Treatment of Textile wastewater using Hybrid Membrane Bioreactor and Hybrid Sequencing Batch Reactor

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Certificate

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Dedication

We dedicate our project thesis to our parents, friends, faculty members and Environmental Engineering department at IESE, NUST for all their support and appreciation.

This project would not have been possible without the didactic guidelines from our supervisor, Dr. Sher Jamal Khan.

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We are thankful to the faculty of Institute of Environmental Sciences and Engineering for helping us in acquiring special tools related to optimization . Through their vast exposure and knowledge we were able to lay hands on a stupendous project like this.

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Abstract

Pakistan is already one of the most water-stressed countries in the world; a situation which is going to degrade into outright water scarcity The need of the day is to reduce the constantly growing stress on existing water resources for sustainable development. Wastewater pollution is a major environmental and social concern in Punjab and Pakistan.

In this study, three differently configured lab-scale Bio Reactors were operated in parallel under same conditions at IESE-NUST. Hybrid Membrane Bio-reactor (H-MBR) with anoxic/oxic conditions and biofilm carrier and PAC.

Table of Contents

List of Figures

List of Tables

Introduction

1.1 Background

As climate change and political and social unrest take their toll on fresh water supplies, 783 million people lack access to clean or safe water and 37 percent of the world's population doesn't have access to sanitation facilities (UN special report). Only 3 percent of the water resources is not salty, two third of the water is locked up in glaciers and other ice caps. Only 0.08 percent of the remaining water is only used by human being in the ever increasing demand for sanitation, drinking, manufacturing, industries, washing and agriculture (World Bank, 2005). Our best concern in the future is the sustainability of the current and future water resources allocation. As water is becoming scarce, so the need and importance that how it should be managed, used and treated is growing vastly.

Water will remain a critical and limiting resource for sustained economic development of the country. Pakistan is already one of the most water-stressed countries in the world; a situation which is going to degrade into outright water scarcity (World Bank, 2005). The need of the day is to reduce the constantly growing stress on existing water resources for sustainable development.

Wastewater pollution is a major environmental and social concern, particularly in Punjab and generally in Pakistan. The impacts of discharging wastewater without treatment into the environment have significant health and ecological impacts and externalities. The Environmental legislation and other related federal and provincial policies and legislation have set it mandatory to treat wastewater before discharging it into the environment. Industries are also major polluters of environment. Except Faisalabad which only treats 20% of the wastewater, none of the cities treat their wastewater. The capacity of the Water and Sanitation Agency (WASA) and cities to design and operate wastewater treatment plant is limited and needs specialized input to enhance their capacities.

One possible solution to the problem is wastewater reclamation and reuse through treatment. Processes used to make water more acceptable for a desired end-use is termed as wastewater treatment. Groundwater recharging is one of the major benefits of wastewater reclamation. The end product can be used for irrigation, industrial processes, and non potable purposes. Another possible solution is to improve quality of wastewater so that it can be reused for non-potable purposes. Conventional wastewater treatment processes are not effective in removal of pathogens and their effluents causes risk to aquatic life and environment. Current technology may be able to satisfy discharge standards but not suitable for reuse.

Major forces to undergo water recycling today are the increasing water demands due to population growth, change in human lifestyle, urbanization, and fading natural water resources. Moreover, well public alertness about environmental protection has resulted in growingly more inflexible wastewater quality discharge regulations. Disposal of treated wastewater below discharge standards from households or other units can result in adverse soil pollution and surface water contamination (Tanner, 2012). Especially in the textile industry a high quality of water effluent is demanded, since textile wastewater can be a major source of color and contaminants when discharged to the environment. The color from the textile wastewater is mainly due to the intense dyeing process, which involves a wide range of different types of dyes, of which only 50 % is biodegradable. Many of these dyes can cause environmental problems if released into the aquatic environment, thus causing highly environmental concerns. Because of this and local water scarcity which is a problem in many regions, reuse of the water effluent has become an important issue in the textile industry.

1.2 Objectives

- To analyze textile effluent from different industries and determine the composition of synthetic textile wastewater.

- To optimize operation and maintenance of Hybrid Membrane Bioreactor and Hybrid Sequencing Batch Reactor with Powdered Activated Carbon (PAC) for textile wastewater.

Chapter 2

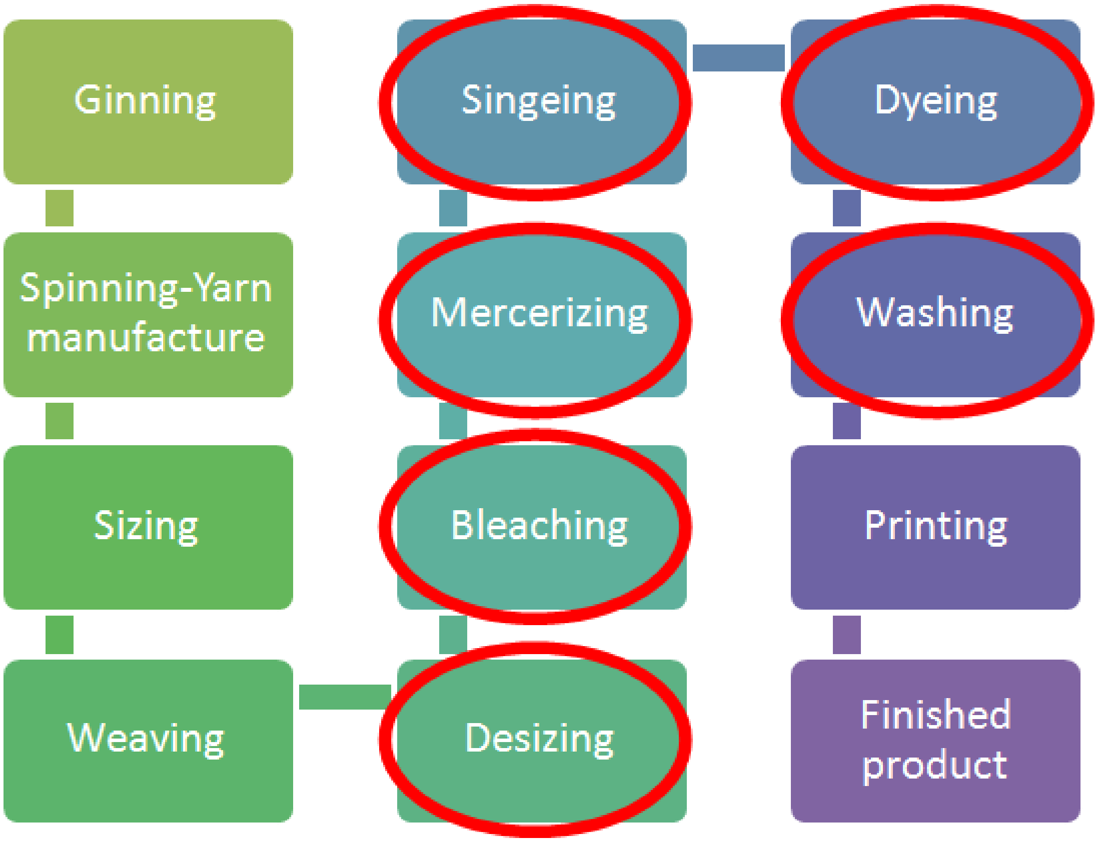
Literature review

2.1 Textile industry processes

The textile industry consumes large amount of water in its different processing operations. In the mechanical processes of spinning and weaving, water consumed is very small as compared to textile wet processing operations, where water is used extensively. According to USEPA a unit producing 20,000 Ib / day of fabric consume 36000 liters of water (Shaikh, 2009).

1) Ginning

The cotton seed grows in to a cotton gin. It separates seed and removes the trash (dirt, stems and leaves) from the fiber. So the process of separating the cotton fibers from the seed pods is termed as ginning. A machine which provides greater productivity then manual separation is termed as cotton gin**.**



Source: Adapted from cresent textile mill

Figure 2.1 Textile Industry Processes

2) Spinning-yarn manufacture

Spinning is the succeeding step to ginning. This process involves the making of yarn from the cotton fiber. The cotton yarns are made of different thickness in this stage.

3) Sizing

Starch is added to the manufactured yarn for the strengthening of the warp to reduce the breakage of yarn. The yarn is run through a size solution and then dried so that it has the strength and stiffness required to withstand the abrasion and friction generated in the weaving operation.

4) Weaving

Weaving is the most important process in the making of cotton cloth. It is the process of interlacing two yarns of similar materials so that they cross each other at right angles to produce woven fabric. In this process, two yarns are placed to make warp and weft of a loom which successively turn them into a cloth. The length way threads are known as the warp, and the cross way threads are known as the weft.

5) Desizing

Depending on the size that has been used, the cloth may be steeped in a dilute acid and then rinsed, or enzymes may be used to break down the size. Removes the sizing compounds applied to yarns to impart tensile strength. The starch sizing compounds are solubilized with alkali, acid or enzyme, and the fabric is washed thoroughly. Alkaline desizing utilizes a weak alkaline solution to facilitate size removal, while acid desizing employs a dilute acid solution to hydrolyze the size and render it water soluble. Enzyme desizing utilizes enzymes to decompose size. After solubilizing the size, the fabric is rinsed clean.

