treatment or advanced treatment involves all operations and processes used to remove the contaminants that are not removed during the conventional treatment. These contaminants may include dissolved and suspended materials such as inorganic compounds of nitrogen and phosphorus, residual organic matters, pathogens, etc. Various processes used in the tertiary treatment include chemical clarification, recarbonation, filtration, activated carbon adsorption, demineralization, etc.

There are three types of water treatment plants, namely,

- Effluent Treatment Plants
- Sewage Treatment Plants
- Water Treatment Plants

Despite of state-of-the-art treatment technologies, industries may face challenges in achieving desired performance during operations. These challenges can be caused due to multiple reasons, like ageing infrastructure, changes in wastewater quality and quantity, presence of emerging constituents, uncertainties associated with operations and others. In order to overcome these challenges, certain customized services maybe required. These customized services include technical audits, treatability studies and membrane autopsy, and pilot-scale testing.

Technical audits can help in restoring plant performance, stabilizing the operations and optimizing operational costs. They can also help in deciding whether retrofitting new technologies or revamping pre-existing technologies is required in order to overcome the challenges faced during plant operation.

Treatability studies, on the other hand, are effective in understanding the characteristics of wastewater. Through treatability studies, characteristics of wastewater can be analyzed and suitable treatment schemes can be determined. These studies help in optimizing chemical consumption requirement for treating wastewater, thereby reducing the operational costs.

Pilot testing includes temporary installation of an equipment in order to study its application and evaluate its feasibility. Pilot scale testing is performed to generate operational data for innovative products and technologies and define their operating conditions and constraints.

Membranes have a broad spectrum of industrial applications. Apart from water and wastewater treatment, membrane filtration technology is widely used in food and beverage processes, chemical processing, pharmaceutical applications and other industrial applications. Membranes are sensitive to deviation in water quality. Any significant deviation in water quality or change in operational parameters can affect the membrane life, affect plant performance and increase operational costs. Membrane autopsy is destructive technique that helps in understanding the membrane health and reasons behind its reduced performance. This can help in preventing repetition of such events in the future.

Such customized services play a crucial role in identification of wastewater characteristics, design challenges and providing innovative as well as cost-effective solutions to various challenges associated with pre-existing treatment schemes.

1.2 COMPANY PROFILE

Thermax Limited in an Indian engineering company that provides sustainable solutions in energy and environment. Headquartered in Pune, Thermax’s portfolio includes products for heating, cooling, water and waste management, and specialty chemicals. Thermax also designs, builds and commissions large boilers for steam and power generation, industrial and municipal wastewater treatment plants, waste heat recovery systems and air pollution control projects. (3)

Thermax operates globally through 29 international offices and 14 manufacturing facilities, 10 of which are in India.

It has three main segments : Energy, Environment and Chemical. Energy includes heating, cooling, power generation and renewable energy. Environment includes air pollution control, waste treatment, and wastewater treatment. Chemicals include water and fuel treatment chemicals, paper and pulp chemicals, oil field chemicals, specialty chemicals and others. (4)

The company's vision for the future is firmly anchored in the belief that to stay competitive, companies need to adopt sustainable development practices.

1.3 OBJECTIVE

During the course of this project, different aspects of multiple projects were covered. The aim was to become familiar with various technical aspects related to water and wastewater treatment. The project objectives are outlined below :

- Perform audit of a sewage treatment plant
- Conduct pilot plant testing of ultrafiltration unit and learn different aspects associated with it
- Analyze and describe membrane autopsy on RO membrane
- Evaluate treatability studies on different industrial wastewaters

CHAPTER 2

LITERATURE REVIEW

2.1 Major Unit Operations and Processes in Wastewater Treatment

2.1.1 Introduction

The aim of sewage treatment is removal of various constituents from the wastewater in order to produce an effluent that can be discharged into the environment without causing health hazards. The sewage treatment involves various operations and processes or their combinations. These operations and processes may be broadly classified into three categories, namely, physical unit operations, chemical unit processes and biological unit processes.

The physical unit operations are those operations where the change is brought about due to the application of physical forces, whereas chemical and biological unit processes are those processes where change is brought about due to the chemical and biological activities. During wastewater treatment, screening, flocculation, floatation, filtration, and comminution are commonly used unit operations. Chemical unit processes commonly employed in wastewater treatment include chemical precipitation, adsorption, disinfection, and dechlorination. Biological unit processes maybe aerobic, anaerobic or facultative.

Depending upon the unit operations and unit processes employed, sewage treatments are distinguished as :

- Preliminary Treatment
- Primary Treatment
- Secondary Treatment
- Tertiary Treatment

2.1.2 Coagulation and Flocculation

The process of coagulation-flocculation is a commonly used process in the treatment of water and wastewater. Coagulation-flocculation followed by sedimentation and filtration is an essential and widely employed in the treatment process before discharging treated water into the environment.. By definition, Coagulation is the process of aggregation of colloidal particles into large aggregates in order to attain better stability. It is an effective, efficient and simple method of treating water and wastewater. Due to the addition of coagulant in the water, the colloidal particles start forming aggregates.

The process of selection of coagulant and the adequate dose required for treatment are quite important. Coagulants maybe inorganic or natural. Inorganic coagulants are frequently used in industrial applications. However, prolonged and excessive use of chemical coagulants can have detrimental effect on human health. Additionally, inorganic coagulants can be ineffective under conditions of low temperature. Furthermore, they also produce significant amount of toxic sludge. Therefore, in contrast, natural, biodegradable coagulants are preferred as they are cheaper, low in toxicity and produce comparatively less sludge. Due to their merits, the use of natural coagulants has been steadily rising in the recent years.

The efficiency of the coagulation process depends upon multiple factors, namely, type of coagulant used, dosage of the coagulant, pH of the effluent, mixing speed and time.

Coagulation is the process of destabilizing the charge of the particles on addition of coagulants. This process involves addition of coagulants or chemicals with charge opposite to those of the suspended solid particulate matter present. Addition of chemicals with opposite charge results in neutralization of the charge on the solids. After the charge is neutralized, the small suspended solids start sticking together. This leads to the formation of micro flocs. Here the key is mixing. During the process of coagulation, mixing is essential. Generally, in this process, rapid mixing takes place with the resident time of about 2-3 minutes.

Following coagulation, flocculation occurs. As the name suggests, it is the part of the process where macro flocs are formed from micro flocs. The micro flocs are brought into contact with each other through slow mixing; the speed is reduced from 300 rpm to 50 rpm. Generally, contact time provided for flocculation ranges from 15-20 minutes to an hour or more. Slow mixing promotes floc formation as flocs continue to grow bigger through additional collisions. After the flocs reach an optimum size, the supernatant is removed through separation processes like sedimentation, floatation or filtration.

Experimentally, jar test is used for calculating optimum dosage and optimum pH required for efficient coagulation and flocculation.

Coagulation-flocculation is a conventional pre-treatment method used to separate the suspended and dissolved solids from the water. Charged species such as suspended minerals, organic constituents, dissolved species such as metal ions, phosphates, fluoride, etc., can be separated by the process of coagulation and flocculation. It has relatively simple technology, low cost and high efficiency in removing suspended and dissolved solids.

2.1.3 Sedimentation

Suspended matters present in the sewage are removed by the process of sedimentation. The sewage undergoes sedimentation before the biological treatment and undergoes sedimentation with coagulation after the biological treatment. The purpose of sedimentation is to separate the settleable solids from the effluent. In the primary settling tanks, plain sedimentation takes place. Secondary settling or secondary sedimentation finds use in settling of the effluents from secondary treatment operations like trickling filter or activated sludge where the flocculated solids produced by the biological treatment are removed.

Principle of sedimentation : Sedimentation is based on the principle that impurities settle down after a period of retention. As turbulence slows down, the suspended solids having specific gravity greater than the specific gravity of water tend to settle down under the effect of gravity.

Factors affecting settling tendencies of particles :

- Velocity of flow – Greater the flow area, lesser is the velocity and the particles settle down easily. Velocity can be reduced by increasing the length of travel of effluent.
- Viscosity of water – Warm, less viscous water offers lower resistance to the settling particles.
- Shape and size of the particles – Particles with greater specific gravity will settle easily. Size of the particles can be altered by the addition of coagulants
- Area of the tank – Greater the area of the tank, more will be the detention period, thereby more will be the settling of particles
- Detention period – Greater the detention period, more will be the settling of particles
- Under normal conditions, sedimentation tank can remove 70% of the suspended particulate matter present in water.

2.1.4 Filtration

As per its definition, filtration is a physical process that removes particulate matter from a liquid or gas using a porous filtering media. The main purpose of filtration is to improve the purity of the filtered material. The filter media acts as a barrier that allows liquid pass through while retaining most of the solids. The filter medium maybe a screen, cloth, paper, or bed of solids. The liquid that passes through the filter medium is called filtrate.

Theory of Filtration :

- **Mechanical Straining –** When water is passed through a porous filtering media, the suspended particles present in water whose size is greater than the size of the voids of the filter media, cannot pass through these voids and are arrested in them. In case of sand filter, most of the particles are removed in the upper sand layers. The arrested particles along with the coagulated flocs form a layer on the top of the bed. This layer additionally helps in straining out impurities from water.
- **Flocculation and Sedimentation –** Particles of size smaller than the size of the voids can also be removed through the process of filtration. This can be explained on the assumption that the void spaces act like tiny coagulation-sedimentation tanks. The colloidal matter previously arrested in these voids acts as a gelatinous mass that can attract other finer particles. These finer particles thus are adsorbed, settle down in the voids and are removed.
- **Biological Metabolism -** Certain microorganisms and bacteria may reside as coatings over sand grains or they may be trapped in the voids during the initial process of filtration. These organisms consume organic impurities present and convert them into harmless compounds through the process of biological metabolism. The harmless compounds formed through biological metabolism generally form a layer on the top of sand layer, which further help in absorbing and removing impurities.
- **Electrolytic Changes -** The purifying action of filter can also be explained by the theory of ionization. According to the theory of ionization, filter helps in purifying water by changing the chemical characteristics of water. This may be explained by the fact that the sand grains of the filter media and impurities in water carry electrical charges of opposite nature. When these oppositely charged particles and impurities encounter each other, they neutralize each other, thereby changing the characteristics

of water and making it purer. After a certain interval, the electrical charges of sand grains get exhausted and have to be restored by cleaning the filter.

2.1.5 Membrane Filtration

The basic principle behind membrane filtration involves using a semi-permeable membrane to separate a liquid into two distinct streams.

Pumping the liquid across the surface of the membrane creates a positive trans-membrane pressure that forces any components smaller than the porosity of the membrane to pass through, forming the permeate. Any components larger than the pore size simply cannot pass through, and remain behind in what is called the retentate.
Trans-membrane pressure refers to the difference in pressure between the two sides of the membrane. It describes the amount of force required to push the feed through a membrane. A low trans-membrane pressure indicates a clean, well-functioning membrane, whereas, a high trans-membrane pressure indicates a fouled membrane with reduced filtering abilities.

The principle of most membrane separations is the selective filtration of influent through pores of different sizes.

Membrane processes can be classified into different categories. Membrane processes differ because of membrane configuration, material of construction of membrane, driving force, separation mechanism, and size range of the constituents removed. There are four types of membrane commonly used, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RF). These membrane systems differ on the basis of their pore size. As the pore size decreases, the processes require more driving force. These technologies are often categorised as low pressure (MF,UF) and high pressure (NF,RO) membrane technologies.

2.1.5.1 Ultrafiltration

Filtration is a physical process that removes particulates from liquid by passing it through a porous filtering media. Membrane filtration is based on the principle of separation of liquid into two distinct streams using a semi-permeable membrane. Liquid is pumped across the surface of membrane. This creates a positive trans-membrane pressure that forces any components of size smaller than the pore size of the membrane to pass through, generating permeate. Any components that are larger than the pore size of membrane are retained as retentate or reject.

Trans-membrane pressure refers to difference in pressure between the two sides of the membrane. It describes the amount of force required to push the feed through a membrane. A low trans-membrane pressure indicates a clean, well-functioning membrane, whereas, a high trans-membrane pressure indicates a fouled membrane with reduced filtering abilities.

Membrane processes can be distinguished into different types, based on membrane configuration, material of construction of membrane, driving force, and size range of the constituents removed. Four membrane types commonly used industrially are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These membrane systems are classified in order of decreasing pore size. With decreasing pore size, the amount of driving force required by the process increases. (6)

Ultrafiltration involves pressure driven separation of components from feed solution. It is a low-pressure membrane process that is used to separate bacteria, virus, high molecular weight compounds, colloidal and particulate matter from feed. UF has pore size ranging from 0.01 to 0.1 µm. (7)

There are four main types of membrane configurations.

- Plate-and-Frame
- Tubular
- Hollow-fibre
- Spiral-wound

A spiral-wound element consists of membranes, feed spacers, permeate spacers and a permeate tube. Spiral module is constructed by attaching membrane sheets to the central permeate tube. Feed spacers are placed between the membrane sheets. Feed spacers provide space for water to flow between membrane surfaces and ensure uniform flow between membrane sheets. After attaching the sheets to the permeate tube, they are rolled such that a spiral structure is formed. At the outlet end of each spiral, an anti-telescopic device is present to prevent deformation of membrane due to pressure of liquid. (8) (9)

In spiral-wound elements, feed travels tangentially across the length of the element. Filtrate with size smaller than the pore size will pass across the membrane surface into the permeate spacer and move towards the permeate tube. The retained constituents become concentrated at the end of the element body. (10)

Advantages of spiral-wound membrane : (9)

- Spiral wound elements have very high packing density as compared to other configurations
- They have smallest footprint and a robust design that prevents membrane breakage
- They offer high flux per membrane area
- They have relatively low capital and operating costs
- They can be easily cleaned through Cleaning-in-Place (CIP)

Disadvantages of spiral-wound membrane :

- Fouling in spiral-wound membrane is greater than fouling in tubular module
- Due to high packing density, TSS in the feed stream should be minimum in order to prevent clogging of membrane
- These elements cannot handle mechanical cleaning

Common problems with UF :

1. Membrane Fouling – Fouling occurs when particulate matter adheres to the surface of membrane. Unchecked build-up of particulate matter will ultimately lead to reduced efficiency, pressure drop across the system and increased energy consumption. There are four types of fouling commonly observed in UF operations – particulate fouling, biological fouling, inorganic fouling and organic fouling. Particulate fouling is caused by suspended solids and can be removed through air scour and backwash. Biological fouling is caused by growth of microorganisms. Biological fouling can be reduced by chemically enhanced backwash using oxidizers and/or biocides. Inorganic fouling is caused by precipitation of inorganics on the membrane. Chemically enhanced backwash with acid is commonly used for the removal of inorganic fouling. Organic

fouling is caused by adsorption of organic compounds on the membrane surface. Common cleaning method for removal of organic fouling is CEB with alkali. Proper pre-treatment in the upstream processes and a robust cleaning regimen with various cleaning solutions can help in reduction of membrane fouling and augmented life of membrane.

2. Increased permeate contamination : Decrease in the quality of permeate or presence of contaminating solids in permeate are general indicators of compromised membrane. Membranes can be worn out over time. High temperature or pH level can degrade the membrane quickly. Presence of heavy metals can cause irreversible damage. Integrity testing is a technique that can be used to test the effectiveness of the membrane. (11)

2.1.6 Biological Treatment Processes

The objectives of the biological treatment of sewage are to coagulate and remove the non-settleable colloidal solids and to stabilize the organic matter with the help of microorganisms. The biological conversion of organic matter can be accomplished both aerobically and anaerobically. The biological treatment processes, which involve aerobic conversion, are usually preferred because aerobic bacteria are about three times more active than anaerobic bacteria at normal temperature. Hence, the rate of aerobic conversion is significantly more rapid than that of anaerobic conversion. Moreover, aerobic conversion does not produce bad smells and gases as are produced by anaerobic conversion. The microorganisms responsible for the conversion of organic matter can be maintained in suspension or attached to a fixed or moving medium.

2.1.6.1 Activated Sludge Process

Activated sludge process is the oldest bio-treatment process that is used for the treatment of wastewater. Typically, after the removal of suspended impurities, wastewater is treated in an activated sludge process. It is a biological treatment system that comprises of aeration tank and clarifier.

The raw sewage coming out after the primary treatment is mixed with the required quantity of activated sludge called return sludge and is sent to the aeration tank. In the aeration tank, the mixed liquor, thus formed is aerated and agitated for several hours depending upon the degree of purification desired. As a result, organic matter present in the sewage is oxidized and the suspended and colloidal matter coagulates and form flocculent masses, which are readily settleable. The aerated mixed liquor is sent to the clarifier, where the sludge settles. The effluent from the clarification tank is clear and has low BOD. A part of the settled, activated sludge from the secondary settling tank is recirculated in the aeration tank as seed for the raw sewage. The excessive sludge generated is treated and disposed of.

2.1.6.2 Membrane Bioreactor

Membrane bioreactors combine both biological treatment and physical separation. An advanced technology that integrates a membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor. It constitutes of a conventional activated sludge process and a submerged or external MF/UF membrane process. In the conventional activated sludge process, the organic matters present in the wastewater are reduced by the action of microorganisms. Membrane bioreactor consists of an aeration tank for biological degradation and a secondary clarifier where the sludge is separated from the treated effluent. The effect of the membrane is to increase the concentration in the biological reactor, to retain the particulate matter within the reactor and allow the treated permeate to pass through. In MBRs, biodegradation of organic matter and membrane separation are performed simultaneously. This maximizes the efficiency of wastewater treatment.

There are two process configurations of MBRs :

- Submerged MBR – In submerged MBR, membrane is submerged directly into the aeration tank. By the application of vacuum, the effluent is driven through the membrane retaining the solids.
- External MBR – In external MBR, the mixed liquor from the aeration tank is pumped from to the membrane. Due to high cost of pumping, this system is impractical for full-scale wastewater treatment plants.

Working : After the pre-treatment, the effluent enters the reactor where the biological process occurs. The reactor involves rigorous agitation through the process of aeration. Aeration ensures the availability of sufficient oxygen concentration for the growth of bacteria. It also aids in cleaning the surface of the membrane to prevent the build-up of material on the membrane. A complete unit is usually equipped with a backflush system where the discharged wastewater moves counter-flow from the permeate side to the feed side, dislodging the trapped particles accumulating on the surface of the membrane. Air scouring along with the backflush system helps increase the removal efficiency.

The effluent enters the aerobic zone of the biological reactor where the microorganisms present digest the organic matter present in the wastewater in the presence of oxygen. The digested organic matter will clump together producing a sludge. This sludge will enter the immersed membrane where the solids and microorganisms will be separated from the largely disinfected water.

2.1.6.3 Moving Bed Biofilm Reactor

Moving Bed Biofilm Reactor offers an economical solution for wastewater treatment. It is a compact, simple to operate and very efficient process for the removal of BOD, ammonia and nitrogen form the wastewater. MBBR is submerged, attached growth process. MBBR system constitutes of an aeration tank that is partially filled with special plastic carrier media that provide surface for biofilm to grow.

Preliminary treatment of the effluent is done through screening. The effluent is then pumped into the equalization tank, which is used to maintain the desired flow rate of homogeneous nature. The effluent in then pumped to MBBR tank which is a part of the secondary treatment. MBBR system consists of an activated sludge aeration tank with special plastic carriers that provide surface for biofilm to grow. These carrier media are dumped into the aeration tank and mixed with the effluent through aeration. These media may occupy as much as 50-70% of the tank. The efficiency of MBBR is calculated based on volume occupied by the carrier media. These carrier media have a large internal surface area that provides optimal contact with air, water, and bacteria.

Aeration helps in circulating the plastic media throughout the tank and helps in maintaining optimum level of dissolved oxygen within the tank. Proper aeration ensures good contact between the organic matter present in the effluent and the microorganisms present on the carrier media. The microorganisms attached to the media consume the organic waste in the water, leaving it cleaner and safer for reuse or disposal. The type of microorganisms introduced into the tank depends on the type of wastewater. A sieve is present on the outlet of the tank to prevent the escape of the carrier media.

CHAPTER 3

METHODOLOGY

3.1 EXPERIMENTAL PROCEDURES

Various analytical experiments were performed during the course of this project.

S.No.	Name of the Test	APHA Method	Method Selected	Reason
1.	COD	• Open Reflux Method • Closed Reflux, Titrimetric Method • Closed Reflux, Colorimetric Method	Closed Reflux Method	Closed reflux methods are more economical. However, open reflux method is more suitable for a wide range of wastes where a large sample size is preferred. For these experiments, initially open reflux method was opted. However, it was switched to close reflux method as it was more economical
2.	Turbidity	• Nephelometric Method	Nephelometric Method	

Table 3.1: List of analytical experiments performed

3.2 METHODOLOGY

3.2.1 Chemical Oxygen Demand

Chemical Oxygen Demand (COD) refers to the amount of oxygen needed to oxidize the organic matter present in the wastewater. Basically, the organic matter is decomposed through the utilization of oxygen present in the chemicals. These chemicals are called oxidizing agents. In other words, Chemical Oxygen Demand is defined as the amount of oxidant that reacts with the sample under controlled conditions. Generally, Potassium dichromate and Potassium permanganate are used as oxidizing agents. However, Potassium dichromate is preferred as it is more economical and a clear solution.

COD is often used as a measurement of pollutants in wastewater.

3.2.1.1 Open Reflux Method

Principle : The sample is refluxed in strong acid solution along with a known quantity of potassium dichromate. The standard reflux time of 2 hours is provided. After digestion at 150℃ for 2 hours, the remaining unreduced potassium dichromate is titrated with Ferrous Ammonium Sulphate (FAS), in order to determine the amount of potassium dichromate consumed.

Apparatus : COD vials, condensers, Pipettes, gloves

Reagents :

- Standard Potassium Dichromate solution
- COD reagent/ Sulphuric acid reagent
- Ferroin indicator solution
- Standard ferrous ammonium sulphate (FAS)

Procedure :

- Take 5 ml of potassium dichromate in the COD vial
- Add 15 ml of COD reagent to it
- Add 10 ml of water/wastewater sample to the COD vial
- Prepare duplicate samples
- Shake gently

- Boil the sample for 2 hours at 150℃ in COD digester
- Cool the sample
- Add 2-3 drops of Ferroin indicator.
- Sample turns greenish-yellow in colour
- Titrate the sample with Ferrous ammonium sulphate (FAS) till end point appears
- Endpoint, brick red colour persists.

Calculation :

COD as mg O_2/L = $\frac{(A-B)\times 8\times 1000M}{volume\ of\ sample}$

where :

A = volume of FAS used for blank

B = volume of FAS used for the sample

M = molarity of FAS

Remarks : The sample should not turn green before the addition of ferroin indicator. If greenish colour appears any time before titration, it indicates that more dilution is required.

3.2.1.2 Closed Reflux Method

Principle : The sample is refluxed in strong acid solution along with a known quantity of potassium dichromate. The standard reflux time of 2 hours is provided. After digestion at 150℃ for 2 hours, the remaining unreduced potassium dichromate is titrated with Ferrous Ammonium Sulphate (FAS), in order to determine the amount of potassium dichromate consumed.

Apparatus : COD vials, Digester, pipette

Reagents :

- Standard potassium dichromate solution
- COD reagent
- Ferroin indicator solution
- Standard ferrous ammonium sulphate

Procedure :

- Take 1 ml of potassium dichromate in the COD vial or ampule.
- Add 3 ml of the COD reagent to it
- Add 2 ml of the sample to the prepared solution
- Shake gently
- Place the tubes in the digester preheated at 150℃.
- Reflux for 2 hours
- Cool the vessels to room temperature
- Add 2-3 drops of Ferroin indicator, sample turns green in colour
- Titrate with standard ferrous ammonium sulphate solution till the end point appears
- Reddish brown colour is the end point.