6) Bleaching

Bleaching improves whiteness by removing natural coloration and remaining trace impurities from the cotton; the degree of bleaching necessary is determined by the required whiteness and absorbency. Cotton being a vegetable fiber will be bleached using an oxidizing agent, such as dilute sodium hypochlorite or dilute hydrogen peroxide. If the fabric is to be dyed a deep shade, then lower levels of bleaching are acceptable. However, for white bed sheets and medical applications, the highest levels of whiteness and absorbency are essential. Bleaching chemicals include sodium hypochlorite, hydrogen peroxide, and sodium perborate, as well as optical brighteners. Batch bleaching is done in dyers where fabric is tacked for a given period to allow the chemical to work before goods are withdrawn from the bottom of the box. Bleaching is followed by thorough rinsing.

7) Mercerizing

In this process the fabric is treated with caustic soda solution to cause swelling of the fibers. This results in improved lustre, strength and dye affinity. Cotton is mercerized under tension, and all alkali must be washed out before the tension is released or shrinkage will take place. Mercerizing can take place directly on grey cloth, or after bleaching.

8) Singeing

Singeing is designed to burn off the surface fibers from the fabric to produce smoothness. The fabric passes over brushes to raise the fibers, and then passes over a plate heated by gas flames. Sometimes different chemicals are also used.

9) Dyeing

This process involves the changing of fabric color by the treatment of dye. Finally, cotton is an absorbent fiber which responds readily to coloration processes. For improved fastness to washing, rubbing and light, other dyes such as vats and reactive are commonly used. These require more complex chemistry during processing and are thus more expensive to apply.

10) Washing

Chemical washing process is carried out on cotton fabric to remove natural wax and non-fibrous impurities from the fibers and any added soiling or dirt. Some of the dyes also need to be washed from the surface of the cloth.

11) Printing

Printing, on the other hand, is the application of color in the form of a paste or ink to the surface of a fabric, in a predetermined pattern. It may be considered as localized dyeing. Printing designs on to already dyed fabric is also possible.

12) Finished product

The primary purpose of the finishing process is to alter properties affecting the care, comfort, durability, environmental resistance, aesthetic value, and human safety associated with the fabric. Finishes can be applied, for example, to make fabric wrinkle resistant, crease retentive, water repellant, flame resistant, mothproof, mildew resistant, and/or stain resistant. Finishes include a very large and diverse group of chemicals ranging from antistatic to shrink-resistant finishes. In wet-finishing, the sequence of steps typically includes chemical finish application together with mechanical techniques, the advantages of the latter being improved feel, strength and abrasion resistance and lower chemical consumption and waste (Snowden-Swan, 1995). Finishing is usually a continuous process that produces little or no wastewater (Noyes, 1993). At this stage the cloth is prepared to be dispatched to the market.

Table 2.1 Amount of wastewater generated from each wet process and characteristics of wastewater

Process	Requirements in litres/1000kg of the product	Characteristics of wastewater
Desizing	2500-21000	High COD, High Total Solids, pH Neutral
Bleaching	2500-25000	H_2O_2, High pH
Mercerizing	17000-32000	Alkaline, Low TDS, Detergents
Singeing	500-8200	Different chemicals, High COD, Alkaline
Dyeing	10000-300000	High COD, High TDS, Neutral to alkaline
Washing	20000-45000	High phosphates

Source: Adapted from Water conservation in textile industry (Shaikh, 2009)

2.2 Textile wastewater effects on the environment

Textile industry is characterized by large quantity of water consumption and a variety of chemical used. Water is used in wet process and lies in a range of 80-150 m^3 per 1000 kg of the product (Haydar & Bari, 2009). Wet process generates wastewater. In Pakistan textile industry discharge highly polluted wastewater into the fresh water bodies adversely affecting the aquatic life and human health. Different process involved in textile industry produce different impacts on wastewater generated. This impact starts with the use of pesticides during the cultivation of natural fibers. However world's wide environmental problems of textile industry are those which are linked with the water pollution caused by discharge of untreated effluent. Moreover, these chemicals can harm consumers if they are retained in the fiber (Haydar & Bari, 2009).

The impact of environmental regulations on the textile sector of Pakistan can be classified according to various parameters of wastewater. The wastewater generated by textile industry is high in COD, pH, temperature, color, turbidity and toxic chemicals. Direct discharge of this wastewater in rivers or lakes can affect flora and fauna. Effluents of textile industry are generally hot, alkaline, and strong smelling, and colored by chemicals used in dying process. Some of the chemicals, including dyes and pigments, are toxic or can lower the dissolved oxygen content of receiving waters, threaten aquatic life and damage general water quality downstream (Shaikh, 2009).

Effects on organisms in the environment can be either short term (acute) or long term (chronic). Many add-ons in dyeing namely carriers, dye-fixing agents, cationic retarders and heavy metal salts are difficult to biodegrade and therefore have a negative impact on the environment. In textile wastewater the toxic effect of heavy metals on animal and aquatic life is dependent on their physico-chemical form. In dye house effluent, heavy metals occur as a consequence of the heavy metals salts used in dyeing, the use of metal-complex dyes, or from the presence of impurities in dye stuffs. It has been observed that dyeing losses contribute to only 10- 30% of total BOD , while respect to COD, the contribution of virgin dyes the is around 2-5%, while that of dye bath chemicals is as high as 25-35% upto 50% of dyes may be lost directly into the waterways when using reactive dyes. Acetic acid used in disperse dyes on polyester exerts a high BOD and can account for 50- 90% of dye house BOD. The presence of dyes in waterways is easily detectable even when released in small concentrations (Shaikh, 2009).

Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria. The breakdown products of dyes are toxic and mutagenic to life. Dye used varies from day to day and sometimes even several times a day primarily because of the batch wise nature of the dyeing process due to which a large pH swing is especially troublesome because the pH tolerance of conventional biological treatment is very limited the dye waste effluent is varied in color from purple, dark red, brown, grey, dark blue or black. There are almost more than 2000 different chemicals are used in textile industry from dyes to transfer agent. Being a chemically intensive industry textile industry is number one polluter of clean water after agriculture. It takes about 500 gallons of water to produce enough fabric to cover one sofa. Half a billion people already live in regions prone to chronic drought, and by 2025, that number is likely to increase by five-fold, to between one third and one half of the entire world population (Iqbal, 2011).

Global consumption of fresh water is doubling every year. The basic chemical discharges in mill drainage are dyes, dextrin, gums, alcohol, fatty acids, soaps, detergents, sodium hydroxide, carbonates, sulfides, sulfites, carboxymethyl cellulose, gelatin, peroxides, resins chlorine, formaldehyde, acetic acid, starch along with heavy metal such as lead and mercury. There are number of problems which can be caused by dyes. Depending on exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms. The presence of very small quantities of dyes in water less than 1 ppm is highly visible due to their brilliance. The primary concern about effluent color is not only its toxicity but also its undesirable aesthetic impact on receiving waters (Kiron, 2011).

The color of reactive dyes is due to the presence of N=N azo bond and chromophoric group. These dyes in both ordinary and hydrolyzed form are not easily biodegradable and thus even after treatment color may be present in the effluent. The greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water. Light absorption diminishes photosynthetic activity of algae and seriously influence on the food chain. Dyes can remain in the environment for an extended period of time, because of high thermal and photo stability. Many dyes and their breakdown products are carcinogenic, mutagenic and toxic to life. There is ample evidence of their harmful effects. Primary cancers involving kidney, urinary bladder and liver of dye workers have been reported in a past several years. A lot of investigations of respiratory diseases in workers dealing with reactive dyes have been made. Certain reactive dyes have caused respiratory sensitization of workers occupationally exposed to them. Most of the dyes, used in the textile industry are known only by their trade name, while their chemical nature and biological hazards are not known (Kiron, 2011).

Textiles industry also have a huge impact on the environment from growing natural fibers to the finishing and dying process, to the substantial amounts of water and energy used to clean the textiles once in hand of the final user. For examples; Cotton is a water intensive crop and is often grown in water-scarce areas. Cotton requires a lot of toxic pesticides to grow and accounts for 16% of the global pesticide use, even though it's only 2.5% of all crops. These pesticides runoff and pollute local ground water. The discharge of organic pollutant either BOD or COD to the receiving stream can lead to the depletion of dissolved oxygen and thus creates anaerobic condition. Under anaerobic condition, foul smelling compound such as hydrogen sulfides may be produced. This will consequently upset the biological activity in stream (Jadeacres, 2011).

Lupica (2013) investigated the effects of untreated wastewater on the body weight and the weight of reproductive organs of animals. The researchers orally administered both treated and untreated wastewater to two groups of animals. They found that the group ingesting the untreated wastewater had significantly reduced body weights and their reproductive organs were up to 44% smaller. Additionally, they found very unhealthy reductions in total protein concentrations of up to 70% and cholesterol was depleted by up to 9%.

The dyes i.e. Disperse, Vat, Reactive and Pigment dye were given by the cresent textile mill. Following is a brief description of the above mentioned dyes.

Table 2.2 Description of Dyes

Dye Class	**Description**	**Main application**
Disperse dye	➢ Moderate price ➢ Complete color range ➢ Normally dispersed in water for application ➢ Good fastness	Mostly used for ➢ Polyester, ➢ Acetate, ➢ Nylon, ➢ Acrylic.

Vat dye	➢ Difficult to apply ➢ Expensive ➢ Incomplete color range ➢ Good fastness ➢ Tending to decrease in popularity due to increasing use of reactive dyes	Mostly used for ➢ High quality cotton goods, e.g. towel; ➢ Specially used in the dyeing of denim fabric.
Reactive dye	➢ Easy application; ➢ Moderate price; ➢ Complete color range; ➢ Good fastness as direct reaction with fibers occurs.	Mostly used for ➢ All cellulosic goods ➢ Selective dyes can also be applied on wool, silk & rayon ➢ Increasingly used in printing due to good fastness. ➢

Source: Adapted from dye class

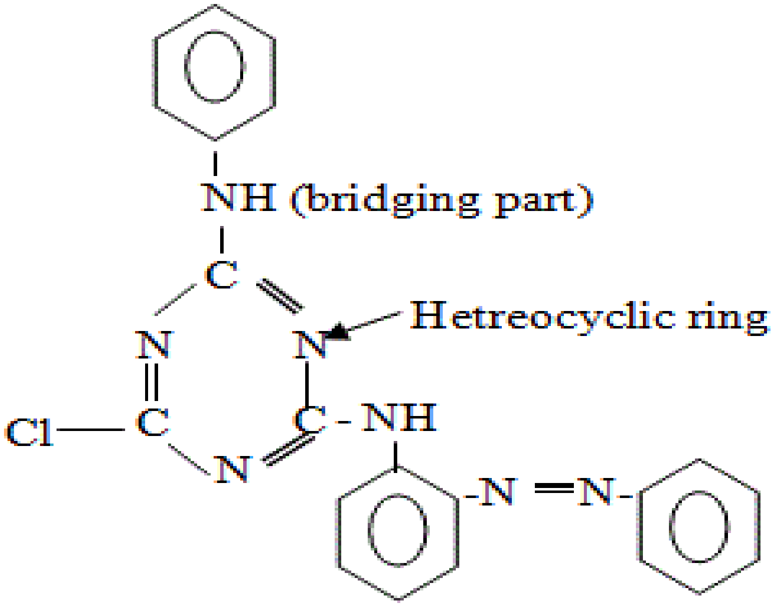


Figure 2.2 Reactive Dye formula

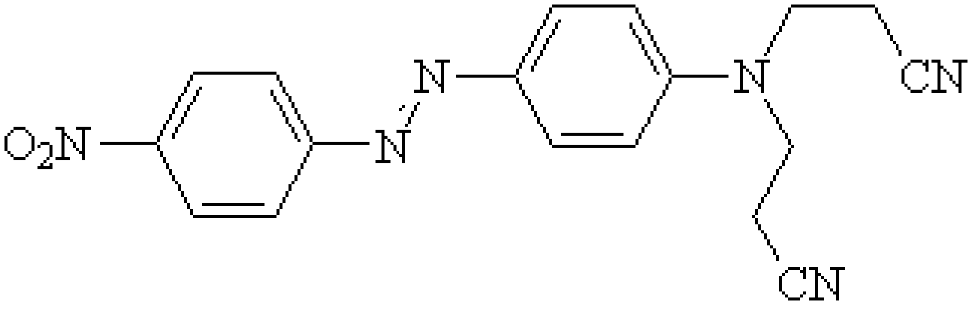


Figure 2.3 Disperse Dye Formula

2.3 Treatment Technologies

During the past two decades, several treatment techniques have been reported, few of which have been accepted by industries. There is a need to find alternative treatments that are effective in removing dyes and colorants from large volume of effluents. The color of effluent is as indication of pollution if it discharges into water bodies. The color of water, polluted with organic colorants, reduces when the cleavage of the –C=C-bond the –N=N- bond and heterocyclic and aromatic ring occurs.

There are various methods which are formed by the physical, chemical and biological methods for treatment of textile industry wastewater are follows;

2.3.1 Physical method

Some physical methods like adsorption, irradiation and ion-exchange are effective and proven technology having potential application in industrial wastewater treatment. Some absorbents like chitin, which contain amino nitrogen, tend to have a significantly larger adsorption capacity in acid dyes. Many adsorbents made from waste materials, for removal of dye and colored organic matters from aqueous media are of low cost (Bousher ,1997). The activated carbon having a high adsorption capacity for basic dyes, is most common method of dye removal by adsorption (Nassar et al., 199l).The adsorption method has difficulties in the treatment of insoluble dye stuffs wastewater and it is difficult to find the desorption process (Kuo.et al.,1992, Kim et al.,2002). Irradiation process is effective for removal of a wide range of colorants at low volume, but in this treatment dissolved oxygen requirement is very high. Ion exchange cannot accommodate a wide range of dyes and further perform poorly in the presence of other additives in wastewater.

2.3.2 Chemical method

Chemical methods like coagulation and flocculation are generally used in order to eliminate organic materials. Coagulant materials are usually effective on decomposed dyeing substance. Coagulation is effective for treatment of insoluble dyestuff wastewater but not so effective for soluble dyestuff wastewater (Kang et al., 2000, Kuo. et al., 1992). The disadvantages of the method are excessive cost, excessive chemical sludge and cost for removing it (Gaehr et al., 1994). The high cost of chemicals for precipitation as well as for pH adjustment, problem associated with dewatering and disposing of generated sludge and high concentration of residual levels which remains in the supernatant are some of the limitations of this method.

2.3.3 Biological method

Most of the biological processes are effective in removing chemical oxygen demand (COD) and turbidity whereas they are not effective in removing color (Lin et al., 1997). An anaerobic step followed by an aerobic step may represent a significant advancement in biological treatment and decolorization in future (Bahorsky, 1998, Ong et al., 2005).

2.4 Membrane Bioreactors (MBR)

Though MBR technology was developed over a decade ago, its applicability for textile wastewater treatment remained elusive due to the involvement of heavy capital investment and the requirement of specific skills for its operation and maintenance. However, as the technology evolved, the costs have been brought down. With process automation, now MBR has found its way into the textile wastewater treatment in many parts of the world.

Membrane Bioreactor is advancement over the conventional Activated Sludge Process (ASP) with the use of ultrafiltration or, microfiltration membrane which helps to maintain higher levels of Mixed Liquor Suspended Solids (MLSS) concentration and attain better treated water quality. Utilization of membrane filtration results in the retention of active micro-organisms, extra cellular enzymes generated by these micro-organisms for degradation of the organics present in the effluent, organics resulting from cell-lysis, and other heavy molecular weight organics typical of textile effluent. Since some micro-organisms, especially nitrifiers, are slowly growing one, their loss shall reduce the efficiency of the treatment system and nutrient removal. Under conventional biological treatment these micro-organisms might escape from the aeration tank and the weirs of clarifier. In the MBR, these organisms are retained and a better treatment is achieved thereof. In addition, retention of active enzymes secreted by micro-organisms taking part in the metabolization of organics present in the textile wastewater is an important aspect of MBR technology. Maintenance of higher concentration of these enzymes shall result in rapid and better degradation of complex organic molecules present in the textile wastewater. Thus, the overall efficiency of BOD and COD removal is improved, detention time required to achieve specific BOD and COD is brought down, and required footprint is also minimized.

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

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

MBRs can be designed with various configurations; in general, submerged MBRs are well suited for textile wastewater treatment. Submerged MBR is normally designed to incorporate two zones i) ano*xic*; ii) *oxic*. The membrane is placed inside the oxic chamber.

The bacteria growing under anoxic condition has the capability to break down recalcitrant macromolecules, which is then digested by the aerobic bacterial population persisting in the oxic zone. In this way, a significant portion of the dye stuff and other organics could be broken down and oxidized. Thus, anoxic biological degradation is an important step if we consider MBR treatment for textile wastewater.

MBRs can be operated effectively under low food/micro-organisms (F/M) ratio. When F/M ratio is low, the settle ability of the sludge is increased. This is because; under low F/M ratio the micro-organisms are under food-limited condition. Once food is limiting, the rate of metabolism rapidly declines until the micro-organisms are in the endogenous *respiration* phase with cell-lysis and re-synthesis taking place. Since microbial activity remains high due to their retention by the membrane, low food/biomass ratio is maintained, leading to higher BOD removal and good sludge settleability. Even if the sludge fails to settle down, the MBR membrane blocks the suspended flocs (biomass) from leaving the digester. However, in the case of conventional biological treatment, sludge retention is mainly dependant on its settle ability in the clarifier.

2.4.1 Membrane Operational Modes

Membrane can be operated either under dead-end filtration or cross-flow filtration mode depending upon the nature of use. Dead-end filtration is also known as direct filtration in which the flow of direction is perpendicular to the membrane. The particles retained by the membrane result in cake formation on the membrane surface. The cake may damage and clog the pores of the membrane. Figure 2.4 illustrates dead-end filtration.

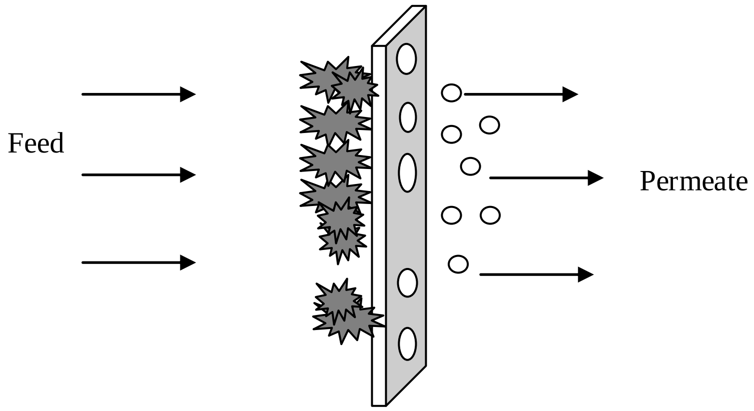


Figure 2.4 Dead end filtration

In cross-flow filtration, the flow is tangential across the surface of the membrane. A portion of feed passes through the membrane which is called permeate and the rest is rejected. Cross flow filtration opposes cake formation as it scours the membrane surface along with the flow, until adhesive forces binding the cake to the membrane are balanced. Upon this equilibrium a steady state is achieved resulting in higher permeate flow. Figure 2.5 shows mechanism of cross flow filtration.