Calculation :

COD as mg O_2/L = $\frac{(A-B)\times 8\times 1000M}{volume\ of\ sample}$

where :

A = volume of FAS used for blank

B = volume of FAS used for the sample

M = molarity of FAS

3.2.1.3 Closed Reflux Colorimetric Method

Principle : When the sample is digested, COD content in the sample is oxidized by the dichromate ion. This results in change of chromium from hexavalent (VI) state to trivalent (III) state. Both of the chromium species are colored and can absorb in the visible region. The chromic ion absorbs strongly in the 600 nm region, whereas dichromate ion has nearly absorption in this region. On the other hand, chromic ion has minimum absorption in the region of 400 nm. For COD values between 100-900 mg/l, increase in Cr^{3+} in the 600 nm region is determined. For COD values of 90 mg/l or less, decrease in $Cr_2O_7^{2-}$ at 420 nm is determined.

Apparatus : COD vials, digester, spectrophotometer, reagents

3.2.2 Turbidity

Clarity of water is considered as an essential determinant of its condition and productivity. Turbidity is defined as cloudiness or haziness of fluid caused by a large number of individual particles. Measurement of turbidity is a key test of water quality. Turbidity in water is caused by suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter and other microscopic organisms.

Electronic nephelometers are the preferred instruments for turbidity measurement. Its precision, sensitivity, and applicability over a wide turbidity range make the nephelometric method preferable to visual methods. Turbidity is measured in nephelometric turbidity units (NTU).

CHAPTER 4

AUDIT OF SEWAGE TREATMENT PLANT

4.1 INTRODUCTION

Technical plant audits aid in restoring plant performance. Audits allow technical experts to understand the reason behind reduced plant performance. It helps in identifying areas of improvement, stabilising and optimising unit operations and processes, and restoring plant performance. Due to factors like changing feed quality and quantity, aging infrastructure and other uncertainties, there may be various challenges during operation. Through plant audits, solutions to such challenges can be ascertained. Audits help in formulating efficient ways to improve an existing treatment. Audits can also help in deciding whether retrofitting new technologies or revamping existing technologies is required to resolve the problem and achieve desired performance.

4.2 OBJECTIVE

The objective was to check the performance of existing sewage treatment plant.

4.3 BACKGROUND

An audit was conducted on a MBBR based sewage treatment plant. A large housing complex had an MBBR based sewage treatment plant of capacity 500 m^3/day for treating the wastewater generated. The treated water from the existing STP was supposed to be used for gardening and flushing purposes. However, due to major operational challenges, the wastewater was being sent to the municipal corporation for further treatment. An Audit was conducted to evaluate the plant performance and suggest corrective measures to achieve the desired outlet water quality.

In this plant, raw sewage enters the equalization tank. Sewage is pumped to fluidised aerobic bioreactor (FAB) followed by flocculator and clarification tank. Poly Aluminium Chloride

(PAC) and Polyelectrolyte are dosed in the flocculation tank. Water from the clarisettler is pumped to chlorine contact tank where sodium hypochlorite is dosed for disinfection. Water is then filtered through Dual-Media Filter (DMF) and Ultrafiltration (UF) unit. Treated water was being used for gardening and flushing. Due to complaints regarding reduced performance of STP, an audit was conducted to evaluate its performance. Figure 4.1 depicts schematic diagram of the sewage treatment plant.

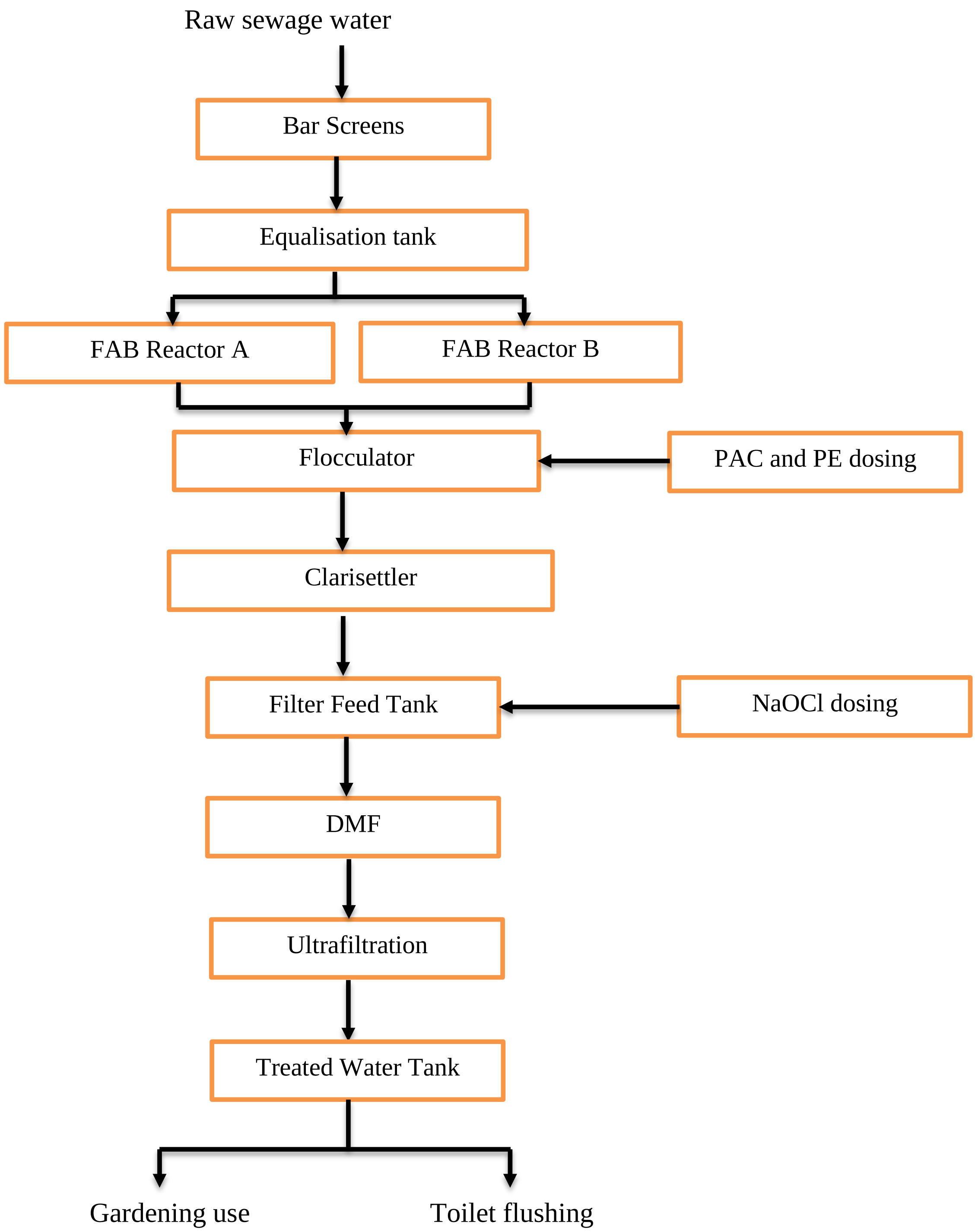

Figure 4.1 : Schematic of the sewage treatment plant

4.4 OBSERVATIONS

The major causes for reduced performance of the sewage treatment plant were due to increased solid load, ineffective screening, lack of proper chemical dosing and fouling of filtration units in the tertiary treatment. Observations and their impacts are summarised in the table. Along with the observations, a detailed list of equipment was prepared to understand their status.

Observations	Impact
Collection tank had excess plastic waste. Bar screen was choked. Diffusers in the equalization tank were not in operation due to which homogeneous feed conditions could not be maintained.	Heavy solid loading had clogged the bar screen, affecting the performance of the preliminary treatment. This waste can damage the pump and affect the feed quality.
Media carriers were found outside near FAB reactors	Overflow in FAB reactors in the past could have caused media to flow-out. This can affect the performance of FAB reactor. Designed media to organic load ratio needs to be maintained for effective reduction.
Inefficient chemical treatment and mixing in flocculator. Poor floc formation. Polyelectrolyte was dosed manually	Ineffective chemical treatment will affect floc formation and consequently lead to carryover of sludge in the downstream
Sludge carryover was observed in outlet of clarification unit	Sludge carryover can adversely affect the performance of filtration units
Sodium hypochlorite was not being dosed in the chlorine contact tank	This can result in bacterial growth which can foul the filtration units.
DMF was choked, hence it was not in operation	Sludge carryover led to choking of filter media which ultimately led to system failure
Ultrafiltration system was not in operation	Sludge carryover in the past and lack of appropriate chemically enhanced backwash (CEB) led to choking

Centrifuge was not in operation. Conventional bag filters were used for sludge dewatering	Due to fault in civil foundation, centrifuge could not be operated.
There was lack of proper air ventilation system in the plant	Excess ammonia produced and strong smell of other chemicals are risky for workers health and hence proper ventilation should be maintained
Most of the mechanical equipment were faulty or not working	Plant operations were challenging with faulty equipment

Table 4.1: Summary of observations and their impact

4.5 DISCUSSION

For restoration of plant performance, raw water analysis is required. Raw water analysis will aid in quantification of plant performance. All the faulty equipment and flow meters need to be repaired or replaced. Daily influent flow rate needs to be validated. Bar screens need to cleaned at regular intervals. Additional unit maybe required to control flooding of sewage in the equalization tank. Figure 4.2 shows the status of raw sewage collection tank.

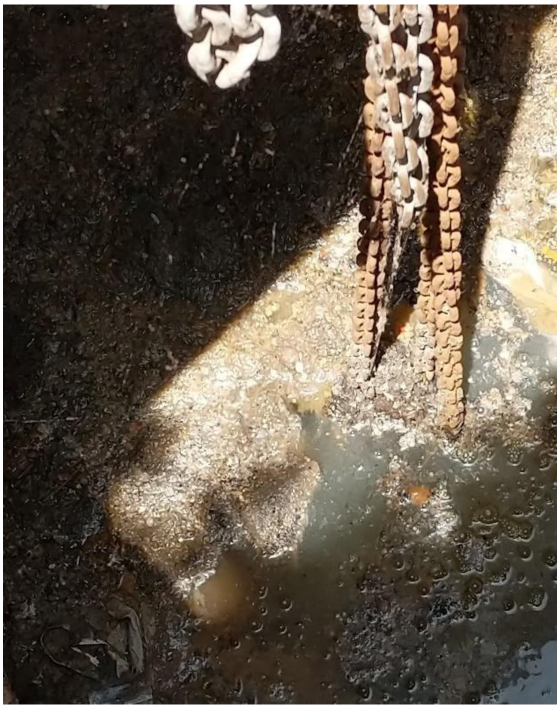

Figure 4.2: Collection tank overloaded with solids

FAB tanks were operating with full capacity. Carrier media appeared to have sufficient growth as shown in figure.

Figure 4.3: Biological growth in the carrier media

Since there was overflow of carrier media in the past, quantity of media carriers need to be verified and added as per requirement.

Due to ineffective chemical treatment in the flocculator, there was sludge carryover in the downstream. Sample water was collected from the outlet of clarification unit.

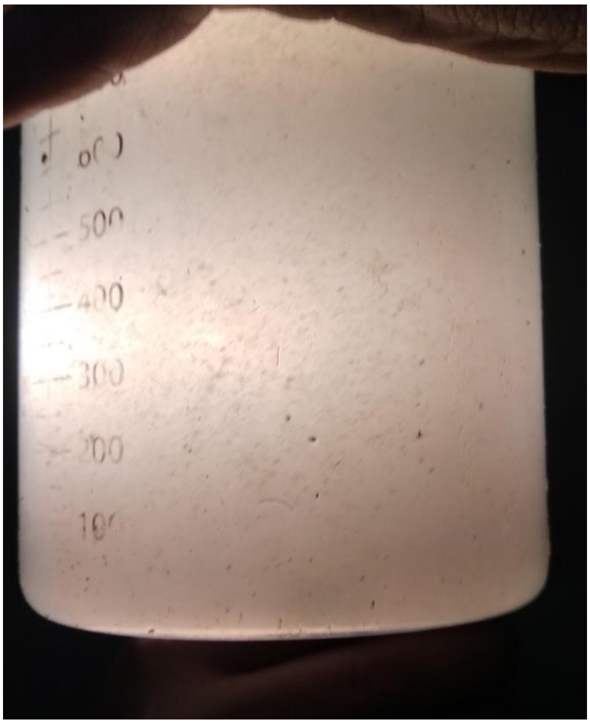

Figure 4.4: Sample from clarisettler outlet

From the figure 4.4, it can be observed that there is a significant presence of suspended solids in the water. This was a clear indication that the flocculation and clarification units were not working efficiently. Dosing of PAC and Polyelectrolyte in the flocculator needs to be redefined as per the quality of wastewater. Sodium hypochlorite needs to be dosed in chlorine contact tank to prevent bacterial growth. Due to sludge carryover, there was increase in differential pressure across the sand filter, which led to choking of DMF. Both DMF and UF units need to be thoroughly cleaned in order to restore their performance.

CHAPTER 5

PILOT TESTING USING SPIRAL-WOUND ULTRAFILTRATION MEMBRANE

5.1 INTRODUCTION

Pilot scale testing includes temporary installation of an equipment in order to study its application and evaluate its feasibility. Pilot scale testing is performed to generate operational data for innovative products and technologies and define their operating conditions and constraints. It is conducted to obtain operational data, estimate the operational and maintenance cost, to research how to optimize the process. (5)

5.2 OBJECTIVE

- To evaluate the performance and define treatment capacity and cleaning frequency of novel spiral-wound ultrafiltration membrane
- To conduct a comparative assessment of spiral-wound and hollow-fibre membrane ultrafiltration module system

5.3 BACKGROUND

A novel spiral-wound UF membrane was commissioned at STP-Environment House, Thermax Limited. STP at Environment House was designed for treating 50 m^3/day of sewage. A schematic depicting the process flow diagram of STP is shown in figure.

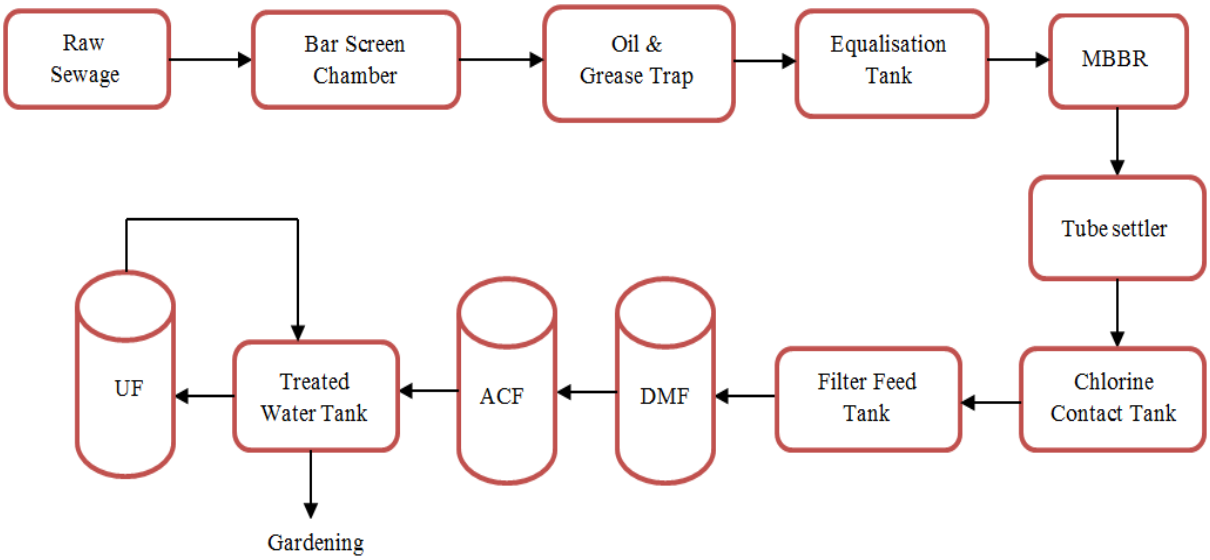

Figure 5.1: Process Flow Diagram of STP-Environment House

Sewage from the equalization tank is pumped to BioCask, which is a moving bed biofilm reactor. After the biological treatment, water enters the tube settler where PAC and Polyelectrolyte are dosed. Water from tube settler goes to chlorine contact tank where sodium hypochlorite is dosed for disinfection. Treated water is filtered through dual media filter and activated carbon filter. Filtered treated water is used for gardening purposes.

For the pilot scale testing, an automated UF system was installed after ACF. Treated wastewater from ACF was collected in treated water tank and used as feed to UF unit. The ultrafiltration system was operated for 24 hours. Operational and analytical parameters were monitored at an interval of 15 minutes.

5.4 EXPERIMENTAL SETUP AND PROCEDURE

The pilot plant showed in the figure was used for conducting this study.

Figure 5.2: Initial setup of Ultrafiltration unit

5.4.1 EXPERIMENTAL SETUP

Initially, the ultrafiltration system commissioned had an arrangement of four elements working in a parallel set-up. The system was designed to provide permeate flowrate of 4500 LPH at 3 bar. However, it could provide a flowrate of 2000LPH only. In order to optimize the system, an additional tank was installed. Water from treated water tank was pumped to UF Feed Tank from where it was pumped to UF. This provided flooded suction to UF feed pump. The current set-up of UF for the pilot test is as shown in figure 5.2. At present, this system is expected to provide permeate at a flowrate of 2000 LPH at 3 bar. Surface area of the membrane is assumed to be 30 m^2.

Figure 5.3: Present setup of Ultrafiltration unit

5.4.2 WORKING OF UF

The pilot plant set-up for this study was an automated plant.

- Treated water from ACF was collected in treated water tank. Water from treated water tank was pumped to UF through microfilters, cartridge filter of 5 micron.
- During service, water enters the module from bottom-side
- Treated water is removed from the top
- A sensor placed after the rotameter displays the flowrate of permeate on the LCD
- UF permeate is bifurcated to permeate tank and treated water tank
- Reject from UF is removed from top-side of the module and goes to the equalization tank
- Water from permeate tank is used during backwash
- At present, backwash with flow rate of 4500 LPH at 0.2 bar is provided after 2 hours of service cycle. For chemically enhanced backwash, Citric acid (1%) and NaOH (0.3%) is provided.

- After a single service cycle, forward flush is provided. In forward flush, UF feed is pumped through the element and removed as reject to the equalization tank.

Time duration for different steps is summarised in the table below.

Service cycle	1 hour
Forward Flush	1 min
Service cycle	1 hour
CEB Dosing 1 (Citric Acid)	120 sec
Soak	6 min
Backwash	1 min
CEB Dosing 2 (NaOH)	120 sec
Soak	6 min
Backwash	120 sec
Forward Flush	1 min
Service	1 hour

Table 5.1: Steps involved in the operation of the ultrafiltration unit

These time durations are preset. In case of change in feed quality, the aforementioned steps can be altered. The duration of backwash can be changed as per requirement.

5.5 DATA GENERATION

During the course of this pilot study, operational parameter, i.e., permeate flowrate, pressure and analytical parameters, i.e., pH and turbidity were monitored. List of the parameters monitored and the frequency of monitoring is summarised in the table

	Parameter	Frequency
Operational Parameters	Permeate Flow rate	15 minutes

	Pressure	15 minutes
Analytical Parameters	Turbidity	15 minutes
	pH	15 minutes

Table 5.2: List of parameters monitored and their frequency

Flux is an important operating parameter that is used to evaluate membrane performance. Flux was calculated based on flowrate monitored. Membrane fouling depreciates the flux rate. Therefore, through the flux values, the need and frequency of CIP can be estimated. This will ensure smooth operations of the plant and extend membrane life.

5.6 OBSERVATIONS

The plant was operated for 24 hours over the time period of 10 days. During this period, operational parameters and analytical parameters were monitored. Data generated during the pilot study is present in Annexure.

The result of this study is depicted in the form of graphs in figure 5.4 and 5.5.