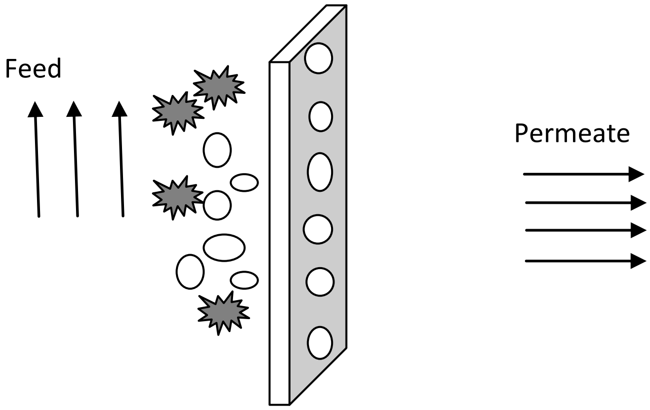


Figure 2.5 Mechanism of cross filtration

2.4.2 Advantages and Disadvantages

MBR is effective technology used for textile wastewater treatment to achieve higher effluent quality that is difficult to achieve with the conventional activated sludge process. The advantages of MBR are:

- Membrane Bioreactors have proven to be quite effective in removing both organic and inorganic contaminants as well as biological entities from wastewater. The removal of organic, inorganic, and microbiological organisms along with suspended material present an excellent output from these systems whereby the biofouling and chemical scaling of the reverse osmosis system could be drastically minimized. It also minimizes use of cleaning chemicals in the secondary treatment.

- Since suspended particles are not lost, total separation and control of the solid retention time (SRT) and hydraulic retention time (HRT) are possible, enabling optimum control of the microbial population and flexibility in operation.
- MBRs operate at low F/M ratio and long SRT. This means less sludge generation. This reduces costs of sludge disposal and hassles associated with it. Further, sludge produced in MBR is of better quality that eliminates sludge bulking.
- Since MBRs are operated under low F/M ratio, it minimizes oxygen consumption since microbes are in endogenous respiration phase and not in growth phase.
- Due to membrane separation, the need for clarifier is avoided; at the same time, due to total retention of microbes, slow-growing species (nitrifying bacteria and bacteria capable of degrading complex organic compounds) are allowed to persist in the system, improving nitrification and biological degradation. The membrane not only retains microbes, but also extra cellular enzymes and soluble oxidants synthesized by these organisms, thereby

creating a more conducive bio-reactive environment capable of degrading a wider range of organic compounds.

- Better removal of phosphorus associated with suspended solids (bacteria and colloids) is also archived with the use of MBR.
- High molecular weight organic compounds, which are not readily biodegradable in conventional systems, are retained in MBR. Thus, their residence time is prolonged and the possibility of biodegradation is improved.
- Higher strength wastewater can be treated and lower biomass yields are realized. This also results in more compact system than conventional processes, significantly reducing plant footprint and making it desirable for water recycling applications.
- The system is also able to handle fluctuations in nutrient concentration due to extensive biological assimilation and retention of decaying biomass. If some portion of complex organics is not digestible by MBR, they shall be retained by the membrane within the system, and let out as sludge.
- Membrane Bioreactor rejects Total Suspended Solids (TSS) in addition to reducing COD to the desired levels and effluent quality is so high that it leads to no post treatment requirements. Membranes provide final barrier for pathogens and suspended solids.

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

- MBR is expensive to install and operate.
- Frequent monitoring and maintenance of membrane is required.
- Certain limitations are caused by temperature, pressure and pH to meet membrane tolerances and the sensitivity of membranes to some chemicals.
- Oxygen transfer may be less efficient because of high MLSS concentration and also if there is surplus sludge, its treatability is difficult (Melin et al., 2006).
- Membrane fouling reduces membrane filtration capacity by reducing filtration flux (Dias et al., 2003). Microbes responsible for treatment of wastewater are also responsible for biofouling of the membrane (Wagner and Loy, 2002).

Chapter 3

Methodology

3.1 Materials

Textile wastewater was prepared synthetically in the laboratory with a COD of 1000 mg/L and its COD: N: P was maintained at 100:20:6. The activated sludge was taken from I-9 sewage treatment plant, Islamabad and was acclimatized with synthetic textile wastewater for 3 weeks in MBR along with Kaldnes media (K-1) with an initial MLSS of 10g/L in Water and Wastewater laboratory, IESE-SCEE, NUST.

3.2 Wastewater characteristics

The MBR was provided with the synthetic textile wastewater throughout the whole period of study. The wastewater characteristics include high strength textile wastewater having an average COD value of 1000 mg/L. Synthetic textile wastewater stock-solution composed of Hydrated glucose (1000 mg/L), Ammonium Chloride (760 mg/l), Potassium di-Hydrogen phosphate (220 mg/L), Calcium Chloride (10 mg/L), Magnesium sulphate (10 mg/L), Ferric chloride (3.3 mg/L), Magnesium Chloride (2 mg/L) and Sodium bicarbonate (800 mg/l) was added as a buffer solution to adjust pH .The stock-solution was combined with a tap water in a ratio 1:50 (i.e. 1 liter of stock solution 50 liters of tap water) to make high strength textile wastewater.

3.3 Membrane characteristics

Poly vinyl di fluoride (PVDF) membranes were used because of their higher water infiltration rate and their resistance to acid and base chemicals. The membrane module was developed by Mitsubishi rayon, Japan. A single membrane consists of a bundle of hollow fiber (HF) . The fibers are horizontally connected to module on both ends. Liquid (water) flows from the outside of fibers in to the hollow fibers.

3.4 Biofilm carrier

Kaldness® media was introduced as a biofilm carrier in A/O-MBR. The biofilm carriers are prepared of high-density polyethylene plastic material and their shape is like cylinders, having a cross on the inner side of the cylinder and rough tooth on the outside of the cylindrical shaped carrier. The size of each cylindrical shaped media was 10 mm in diameter and 7 mm in height.

Table 3.1 Chemical composition of synthetic textile wastewater

Chemicals	**Formula**	**Quantity (mg/L)**
Glucose	$C_6 H_{12} O_6$	1000
Ammonium Chloride	NH_4Cl	760
Potassium di-Hydrogen Phosphate	KH_2PO_4	220
Calcium Chloride	$CaCl_2$	10
Magnesium Sulphate	$MgSO_4.7H_2O$	10
Magnesium Chloride	$MgCl_2$	2
Ferric Chloride	$FeCl_3$	3.3
Sodium bicarbonate	$NaHCO_3$	800
Disperse dye	-	100
Vat dye	-	100
Reactive dye	-	100
Pigment dye	-	100

Table 3.2 Specific properties of plastic (Kaldness® media)

Properties	Description
Dimensions	1 cm dia.
Dry Volume	20%
Wet volume	8%
Material	K3 Type Plastic

Table 3.3 HF-PVDF membrane characteristics

Item	Characteristics
Manufacturer	Mitsubishi rayon engineering Co. Ltd., Japan
Membrane material	Polyethylene
Pore size	0.1 µm
Filtration area	0.2 m^2
MLSS	8 g/L
Filtration flow rate	Constant
Suction pressure	10-30kPa
Temperature	15-35^o C

3.4 Experimental setup

The anoxic/oxic MBR system was installed at Water and Wastewater Laboratory, IESE-SCEE, NUST. The working volume of the tank was approximately 16 L. A perforated plate divided this reactor into two compartments, with a ratio of 1:2 of the total volume. Membrane was installed in the smaller compartment with diffused aeration and a mechanical mixer (Cole- Parmer, Model 50007-25, USA) was installed in the larger compartment to create anoxic conditions. It operated in cyclic mode as 2 minutes relaxation and 10 minutes filtration mode. This MBR was named as Anoxic/Oxic MBR (A/O-MBR) as it had two zones of dissolved oxygen. Anoxic zone in which mechanical mixer was provided with a Dissolved Oxygen (DO) of 1-2 mg/L and Oxic zone with diffusers had DO of 5-6 mg/L. Kaldnes media was also used as a biofilm carrier in the anoxic zone so that hybrid growth environment can be introduced. Synthetic textile wastewater was filled into the influent tank from where it passed under gravity to the control tank where a relay unit is installed in the control tank to maintain the wastewater level in bioreactor. The system was fed with textile wastewater at a rate of 1.5 L/h.