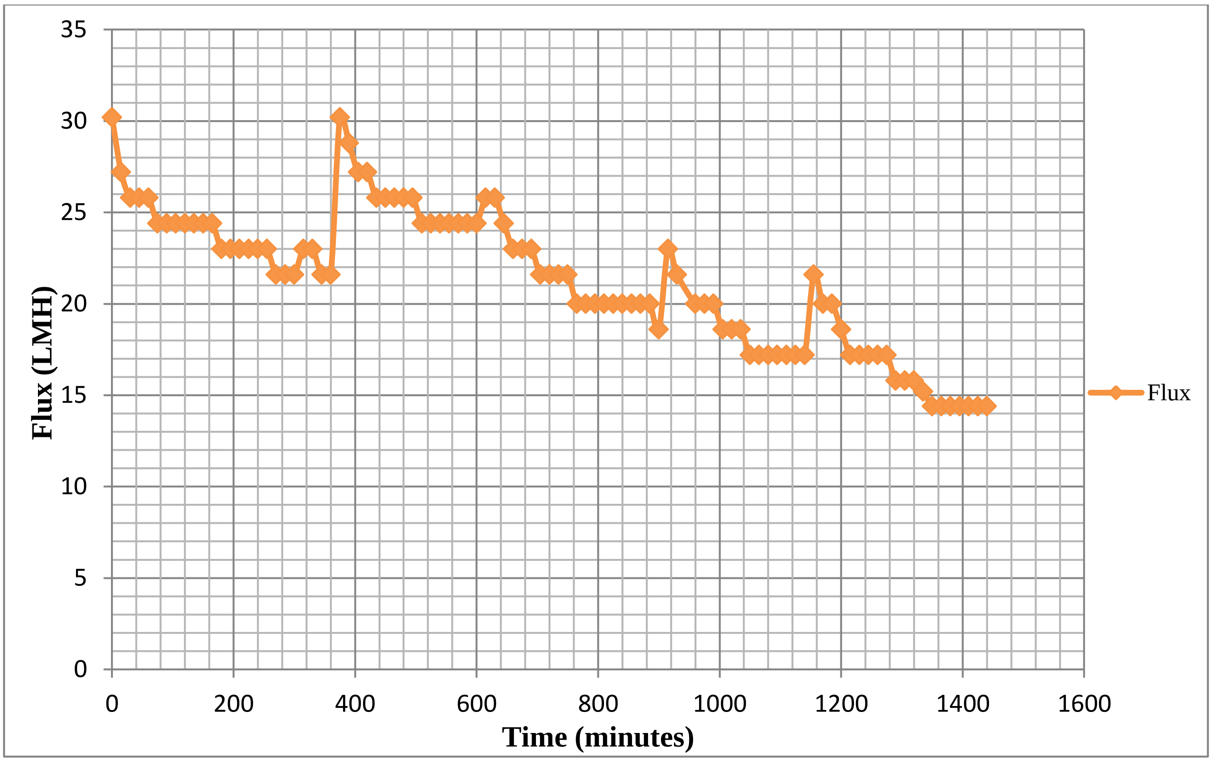

Figure 5.4: Graph - Flux vs Time

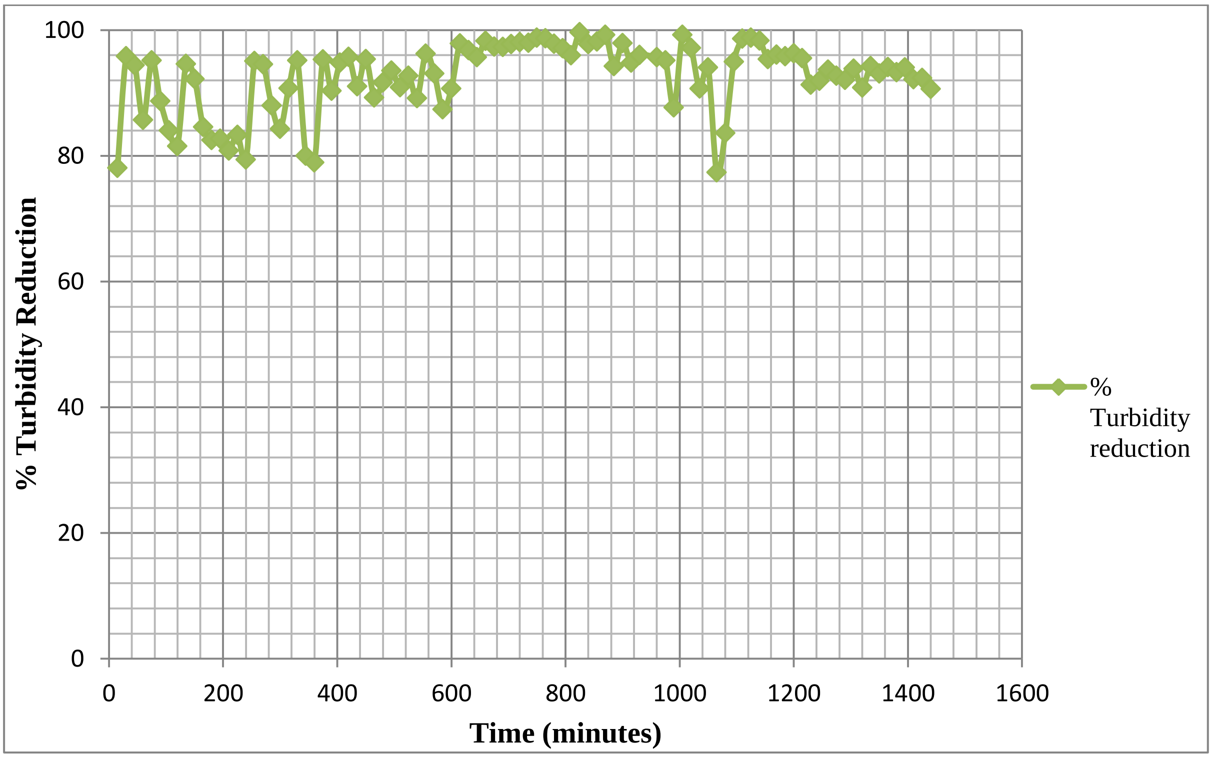

Figure 5.5: % Turbidity Reduction vs Time

5.7 RESULTS AND INFERENCE

During the course of this pilot study, the ultrafiltration unit was operated for 24 service cycles over a period of 10 days. Initially, the permeate flow across the ultrafiltration system was 1.51 m^3/hr. In the beginning, this system could generate flux of 25.16 LMH at 3 bar system pressure. Inspite of regular backwash after 2 hours of service cycle, rapid flux decline was observed. By the end of 24 service cycles, flux declined by 52%.

Despite of rapid flux decline, on an average, 92.7% reduction in turbidity was observed. This makes spiral-wound membrane advantageous as compared to other membrane configuration. Maximum turbidity reduction observed was 99.6 %. Due to its high packing density, it is able to produce permeate with high turbidity reduction despite decline in flux. From the data generated so far, it can be inferred that with a robust cleaning regimen and periodic CIP, spiral-wound membrane could be a viable solution. A more accurate assessment regarding the viability of spiral-wound membrane can be made after the completion of pilot study.

Currently, the ultrafiltration unit is installed after ACF. After a time period of 30 days, this unit will be installed after DMF in order to target water containing comparatively higher quantity of suspended solids. Treated water from DMF will be used as feed for the UF unit. This will help in analyzing whether replacing one or more filtration units with ultrafiltration unit is feasible or not.

Previously, a pilot-scale testing was conducted using hollow-fibre membrane at STP-Environment House. A comparative analysis between the two pilot tests can provide better insight regarding their applications.

CHAPTER 6

MEMBRANE AUTOPSY

6.1 INTRODUCTION

Membranes have a broad spectrum of industrial applications. Apart from water and wastewater treatment, membrane filtration technology is widely used in food and beverage processes, chemical processing, pharmaceutical applications and other industrial applications. Membranes are sensitive to deviation in water quality. Any significant deviation in water quality or change in operational parameters can impact the membrane life, affect plant performance and increase operational costs.

Reverse Osmosis (RO) is a widely used water purification technology that has versatile commercial applications. It involves physical separation of the contaminants from the water. It is an essential as well as a delicate component in the process of water treatment. RO is often subject to premature degradation and deteriorated performance. Deterioration in performance results in loss of permeate flux and quality, increased differential pressure across the system, lower salt rejection rate and shortened membrane life. Decline in membrane performance could be caused by physical damage to the membrane, fouling of the membrane, provision of inadequate pre-treatment upstream or due to lack of proper operational and maintenance practices. In order to improve the efficiency of RO membrane, it is essential to understand the underlying cause behind loss of membrane performance. (12) (13)

Membrane autopsy is a destructive procedure that is used for the diagnosis of performance loss in the membrane. It is used for the assessment of the condition of membrane. It involves visual and physical examination, followed by dissection of membrane, removal of scale and conducting analytical tests on the deposit collected. It can provide reliable evidence that can be used to remediate pre-existing problem and improve overall plant operation. Membrane autopsy is a destructive technique that helps in understanding the membrane health and reasons behind its reduced performance. This can help in preventing repetition of such events in the future. (14) (15)

6.2 OBJECTIVE

- To conduct membrane autopsy and understand the various aspects associated with this procedure.
- To understand the nature of deposition on the membrane surface and potential reasons of fouling

6.3 BACKGROUND

Two seawater reverse osmosis elements were received. There was deterioration in the quality of permeate and high TDS was observed in the permeate. Rapid increase in differential pressure was observed during operation.

6.4 METHODOLOGY AND PROCEDURE

6.4.1 Methodology adopted

1. RO element was cut and sheets were opened.
2. Visual and physical examination of the membrane sheet and feed spacer was conducted.
3. Deposition was scraped from all the membrane sheets.
4. Powdered scale was dried and various tests were conducted to understand the composition of the scale.
5. Findings were summarised

6.4.2 Detailed Procedure

1. RO element was cut and the sheets were opened.
2. Visual and physical examination of the membrane sheets was conducted.
3. The scale was scraped from all the membrane sheets.
4. Powdered scale was dried at 105°C for 3 hours in order to remove the moisture.
5. A 5% solution was prepared using the dried powder.
6. Solution was heated between 50-80°C for 20 minutes. Solids did not dissolve. They settled at bottom of the beaker.

7. The solution was cooled and 400 mg/L of HCl (10%) was added to the solution. Solids did not dissolve. They settled at bottom of the beaker.
8. The solution was again heated between 50-75°C for 25 minutes. Solution was cooled down filtered using a Whatman 42 filter paper.
9. Analysis was performed on the filtrate obtained. Various analytical experiments were performed on the sample in order to understand the characteristics of the scale.
10. In order to better understand the characteristics of the foulant, sample was sent for Scanning electron microscopy (SEM)-Energy dispersive x-ray spectroscopy (EDS)

6.5 OBSERVATIONS

6.5.1 Visual and Physical Observations

The membrane element received was wrapped in FRP sheet. It had two anti-telescopic devices at the inlet and outlet respectively. Anti-telescopic device provide structural support to the RO membrane. Absence of ATD can cause physical damage to RO membrane and lead to unrecoverable loss of membrane performance. Brine seal was present at one end of the element. Brine seal is present to prevent bypass of feed water around the element. An image of the membrane as received is shown in the Figure 6.1. Activated carbon and sand particles were observed on the ATD as shown in figure. Presence of these particles indicates ineffective operation of upstream filtration systems, damaged strainer at ACF outlet or contamination of the storage tank.

Figure 6.1: RO membrane as received

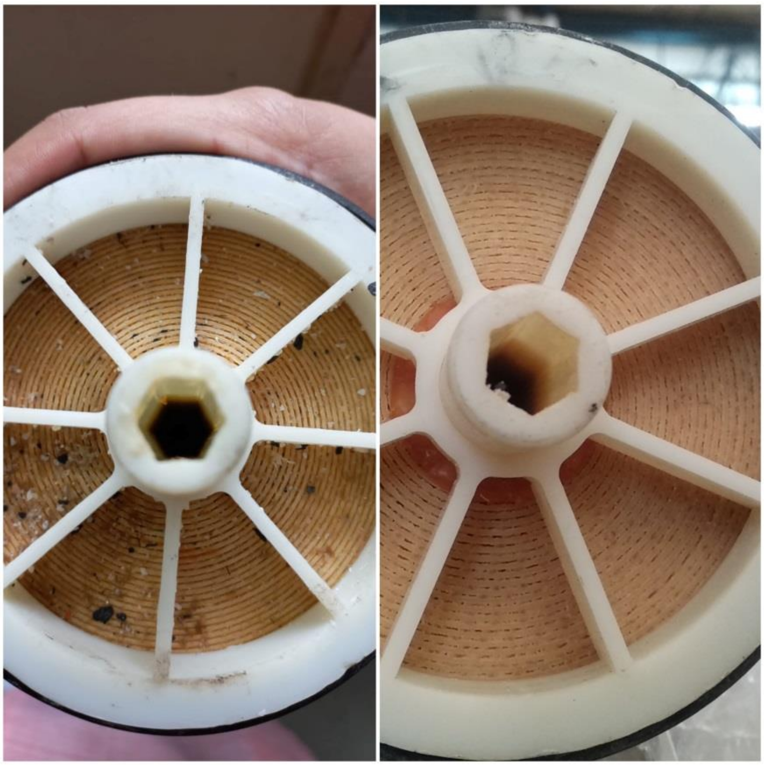

Figure 6.2: Inlet of element

The FRP sheet was cut and the membranes were opened. Membranes were slightly moist. The element comprised of six membrane sheets and feed spacers that were spiral wound around the permeate tube. It was observed that all the membrane sheets, feed spacers and permeate spacers were physically damaged as shown in Figure 6.3. There was a small hole present on the corner of the sheets. Heavy, uniform, off-white coloured scale was accumulated on the membrane surface as shown in Figure 6.4 . The accumulated scale was scraped form the membrane sheets and used for experimentation. Physical and visual observations are summarised in Table 6.1 .

Figure 6.3: Perforation on membrane sheet

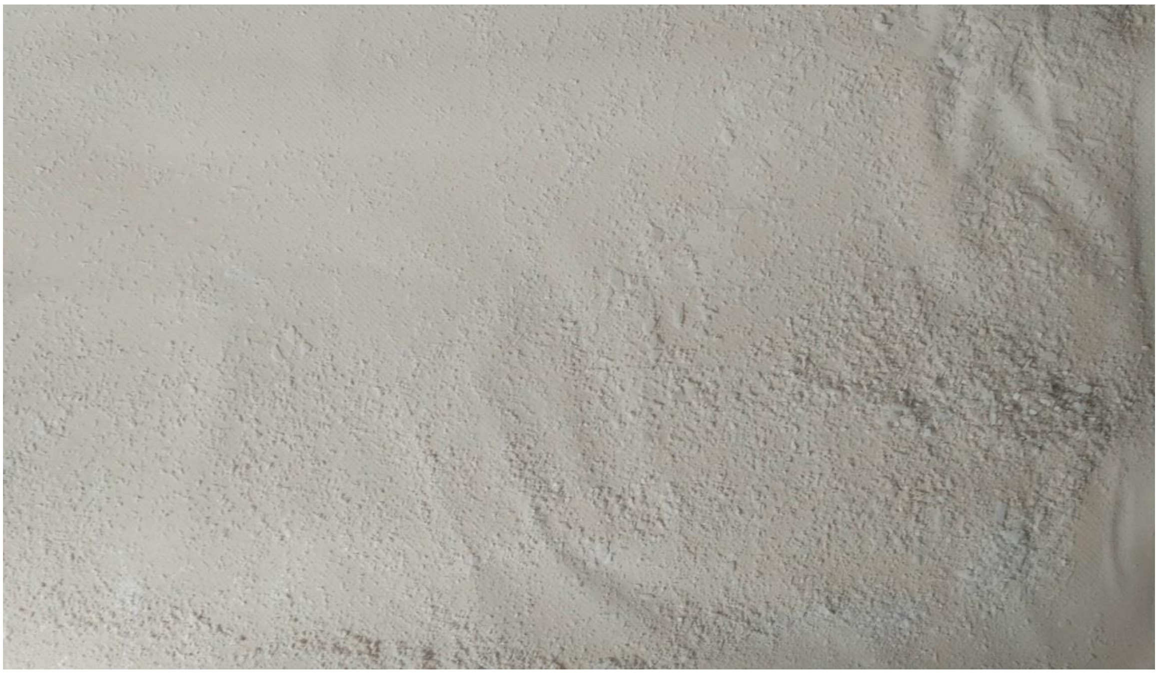

Figure 6.4: Scaling on membrane sheet

Observations	Remarks
FRP sheet	Small white particles distributed unevenly on the surface
Anti-telescopic Device Inlet	Intact, Not damaged
Anti-telescopic Device Outlet	Intact, Not damaged
Brine seal	Intact, firmly placed
Membrane sheet	Small hole present on all membrane sheets
Feed spacer	Small hole present on all feed spacers
Permeate spacer	Small hole present on all permeate spacers
Scaling	Heavy, even and uniform deposition of scale on each membrane
Colour of deposition	Off-white scale
Odour	Mild milky odour
Moisture	Membrane was slightly moist

Table 6.1: Summary of visual and physical observations

A 5% sample solution was prepared using dried scale powder. It was observed that it was hard to dissolve the solids. Solids were settling at the bottom of the beaker as shown in figure 6.5. Analytical experiments were performed on the filtered sample.