Table 3.4 Physical parameter for laboratory scale MBR

Parameter	Value
Volume of anoxic tank	10 L
Volume of oxic tank	5 L
Membrane surface area	0.2 m^2
Pore size	0.1μm

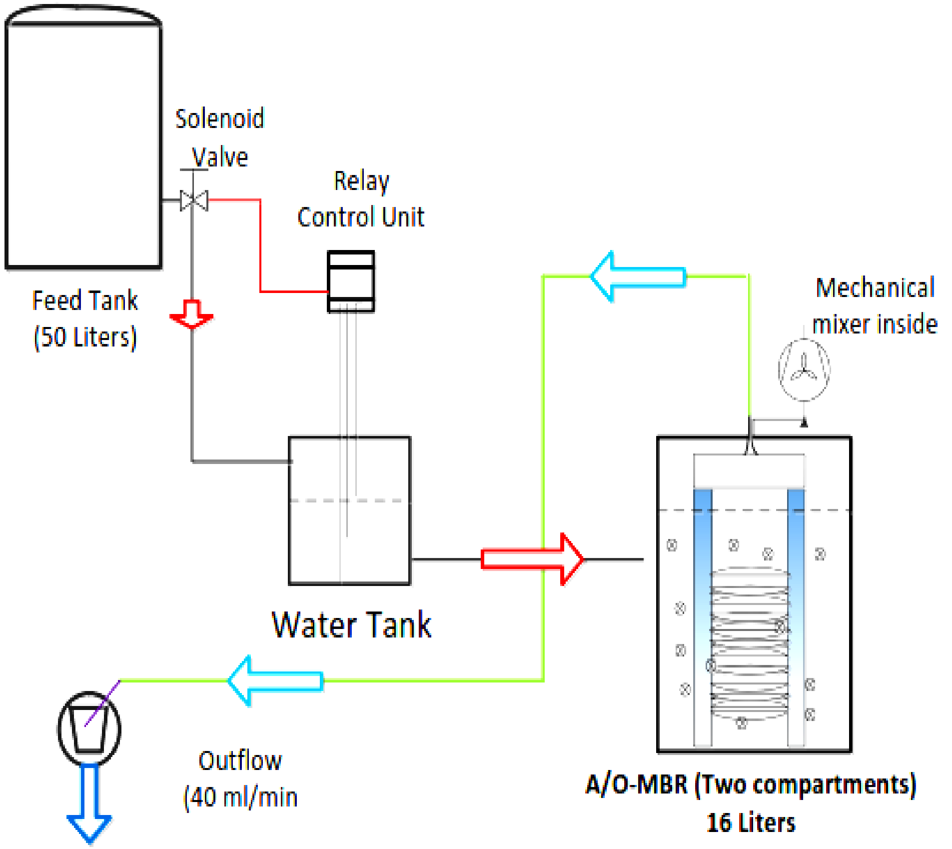


Figure 3.1 Experimental setup of A/O MBR system

Table 3.5 Biological parameters for laboratory scale MBR

Parameters	**Value**
Feed COD	1000 mg/L
MLSS	7000-10000 mg/L
HRT	12 hours
SRT	30 days

3.4.1 Addition of Powdered activated carbon

The low biodegradability of many dyes and textile chemicals indicates that biological treatment is not always successful in the treatment of cotton textile wastewater, in terms of color removal (Pala & Tokat, 2002). In this study, powdered activated carbon (PAC), were directly added into the bioreactor after sludge acclimatization. The optimum sludge retention time and hydraulic retention time were determined as 30 days and 12 hours. The addition of the synthetic wastewater did not change COD removal significantly. However; the color removal efficiency with PAC was 65% for 50 mg/L, 77% for 100 mg/L and 86% for 150 mg/L PAC addition.

3.5 Treatment of textile wastewater in SBR

To treat textile wastewater a conventional technique system using sequential batch reactor also performed for this study. Two reactors SBR and Hybrid SBR (with addition of powdered activated carbon), each having 15 L volumes were used for this study. The operating condition for both the reactors was similar.

3.6 Operating condition

A concentrated volume of 2 L sludge was placed in both the reactors and then filled with textile wastewater. Aeration is provided in both reactors to keep sludge in suspension and for microbes to perform its activity. After maintaining aeration for 12 hours, the aeration was stopped and the sludge was allowed to settle down, the supernatant is removed carefully and stored it for further analysis. The SBR operating condition was completed in four cycles Figure 3.3.

Fill (synthetically prepared textile wastewater was filled into the reactor). During the fill phase, the reactor receives influent wastewater. The influent brought food to the microbes in the activated sludge, creating an environment for biochemical reactions to take place.

React (the system is provided with aeration to let the microbes degrade pollutants for 12 hours). This phase allows for biodegradation of wastewater parameters. During this phase, no wastewater enters the reactor and the mechanical mixing and aeration units are on. Because there are no additional volume and organic loadings, the rate of organic removal increases dramatically. Most of the carbonaceous BOD removal occurs in the react phase. Further nitrification occurs by allowing the mixing and aeration to continue, the majority of denitrification takes place in the mixed-fill phase. The phosphorus released during mixed fill, plus some additional phosphorus, is taken up during the react phase.

Settle (stops aeration and let the sludge to settle down). During this phase, activated sludge is allowed to settle under quiescent conditions, no flow enters the basin and no aeration and mixing takes place.

Decant (the supernatant is then removed from the top) and pass it through the dead end filtration assembly.

Idle This step occurs between decant and the fill phases. The time varies, based on the influent flow rate and the operating strategy. During this phase, a small amount of activated sludge at the bottom of the SBR reactor is wasted, a process called wasting (Ronald F. poltak, 2005)**.**

3.7 Analytical parameters

The parameters analyzed to measure the removal efficiency in the SBR and MBR is shown in Figure 3.2.

Analytical techniques, methods and materials are listed in Table 3.4. It also contains reference protocols used for analysis. Most of the analytical techniques used in this study were adopted from Standards Methods (APHA et al., 2005).

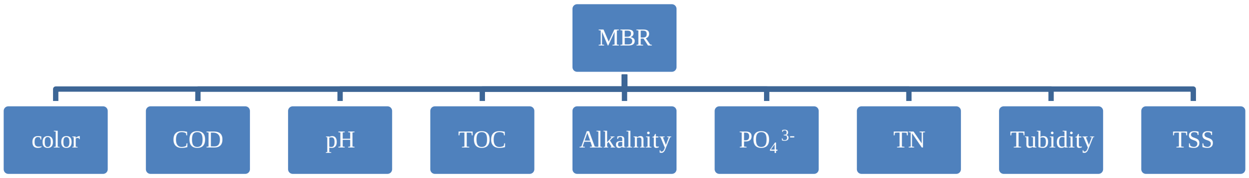
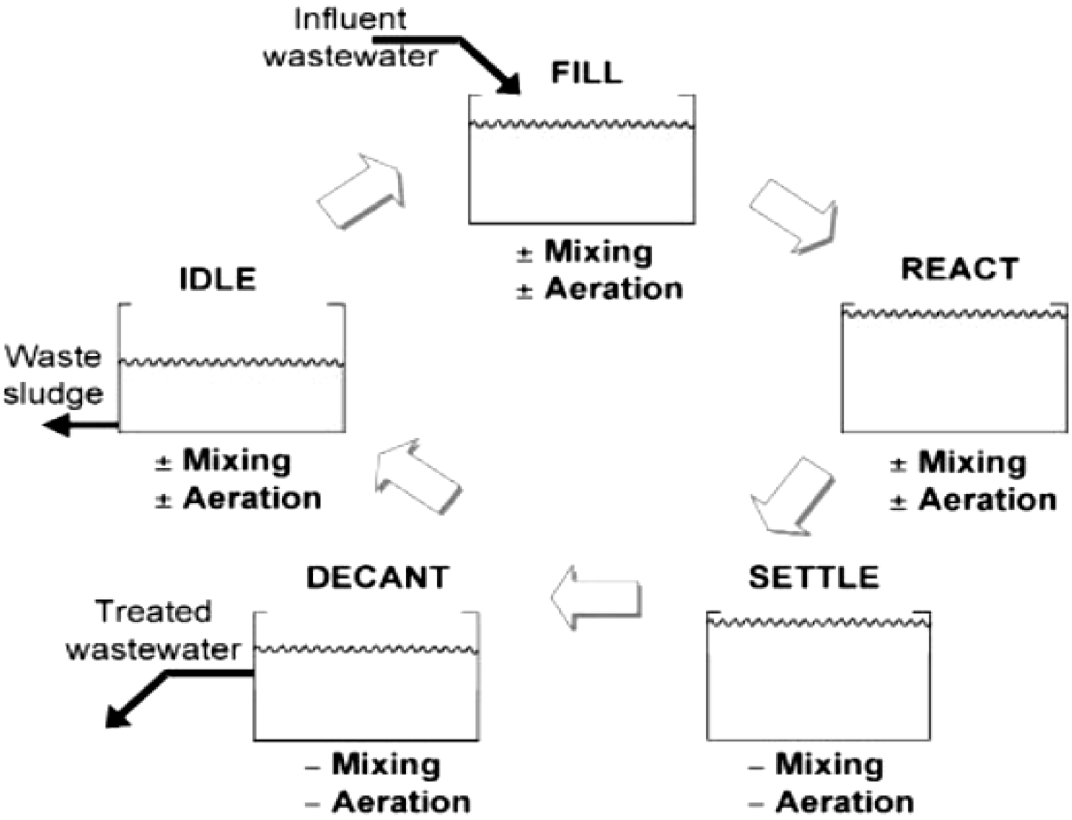


Figure 3.2 Analytical parameters analyzed



Source: University of Florida TREEO Center's Sequencing Batch Reactor Operations and Troubleshooting Manual.