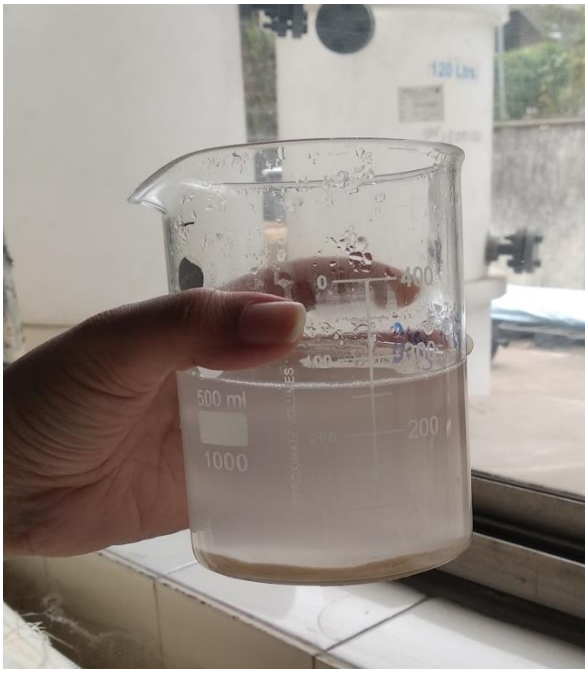

Figure 6.5: Dissolved scale

6.5 RESULTS AND INFERENCE

A 5% solution was prepared using the dried scale powder. Experiments were conducted on the prepared sample. Sample was sent for SEM-EDS testing and AAS for analysis of the deposit. Results of various experiments indicated significant presence sulphate, silica, calcium and carbon. This indicates that the primary constituent of scale maybe Calcium sulphate and silica.

Parameter	**Concentration**
pH	3.30
Conductivity (mS)	2.42
Turbidity (NTU)	12
Total Hardness (mg/l as)	68
Chlorides (mg/l as Cl^-)	44
M-alkalinity (mg/l as HCO_3)	6
Sulphate (mg/l as SO_4)	1465
Silica (mg/l as SiO_2)	17.7
Iron (mg/l as Fe)	BDL
Total Solids (mg/l)	53760
Total suspended solids (mg/l)	50507
Total dissolved solids (mg/l)	3253
Total volatile solids (%)	19
Total fixed solids (%)	81
COD (mg/l as O_2)	90

Table 6.2: Results of analytical procedures

Under the assumption that the primary constituents of scale are calcium sulphate and silica, it can be inferred that presence of these compounds caused scaling on membrane sheets.

Deposition of scale on membrane led to increase in differential pressure and reduced quality of permeate. Perforation of membrane sheets could be due to operation of RO at high differential pressure. Perforation of membrane sheets could also be due to passage of solids from the upstream processes or contamination of feed tank. That is why the upstream processes need to be checked to understand the cause behind perforation of membrane sheets.

Additionally, Silt Density Index can be used to quantify permeate flow. After thorough cleaning of membrane coupons in different solutions, SDI analysis can be conducted. Currently these experiments could not be performed after membrane autopsy due to technical problem with the SDI equipment.

CHAPTER 7

TREATABILITY STUDIES

7.1 INTRODUCTION

Treatability studies are laboratory or field tests that are conducted to evaluate the performance of one or more treatment technology. These studies involve characterization of raw wastewater and evaluation of performance of treatment technology under different operating conditions. Through treatability studies, both qualitative and quantitative results can be achieved. Treatability studies help in the identification of the problem in the wastewater stream and ensure proper implementation of treatment solutions. (16)

7.2 OBJECTIVE

The objective is to conduct treatability tests on wastewaters of different industries

7.3 BACKGROUND

Treatability tests were conducted on different wastewaters of various industries. In order to understand the suitability of a particular coagulant, jar tests were conducted.

This chapter consists of case studies based on treatability tests.

7.4 CASE STUDY 1

The aim of this treatability study was to quantify colour reduction through different treatability methods.

7.4.1 BACKGROUND

The aim was to reduce the colour of the wastewater. Experiments were conducted using coagulants and ozone. Results were quantified on the basis of visual colour reduction and analytical experimements.

7.4.2 EXPERIMENTAL PROCEDURE

- A known volume of sample was taken
- Jar tests were conducted using $FeCl_3$ and PAC.
- 5% (w/v) $FeCl_3$ was prepared
- 10% (w/v) PAC was prepared
- 0.1% (w/v) Anionic PE was prepared
- NaOH was added to increase the pH and Anionic Polyelectrolyte was used as flocculant
- Analytical experiments were performed on the supernatant of jar tests

7.4.2.1 Jar Test 1

- For this analysis, 500 ml of sample was taken.
- 400 mg/L of $Fecl_3$ was dosed
- 1 mg/L of anionic PE was added and the sample was allowed to settle
- Sample was filtered and supernatant was analysed

7.4.2.2 Jar Test 2

- For this analysis, 500 ml of sample was taken.
- 200 mg/L of $Fecl_3$ was dosed
- 1 mg/L of anionic PE was added and the sample was allowed to settle
- Sample was filtered and supernatant was analysed

7.4.2.3 Jar Test 3

- For this analysis, 500 ml of sample was taken.
- 100 mg/L of $FeCl_3$ was dosed
- 1 mg/L of anionic PE was added and the sample was allowed to settle
- Sample was filtered and supernatant was analysed

7.4.2.4 Jar Test 4

- For this analysis, 500 ml of sample was taken.
- 80 mg/L of 5% NaOH was added to increase the pH
- 40 mg/L of 10% PAC was dosed
- 1 mg/L of anionic PE was added and the sample was allowed to settle
- Sample was filtered and supernatant was analysed

7.4.2.5 Treatment with ozone

Four samples were treated with ozone for different time intervals. Concentration of ozone provided to each sample is summarized in Table.

Sample	Time Period(mins)	O_3 (mg/l)
1	1.5	5
2	5	16
3	10	33
4	15	50

Table 7.1: Details of ozone treatment

7.4.3 RESULTS AND ANALYSIS

Supernatant collected after filtration was analysed. Analytical experiments were conducted on samples that showed visible reduction in colour. Figure 7.1 shows supernatant collected after filtration of jar tests.

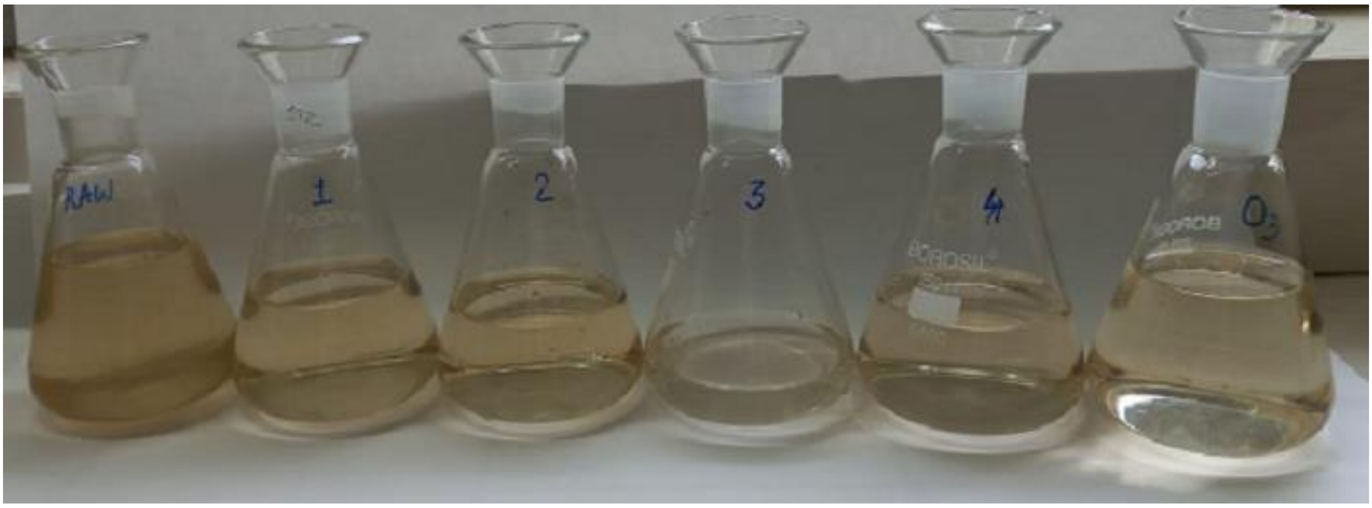

Figure 7.1: Supernatant from Jar Tests and ozone treated sample

As can be observed from figure 7.1, there was no significant colour reduction after addition of coagulants. The supernatant collected was clear but no visible colour reduction was observed. There was no visible colour reduction after treatment with ozone as well. Water quality parameters of the supernatants collected were analysed. The result of water quality parameters analysed is summarized in Table 7.2.

Parameter	**Wastewater**	**Jar Test 1**	**Jar Test 2**	**Jar Test 3**	**Jar Test 4**	**Treatment with Ozone**
Ph	7.6	6.9	7.04	5.7	7.5	8.6
Total suspended solids (mg/l)	226	-	-	163	61	-
Total dissolved solids (mg/l)	2456	-	2540	2600	2640	-
COD (mg/l)	235	-	198	328	219	221

Table 7.2: Water quality parameters

7.5 CASE STUDY 2

7.5.1 BACKGROUND

Wastewater with high quantity of oil was received. Treatability tests were performed to select an effective treatment scheme. Chemical treatment and adsorption was performed in the laboratory. The objective was to quantify COD and colour reduction in the wastewater sample received.

7.5.2 EXPERIMENTAL PROCEDURE

7.5.2.1 Jar Test

A known volume of wastewater was taken. Different polyeletcrolytes were used. The supernatant was obtained and analysed for COD reduction.

- Jar Test 1

  Sample Volume = 500 ml

  PAC (10%) (w/v) = 100 mg/l

  Anionic PE (0.1%) (w/v) = 1 mg/l

  Flocs were formed and settled easily. Supernatant obtained was clear and visible colour reduction could be observed.

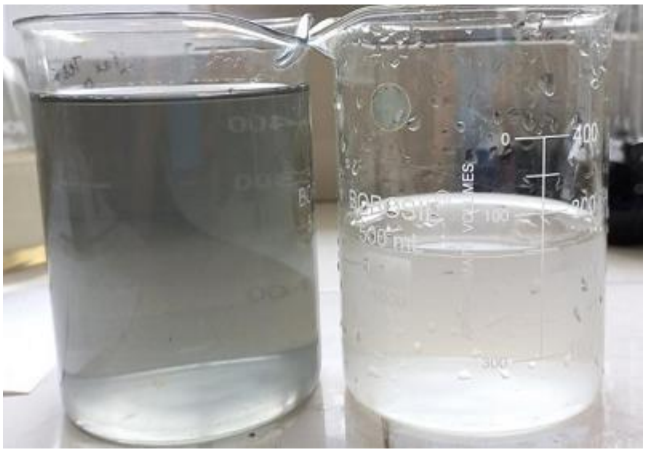

Figure 7.2: Raw wastewater (left) and Supernatant of Jar Test 1

- Jar Test 2

  Sample Volume = 100 ml

PE 2 (1.5%) (w/v) = 15 mg/l

After the addition of PE 2, fine black strands formed and visible colour reduction was observed. However, supernatant received was turbid. Supernatant was filtered and used for further analysis. Cationic polyelectolyte was used during this experiment. Figure 7.3 shows the supernatant of Jar Test 2.

- Jar Test 3

  Sample volume = 100 ml

  PE 3 (0.1%)(w/v) = 5 mg/l

  PE 4 (100%) = 1000 mg/l

  After addition of PE 4, formation of fine black strands was observed. This polyelectrolyte is efficient in colour reduction. Supernatant obtained was clear and good colour reduction was observed. Figure 7.3 shows the supernatant of jar test 3.

- Jar Test 4

  Sample volume = 100 ml

  PE 3 (0.1%) (w/v) = 2 mg/l

  The dosage of polyelectrolyte was lowered during this jar test in order to check the effectiveness of PE 3 at a lower dose. The supernatant obtained was clear but no visible colour reduction could be observed. Figure 7.3 shows the supernatant of jar test 4.

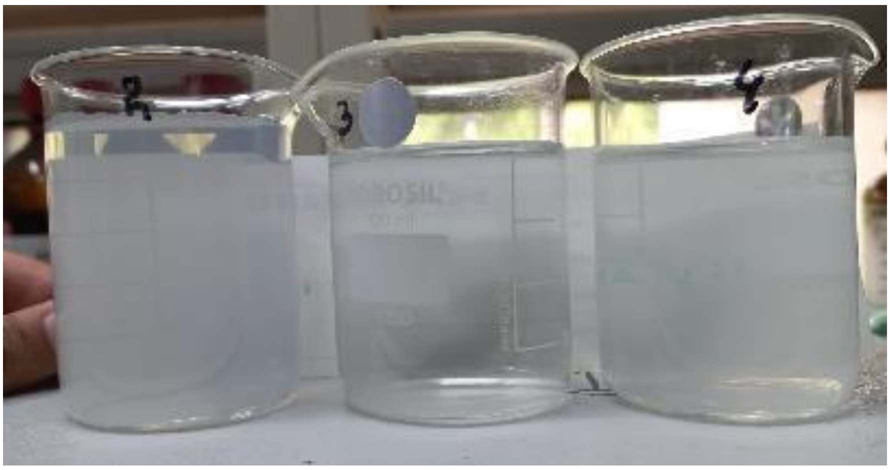

Figure 7.3: Supernatant of jar test 2, 3 and 4

7.5.2.2 Column Test

After jar tests, column test was conducted in order to check if adsorption can be used for reduction in COD and colour. A column was set-up in the laboratory. A novel activated carbon of unknown properties was used as adsorbent during the experimentation. The column was operated with a contact time of 15 minutes. The adsorbent was cleaned and a bed volume of 30 ml was set. Initial volumes were discarded under the assumption that they contained DM water. The next bed volumes were collected and COD analysis was performed on them.

The details of the set-up are summarized in the table below.

Column Height (cm)	20.5
Column Diameter (cm)	1.8
Cross sectional area of column (cm^2)	2.5
Volume of the column (cm^3)	52
Bed depth of activated carbon in column (cm)	11.7
Activated carbon volume filled in the column (ml)	30
Service flowrate (ml/min)	2
Contact time (mins)	15
Free board carbon height (m)	8.3

Table 7.3: Details of column setup

Colourless filtrate was obtained by passing it through adsorption column. The bed volumes collected were clear. Massive colour reduction was observed and high COD reduction was expected.

Column test using a special adsorbent material was performed. Column was operated with a contact time of 15 minutes. Maximum COD reduction of 95% achieved. Clear and colorless filtrate was obtained.

7.5.3 Results and Discussion

The summary of the results obtained is shown in Table 7.4 The initial bed volumes were discarded

	Raw wastewater		Filtered Raw Waste-water	Jar Test Result				Column Test		
Parameter	**Raw1**	**Raw2**	**Raw**	**Jar Test 1**	**Jar Test 2**	**Jar Test 3**	**Jar Test 4**	**5 B.V**	**6 B.V**	**7 B.V**
pH	8.08	7.8	8	7	8.1	8.4	8.4	8.8	8.8	8.4
COD (mg/l)	7173	5871	5903	4026	-	4425	5390	242	222	209

Table 7.4: COD analysis of raw sample, Jar tests and column test

After COD analysis, it was observed that there was higher COD reduction in the filtrate of the adsorption column as compared to the supernatant collected after jar tests. 95% COD reduction was observed on the use of adsorbent. Adsorption had the best results as it could adsorb and remove both negatively charged particles and positively charged particles, thereby removing maximum organics.

During jar tests, both anionic and cationic polyelectrolytes were used. Use of cationic polyelectrolyte showed visible colour reduction and COD reduction by 38%.

A major challenge faced during the experimentation was change in the charcteristcis of the sample. It was observed that the wastewater sample changed colour overtime. After 20-24 hours, the sample had turned colourless and turbid on its own. After change in the sample, tests were conducted again using different polyelectrolytes but no change in colour or floc formation was observed. This indicated that there was change in both appearance as well as charcteristics of the sample. This change in the sample could be attributed to occurance of some biological action in the sample. Therefore, in order to have more conclusive results, these findings should be validated on site.

7.6 CASE STUDY 3

7.6.1 BACKGROUND

Surfactants are widely used throughout the world. Surfactants find their use in various industrial domains. Surfactants are categorized into anionic and nonionic surfactants. Anionic surfactants are the primary constituents in detergent formation. Foaming due to surfactants is a major problem in effluent treatment plants. Due to foaming, suspended solids are carried away along the foam. Presence of suspended solids will affect the downstream processes. Presence of solids can cause organic fouling and affect mixing of chemicals during pre-treatment. That is why removal of foam causing chemicals is essential. (17)

According to the literature, processes like coagulation-flocculation, chemical oxidation, membrane technology, adsorption, biological methods, etc., can be used for the removal of surfactant from wastewaters. Each one of these applications has its own advantages and limitations. Among the aforementioned techniques, coagulation-flocculation is the preferred method of treatment owing to its high removal efficiency. (18) (19)

Literature review was conducted to understand the mechanism of removal of surfactant from wastewater. Both Alum and $FeCl_3$ have been used as coagulants for the removal of surafactant. As per literature, both coagulation/flocculation and adsorption contributes to the removal of surfactants. The cations Fe^{3+} binds itself to aggregate of surfactant molecules which are dispersed in water, it suppresses repulsion between surfactant molecules by neutralizing the charge and binds organic compounds to form flocs. Sulphate groups are adsorbed on the nuclei and crystallites of $FeCl_3$ phases in water. Turbidity and total solids concentration also affect removal efficiency of surfactants. As surfactants are amphophilic in nature they adsorb to the surface of particulate matter present in water thus increasing the removal efficiency. This is due to hydrophobic effect and electrostatic forces of attraction.

7.6.2 OBJECTIVE

The objective of this study was to check the removal of anionic surfactant through chemical treatment.

7.6.3 EXPERIMENTAL PROCEDURE

For this study, a known concentration of Sodium Lauryl Sulphate (SLS) was prepared. The aim of this study was to quantify the removal of SLS from synthetically prepared SLS solution of known concentration. This study involved chemical treatment of SLS with the use of Alum, Ferric chloride, sodium hydroxide , polyelectrolytes and ozone.

For these experiments, 300 mg/l of SLS was prepared synthetically. The reduction was quantified on the basis of initial and final turbidity of the solution and formation of foam after pre-treatment.

- Treatment with ozone : In the first experiment, 300 mg/l of SLS was prepared. Ozone was passed through it for 1 minute. Effect on foam and turbidity was observed.
- Jar Tests : Jar tests were performed using $FeCl_3$ and Alum. NaOH was used for raising the pH. Different polyeclectrolytes were used as flocculant.
  Table 7.5 summaries the dosages of coagulants used in different jar tests.

Jar Test	**Description**
Jar Test 1	500 ml water sample (pH-8.2) + 400 mg/l Alum (10%) (wt/vol), pH 4.5 + 1 mg/l PE – A107 (0.1%) Filtered supernatant was aerated to check foam formation

Jar Test 2	500 ml water sample (pH-8.2) + 500 mg/l Alum (10%) (wt/vol), pH = 4.18 + 1 mg/l PE – C11 (0.1%) Supernatant was filtered and NaOH was added + 60 mg/L NaOH (2%) (wt/vol)
Jar Test 3	500 ml water sample (pH-7.18) + 400 mg/l $FeCl_3$ (10%) (wt/vol), pH = 2.93 + 1 mg/l PE – C11 (0.1%) After filtration, pH = 3.27
Jar Test 4	500 ml water sample (pH-7.2) + 40 mg/l NaOH (2%) (wt/vol), pH = 10.42 + 120 mg/l $FeCl_3$ (10%) (wt/vol), pH = 8.4 + 1 mg/l PE – A107 (0.1%)
Jar Test 5	500 ml water sample (pH-8.07) + 40 mg/l NaOH (2%) (wt/vol), pH = 10.42 + 120 mg/l $FeCl_3$ (10%) (wt/vol), pH = 7.7 + 1 mg/l PE – C11 (0.1%)
Jar Test 6	500 ml water sample (pH-7.2) + 180 mg/l NaOH (2%) (wt/vol), pH = 11.42 + 400 mg/l $FeCl_3$ (10%) (wt/vol), pH = 6.73 + 1 mg/l PE – C11 (0.1%) + 1 mg/l PE – A107 (0.1%)

	pH = 7.30, Turbidity = 18.19

Table 7.5: Dosage of coagulants used in the jar tests

After settling of flocs, the sample was filtered. The filtrate was taken in a 1000 ml measuring cylinder. Aeration was provided through a portable air diffuser. Rise in foam was observed.

7.6.4 OBSERVATIONS

Turbidity reduction and visual observations are summarised in table 7.6.

Jar Test	Initial Turbidity (NTU)	Final Turbidity (NTU)	Observation
Jar Test 1	97.3	2.7	Flocs formed and settled easily. Excess foam formed during aeration.
Jar Test 2	95	1.10	Fine floc formed that settled easily. Clear supernatant and turbidity reduction obtained. No foam formation after 30 minutes of aeration
Jar Test 3	81.9	6.5	Fine floc formation that settled easily. Clear supernatant. Visible reduction in turbidity. No foam formation during aeration
Jar Test 4	90.4	16.84	Fine floc formation that settled easily. Slightly turbid supernatant. Foam formation during aeration
Jar Test 5	90	-	Flocs formed settled easily.

			Aeration not provided.
Jar Test 6	81	18.19	Fine floc formation that settled easily. Slightly turbid supernatant. Foam formation during aeration

Table 7.6: Observations of Jar Tests - Foam Reduction

7.6.5 RESULTS AND INFERENCE

In the first experiment, ozone treatment was provided to the SLS sample prepared. It was observed that there was no effect on turbidity reduction or foam formation. On the contrary, foam formation took place quite rapidly. This could be due to the anionic nature of foam. It can be inferred that due to the anionic nature of foam, no charge neutralization took place, instead foam formation enhanced due to diffusion. During these experiments, 500 ml sample was taken in 1000 ml measuring cylinder. Figure 1 shows the image of foam formation after the sample was aerated for 1.5 minutes.

Figure 7.4: Foam formation after aeration for 1.5 minutes

As shown in figure 7.4, there was enhanced foam formation after aeration was provided for 1.5 minutes. Aeration was stopped as foam height had increased considerably.