Figure 3.3 Major phases of SBR operation cycles

Table 3.2 Summary of analytical approaches

PARAMETER	METHOD	EQUIPMENT/MATERIAL	REFERENCE
COD	Closed reflux tritimetric method	HACH COD reactor	APHA 2005
TOC/TN	TOC differential method	ANALYTIK JINA	Multi N/C 3100
NO□$^{-1}$-N, NH_4^{1+}-N , NO_2^{1-} -N, PO□$^{-3}$ -P	N-tube test	Potable data logging spectrophotometer	HACH DR/2010
MLSS/MLVSS	FILTRATION-EVAPORATION	1.2µm GF/C (whatmann®)filter 105^{o}C (MLSS),550^{0}C (MLVSS)	APHA 2005
pH	-	OAKLON water proof	PH/DO/300 series
TDS/TSS	FILTRATION-EVAPORATION	OAKLON water proof	35631-60 cole permer
Turbidity	-	turbiditimeter	HACH 2100N

			turbiditimeter
Color	Calorimetric method	Potable data logging spectrophotometer	HACH DR/2010
Iron , chromium, copper	Calorimetric method	Potable data logging spectrophotometer	HACH DR/2010
Alkalinity	Titration method	Titration assembly	APHA 2005

Chapter 4

Results and discussions

The aims of this study were to make a comparison among hybrid membrane bioreactor (H-MBR), hybrid sequencing batch reactor (H-SBR) and conventional sequencing batch reactor(C-SBR) in terms of their performance efficiency.

4.1 Performance evaluation of H-MBR, H-SBR and C-SBR

Influent wastewater prepared synthetically having COD value of 1000 mg/L and COD: N: P of 100: 20: 6, was treated through H-MBR and H-SBR and C-SBR. Figure 4.1 shows the influent wastewater while effluent quality is clearly shown in Figure 4.2. The effluent quality of H-MBR and H-SBR was visually clear and aesthetically acceptable while effluent from SBR was hazzy and not aesthetically acceptable. Further analyses were performed to check the effluent quality standards. H-MBR, H-SBR and SBR were checked for their performance efficiency and their comparison was evaluated on the basis of parameters like COD, nutrients (TN, TP) and color which will be discussed below.

Figure 4. 1 Influent to H-MBR, H-SBR and C-SBR

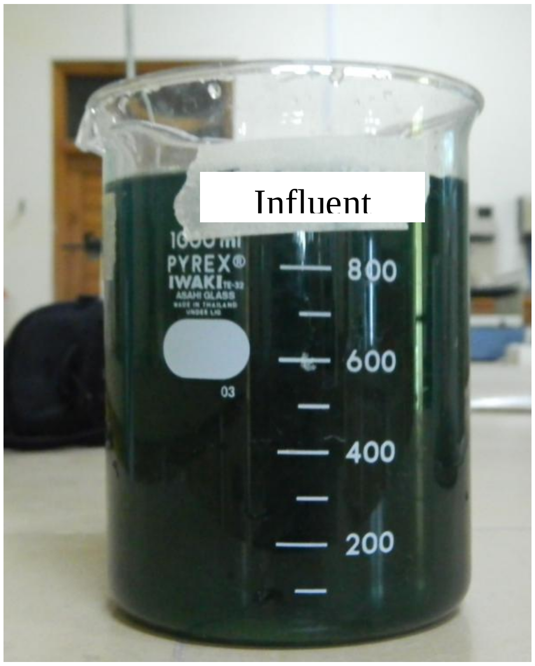
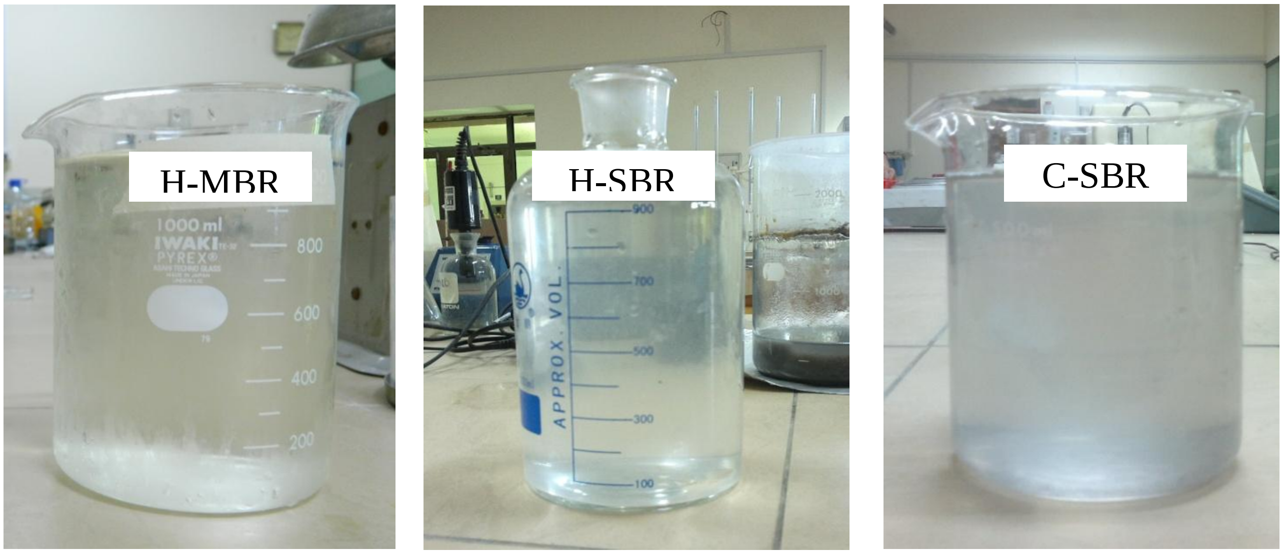


Figure 4. 2 Effluent from H-MBR, H-SBR AND C-SBR



4.2 Chemical Oxygen Demand (COD)

COD analysis over the study period was done and effluent COD was performed and effluent COD was evaluated while influent COD throughout the study was kept constant at 1000 mg/L. The time series analysis of effluent COD is shown in Figure 4.3

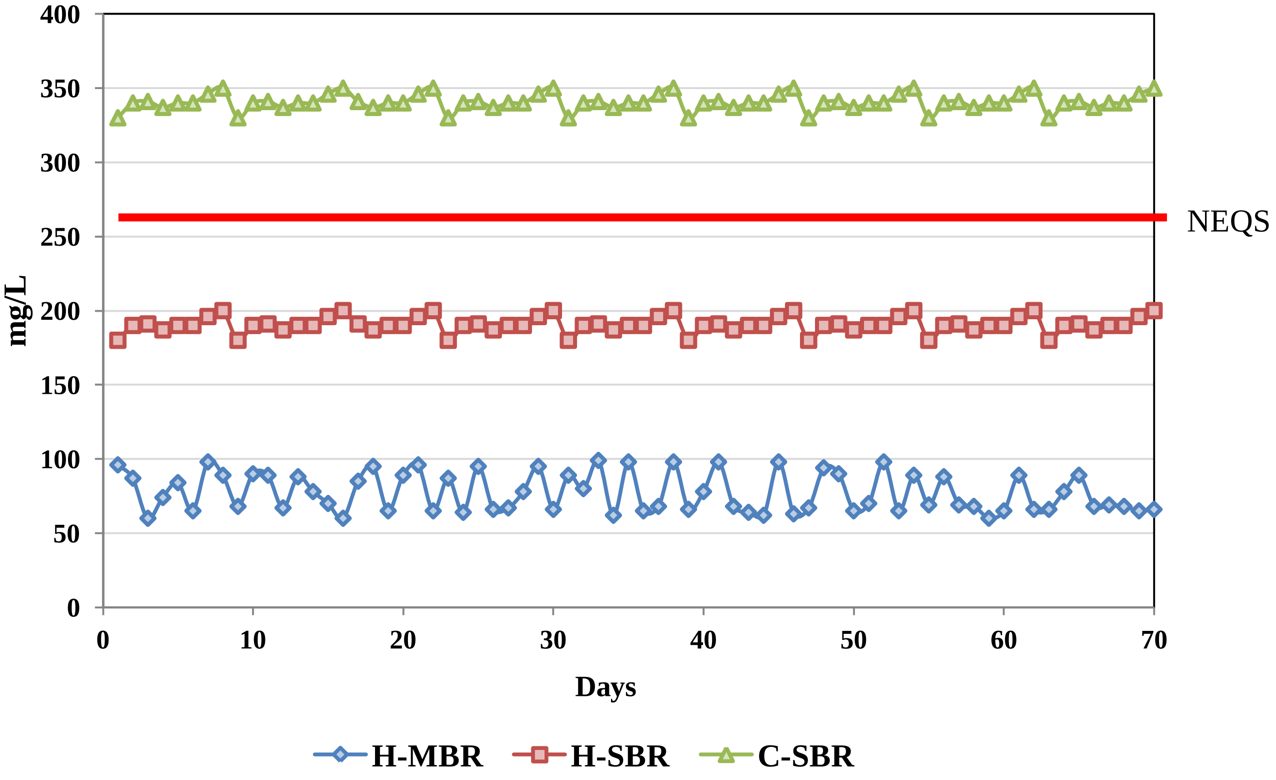


Figure 4.3 Effluent COD in H-MBR, H-SBR and C-SBR

The standard for the effluent treated wastewater COD according to NEQ standards is 150 mg/L. It is shown that C-SBR does not meet the NEQS while H-SBR can meet the discharge requirement. Moreover, the H-MBR not only meets the NEQS requirement but produces high quality effluent for reuse in agriculture and landscaping.