Jar test [3] was performed with $FeCl_3$ at pH of 7.2, 10.5, 11.5 with coagulant dose of 400 mg/l, 120 mg/l and 400 mg/l respectively. Maximum turbidity reduction was observed at pH 7.2. 92% reduction turbidity was observed. The supernatatnt was aerated for 30 minutes. After 30 minutes, there was negligible foam formation. However, the final pH was recorded at 3. This is not ideal for the upstream biological process. Figure 7.5 shows the status of foam formation for jar test 3.

Figure 7.5: Foam formation after 30 minutes - Jar Test 3

Jar tests were also performed using alum as a coagulant. Alum dose of 400 mg/l and 500 mg/l was provided. Turbidity reduction of 97% and 98% was recorded for the two jar tests respectively. Supernatatnt was filtered. In case of jar test 1, where the dose of alum was 400 mg/l, foam formation was observed despite reduction in turbidity. However, in case of jar test 2, where the dose of alum was 500 mg/l, NaOH was added before aeration. No foam formation was observed after 30 minutes of aeration in this case. Figure 7.6 shows the supernatant of jar test 2 after aeration was provided for 30 minutes.

Figure 7.6: Jar Test 2 - Foam formation after 30 minutes of aeration

In case of both Alum and Ferric chloride, the final pH of the supernatant was quite low. This can have an adverse effect on the biological process. Therefore, jar test was conducted while maintaining the pH within the neutral range.

Jar test 6 was conducted. pH was raised using NaOH. After a pH of 11.42 was observed, 400 mg/l of ferric chloride was dosed. After settling, the supernantant was aerated. Heavy foam formation was observed as shown in figure 7.7. Moreover, the turbidity reduction was also reduced.

Figure 7.7: Foam formation after Jar Test 6

Both Alum and Ferric Chloride are able to remove anionic surfactant and show reduction in turbidity and foam formation. However, the final pH is not favourable for upstream biological process. Therefore, more trials need to be performed in order to better understand the optimum pH range. Optimum dose of coagulant required needs to be defined while keeping a check on the pH conditions. Minimum concentration of SLS that does not result in foam formation needs to be evaluated in order to establish a lower limit for which chemical treatment can be applied. Additionally, experiments can be performed to evaluate the efficiency of surfactant removal with the use of activated carbon.

CHAPTER 8

USE OF SODIUM HYPOCHLORITE AS AN OXIDISING AGENT

8.1 INTRODUCTION

Advanced Oxidation Process (AOP) is a method of treatment of toxic, recalcitrant pollutants present in wastewater. In the recent years, use of AOPs has risen exponentially due to their ability to eliminate persistent, recalcitrant compounds present in the water. These persistent compounds are hazardous to both the aquatic biota as well as human life. Thereby increasing the need to obliterate these compounds from the wastewater. Over the recent years, the use of AOPs has risen significantly due to its versatility. Furthermore, this technology has proven to be environmentally sustainable as well. Chlorine has been widely used in both water and wastewater treatment primarily as a disinfectant, but it has also been used for the reduction in oxygen demand and odour. Hypochlorites have been used as disinfectants for years. (20)

When sodium hypochlorite dissolves in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) are formed. Hypochlorous acid and hypochlorite ion play a role in the process of oxidation. By adding hypochlorite to water, hypochlorous acid is formed,

$NaOCl + H_2O \rightarrow HOCl + NaOH^-$

Hypochlorous acid is divided into hydrochloric acid (HCl) and oxygen (O). The oxygen atom is a very strong oxidant. There are a few research papers only where sodium hypochlorite is used for the treatmentof wastewater.

One journal article indicated that there is reduction in the BOD and COD levels after chlorination. However, the COD removal efficiency was not quite high. However, according to an article from the Journal (Water Pollution Control Federation), there is no BOD reduction caused by chlorination and COD remained unchanged before and after chlorination. Presence of a significant amount of ammonia could be the reason behind the lack of effect of chlorination. Their hypothesis was that the chlorine would preferentially and rapidly combine with ammonia and form chloramine. This chloramine formation would tend to suppress oxidation of organic matter in the wastewater. Therefore, effect of sodium hypochlorite on sewage water is unclear. (21) (22)

8.2 EXPERIMENTAL PROCEDURE

For the experiments, wastewater sample was collected from the on-campus sewage treatment plant.

The sewage treatment plant in Thapar Institute of Engineering and Technology comprises of two stage biological process. It has a capacity of 2.3 MLD.

Wastewater enters the wastewater collection tank through the inlet drain and bar screen chamber. The wastewater is then sent to the anaerobic reactor.

The upflow anaerobic sludge blanket reactor (UASB reactor), is a single tank process. Wastewater enters the reactor from the bottom, and flows upward. A suspended sludge blanket is present which filters and treats the wastewater. Microorganisms present in the sludge break down the organic matter by anaerobic digestion. UASB has high removal efficiency of organic pollutants.

Wastewater from the UASB reactor enters the oxidation pond. The sample was collected from the drain connecting UASB and oxidation pond. It was collected before the wastewater could enter the oxidation pond.

Water from the oxidation passes through multi-stage filter and is collected in the treated water collection tank for further reuse.

Table 8.1 lists the experiments that were performed during the course of this project.

S.No.	Name of the Test	APHA Method	Method Selected	Reason
1.	COD	• Open Reflux Method • Closed Reflux, Titrimetric Method • Closed Reflux, Colorimetric Method	Open Reflux Method	Closed reflux methods are more economical. However, open reflux method is

				more suitable for a wide range of wastes where a large sample size is preferred. For these experiments, initially open reflux method was opted. However, it was switched to close reflux method as it was more economical
2.	Turbidity	• Nephelometric Method	Nephelometric Method	Its precision, sensitivity, and applicability over a wide turbidity range make it preferable.

Table 8.1: List of experiments (23)

8.3 RESULTS AND DISCUSSION

Maximum COD reduction was observed when 10 ml of 10 ppm sodium hypochlorite solution was added to the diluted wastewater sample. The maximum COD removal recorded was 62.5%. This is not considered economical. Addition of sodium hypochlorite has an effect on the COD reduction of the wastewater but its effect is not highly significant.

This can be attributed to the presence of ammonia in the wastewater sample. High concentrations of ammonia in the wastewater yield a chloramine residual. A study noted that chlorine would preferentially and rapidly combine with ammonia in the presence of other organic compounds. The formation of chloramine will be considerably rapid such that HOCl and OCl^- will be present momentarily only. Furthermore, the formation of chloramine would have a propensity to suppress the oxidation of other organic matter in the wastewater.

Therefore, a normal dosage of chlorine will be insufficient for the oxidation of soluble organics when the wastewater contains considerable amount of ammonia.

The results obtained corroborate with this hypothesis.

Therefore, the use of sodium hypochlorite for the reduction of COD in the sewage wastewater is not cost-effective.

CHAPTER 9

CONCLUSION

Water pollution is one environmental issue that has a drastic impact on the environment. Water scarcity is deemed as one of the largest threats to humankind. Just a small percentage of the world's water is considered fit for human consumption. Being a natural resource, water is indispensable for human life and critical for the sustainability of the environment. Over the years, states all over the world have taken up initiatives to develop new technologies and practices to mitigate the effect of water pollution. Some of these initiatives include desalination, rainwater harvesting and wastewater treatment. Despite of state-of-the-art treatment technologies, industries may face challenges in achieving desired performance during operations. These challenges can be caused due to multiple reasons, like ageing infrastructure, changes in wastewater quality and quantity, presence of emerging constituents, uncertainties associated with operations and others. In order to overcome these challenges, certain customized services maybe required. These customized services include technical audits, treatability studies and membrane autopsy, and pilot-scale testing. Such customized services play a crucial role in identification of wastewater characteristics, design challenges and providing innovative as well as cost-effective solutions to various challenges associated with pre-existing treatment schemes. During the course of these projects a hands-on experience was gained. An insight on various technical issues faced during the operation of a treatment plant was gained.

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ANNEXURE

Time	Flowrate	Pressure	Flux	% Turbidity Reduction
0	1.51	3.4	30.2	
15	1.36	3.4	27.2	78.0822
30	1.29	3.4	25.8	95.8333
45	1.29	3.4	25.8	94.4444
60	1.29	3.4	25.8	85.7143
75	1.22	3.4	24.4	95.1807
90	1.22	3.4	24.4	88.7324
105	1.22	3.5	24.4	84.058
120	1.22	3.5	24.4	81.56
135	1.22	3.4	24.4	94.6237
150	1.22	3.4	24.4	92.2222
165	1.22	3.4	24.4	84.6154
180	1.15	3.4	23	82.5
195	1.15	3.4	23	82.716
210	1.15	3.4	23	80.8219
225	1.15	3.4	23	83.3333
240	1.15	3.4	23	79.4118
255	1.15	3.4	23	95.0617
270	1.08	3.4	21.6	94.5946
285	1.08	3.4	21.6	88
300	1.08	3.4	21.6	84.2857
315	1.15	3.4	23	90.7692
330	1.15	3.4	23	95.1613
345	1.08	3.4	21.6	80
360	1.08	3.4	21.6	78.9474
375	1.51	3.3	30.2	95.3488
390	1.44	3.3	28.8	90.3614
405	1.36	3.3	27.2	94.8276
420	1.36	3.3	27.2	95.7576
435	1.29	3.3	25.8	91.0828
450	1.29	3.3	25.8	95.3947
465	1.29	3.3	25.8	89.2617
480	1.29	3.4	25.8	91.6667
495	1.29	3.3	25.8	93.5484
510	1.22	3.3	24.4	90.9091
525	1.22	3.3	24.4	92.7536
540	1.22	3.3	24.4	89.1667
555	1.22	3.4	24.4	96.2693
570	1.22	3.4	24.4	93.0769
585	1.22	3.4	24.4	87.395
600	1.22	3.4	24.4	90.6977
615	1.29	3.4	25.8	97.8571

630	1.29	3.4	25.8	96.7972
645	1.22	3.4	24.4	95.6679
660	1.15	3.4	23	98.2639
675	1.15	3.4	23	97.3585
690	1.15	3.4	23	97.3384
705	1.08	3.4	21.6	97.7528
720	1.08	3.4	21.6	98.0695
735	1.08	3.4	21.6	97.992
750	1.08	3.4	21.6	98.7805
765	1	3.4	20	98.7179
780	1	3.4	20	97.8448
795	1	3.3	20	97.0909
810	1	3.3	20	95.9854
825	1	3.3	20	99.6441
840	1	3.3	20	97.7941
855	1	3.3	20	98.1982
870	1	3.3	20	99.2727
885	1	3.3	20	94.2748
900	0.93	3.3	18.6	97.9253
915	1.15	3.3	23	94.8077
930	1.08	3.3	21.6	96.0707
960	1	3.4	20	95.6778
975	1	3.3	20	95.1904
990	1	3.3	20	87.6923
1005	0.93	3.4	18.6	99.2381
1020	0.93	3.4	18.6	97.1602
1035	0.93	3.4	18.6	90.7258
1050	0.86	3.4	17.2	94.0452
1065	0.86	3.4	17.2	77.3547
1080	0.86	3.4	17.2	83.6245
1095	0.86	3.4	17.2	94.9686
1110	0.86	3.4	17.2	98.627
1125	0.86	3.4	17.2	98.801
1140	0.86	3.4	17.2	98.3529
1155	1.08	3.3	21.6	95.4094
1170	1	3.3	20	96.1006
1185	1	3.3	20	95.8549
1200	0.93	3.3	18.6	96.3061
1215	0.86	3.3	17.2	95.5585
1230	0.86	3.3	17.2	91.3098
1245	0.86	3.4	17.2	91.9395
1260	0.86	3.4	17.2	93.7173
1275	0.86	3.3	17.2	92.7397
1290	0.79	3.3	15.8	92.074
1305	0.79	3.3	15.8	93.8619
1320	0.79	3.3	15.8	90.8441
1335	0.76	3.3	15.2	94.2857
1350	0.72	3.2	14.4	93.1129

1365	0.72	3.3	14.4	94.1265
1380	0.72	3.3	14.4	93.2847
1395	0.72	3.4	14.4	94.0506
1410	0.72	3.3	14.4	92.1824
1425	0.72	3.3	14.4	92.3888
1440	0.72	3.3	14.4	90.6725