H-MBR gave almost more than 90% COD removal for entire period. H-SBR gave more than 80% COD removal for entire period and C-SBR gave more than 70% COD removal. So, H-MBR was more efficient in removing COD as compared to H-SBR and SBR as presented in Figure 4.4

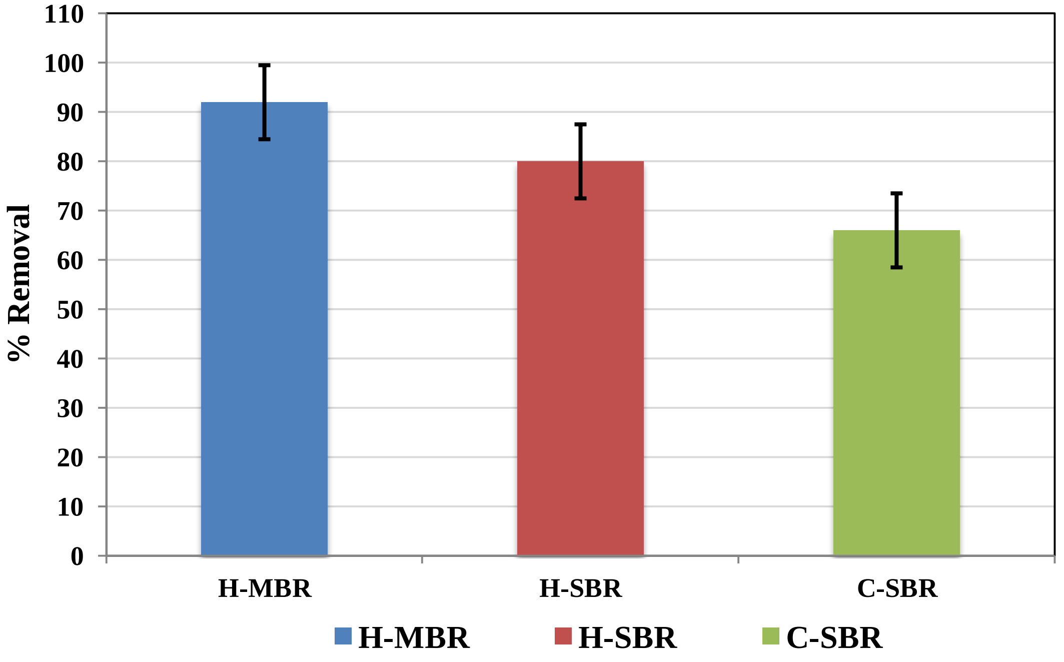


Figure 4.4 Effluent % COD removal of H-MBR, H-SBR and C-SBR

4.3 Color

Color analysis over the study period was performed and effluent color was evaluated while influent color throughout the study was kept at 1540 Pt-Co. The time series analysis of effluent color of H-MBR, H-SBR and C-SBR is shown in Figure 4.5. H-SBR gave almost more than 80% color removal for entire period. H-

MBR gave more than 96% color removal for entire period and SBR gave more than 60 % color removal. So, H-MBR was more efficient in removing color as compared to H-SBR and SBR as presented in Figure 4.6

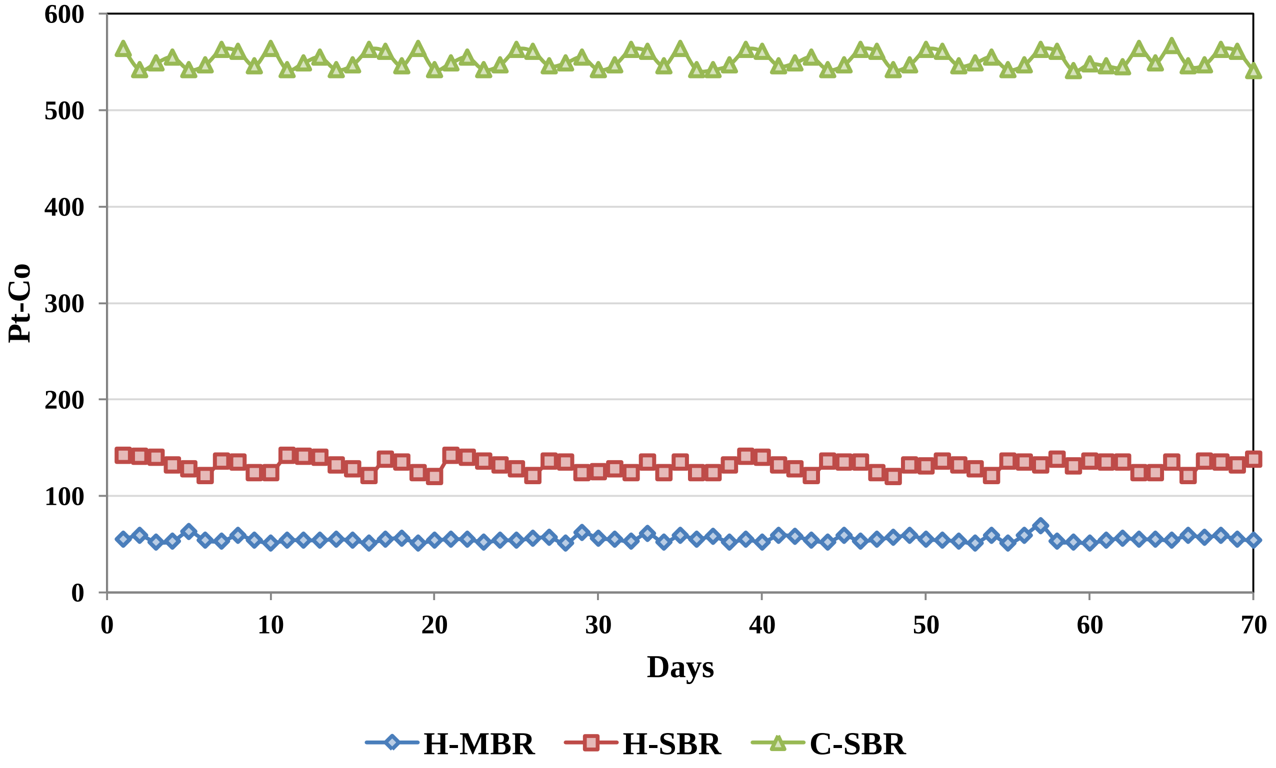


Figure 4.5 Effluent Color in H-MBR, H-SBR and C-SBR

H-MBR was better in removal of color than H-SBR because of PAC as well as membrane while H-SBR contains only the PAC. Moreover, C-SBR was least efficient as it neither contains the PAC nor the membrane. In short, H-MBR and H-

SBR both were efficient in removing color a compared to C-SBR. This indicates that PAC was the major adsorbent for color removal.

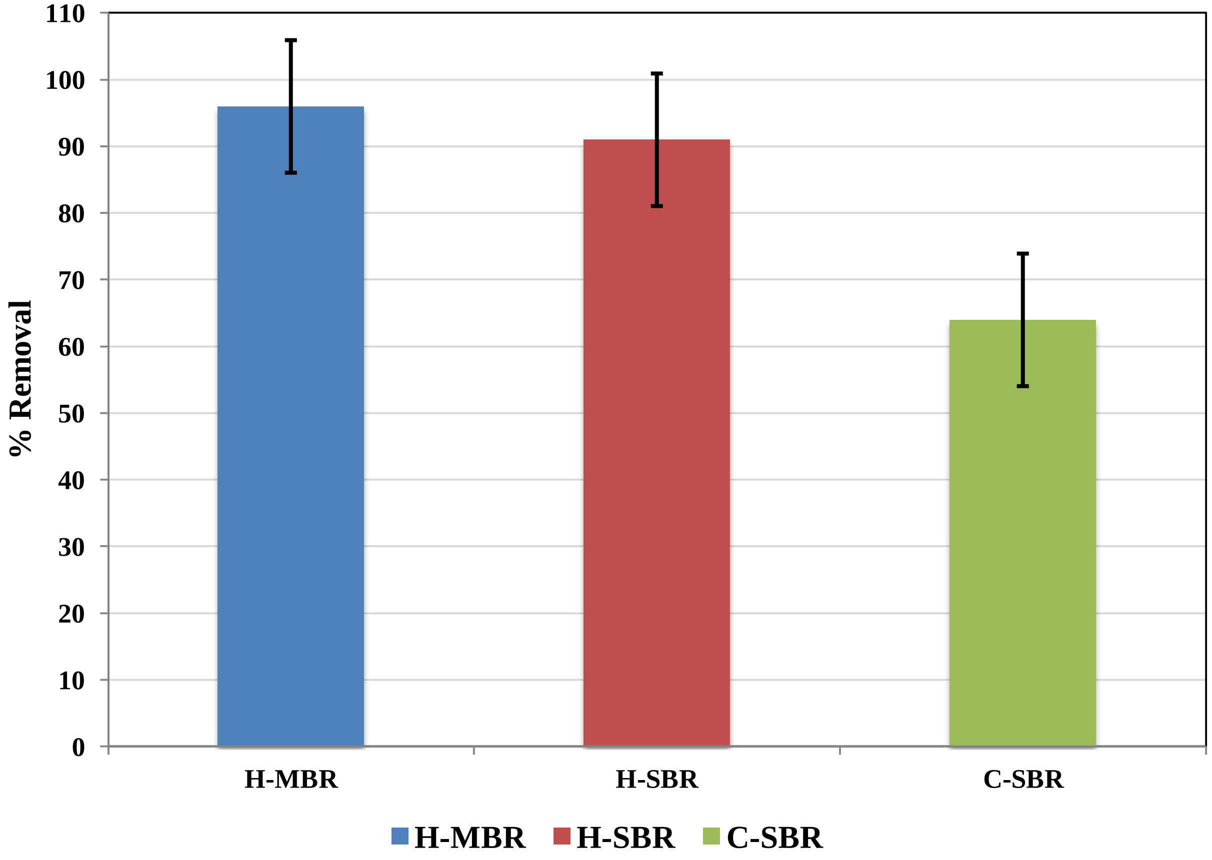


Figure 4.6 Effluent % Color removal from H-MBR, H-SBR and C-SBR

4.4 Total Nitrogen (TN)

Total nitrogen removal is presented in Figure 4.7. As it is clearly visible in the figure that H-MBR was more efficient in removing total nitrogen as compared to H-SBR and SBR. H-MBR gave almost more than 70% TN removal for entire period. H-SBR and C-SBR gave more than 60% TN removal for entire period. It has been previously reported that MBR was the most efficient technology for the TN removal . But the results showed that H-MBR was not efficient in TN removal. The reason can be the presence of amine dyes in the textile waste water, which inhibited the growth of microbes and hence decreased the performance of H-MBR as shown in Figure 4.8.

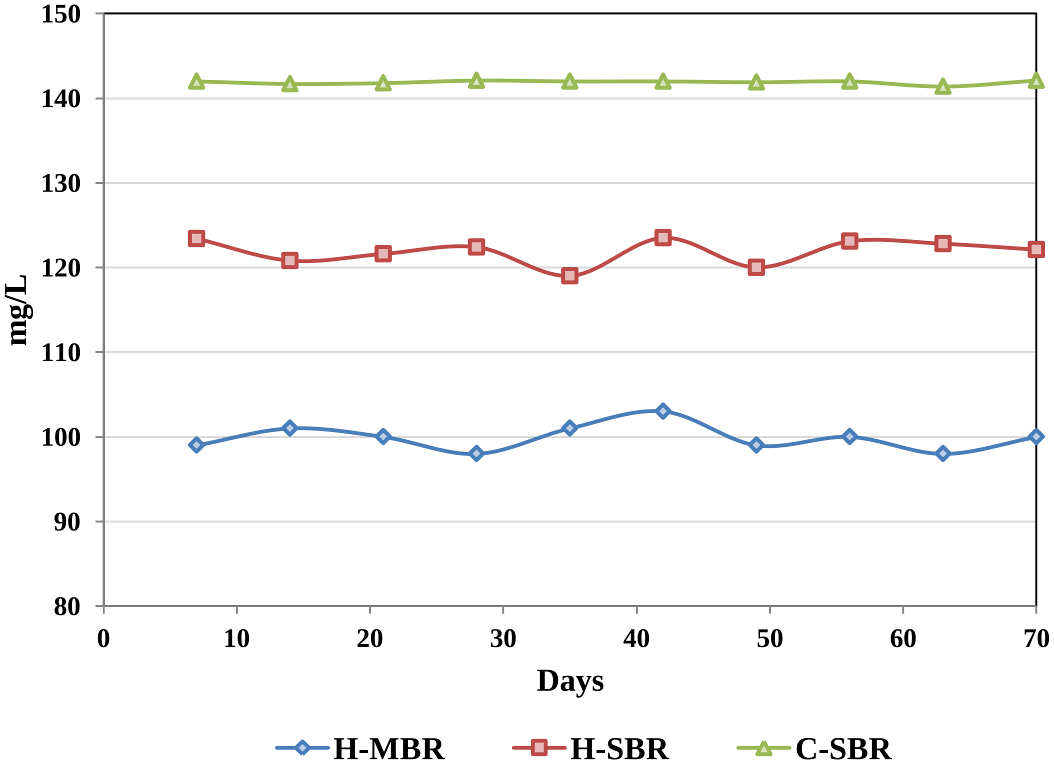


Figure 4.7 Effluent TN in H-MBR, H-SBR AND C-SBR

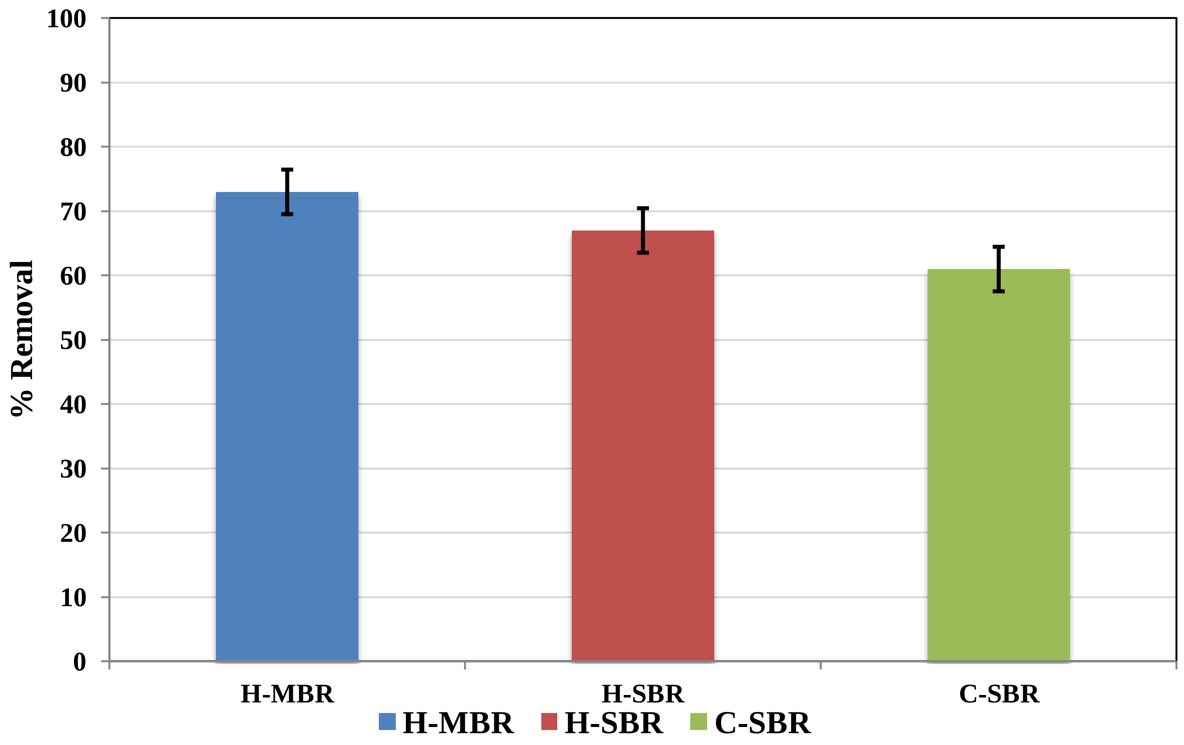


Figure 4.8 Effluent % removal from H-MBR, H-SBR and C-SBR

4.5 Phosphates (PO_4^{-3} – P)

The PO_4^{-3} – P removal is very important parameter in wastewater treatment as it can cause eutrophication. The H-MBR was very efficient in phosphorous removal. H-MBR removed almost 98%phosphorous from influent wastewater. This is shown in the Figure 4.9.

H-MBR gave almost more than 90% Phosphates removal for entire period. H-SBR gave more than 80% phosphates removal for entire period and C-SBR gave almost 70% phosphates removal. This is shown by the Figure 4.10.

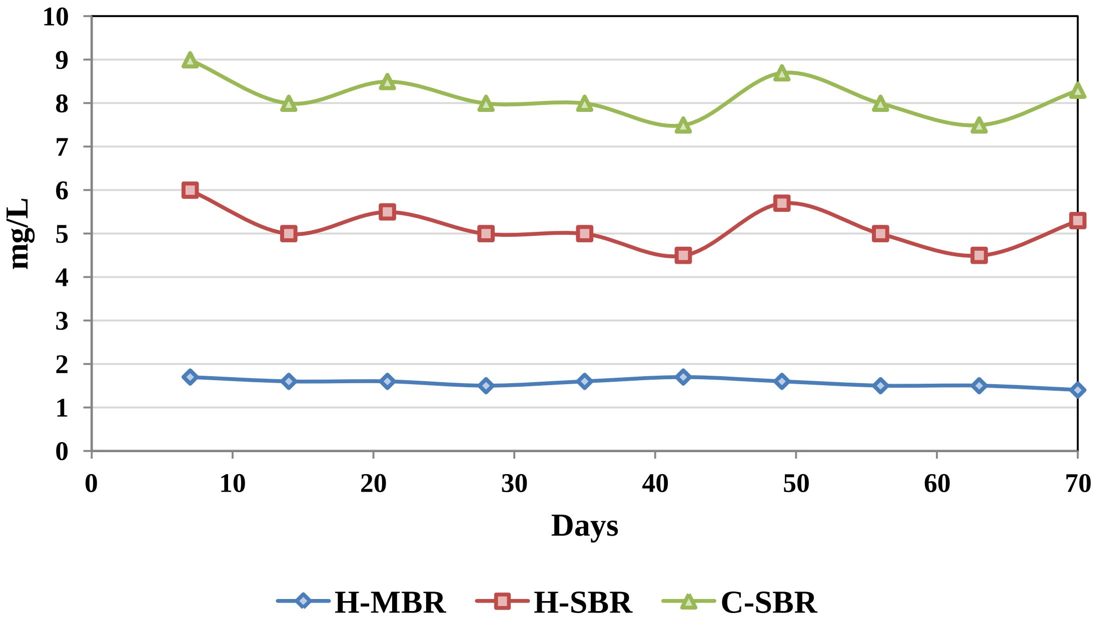


Figure 4.9 Effluent Phosphates in H-MBR, H-SBR and C-SBR

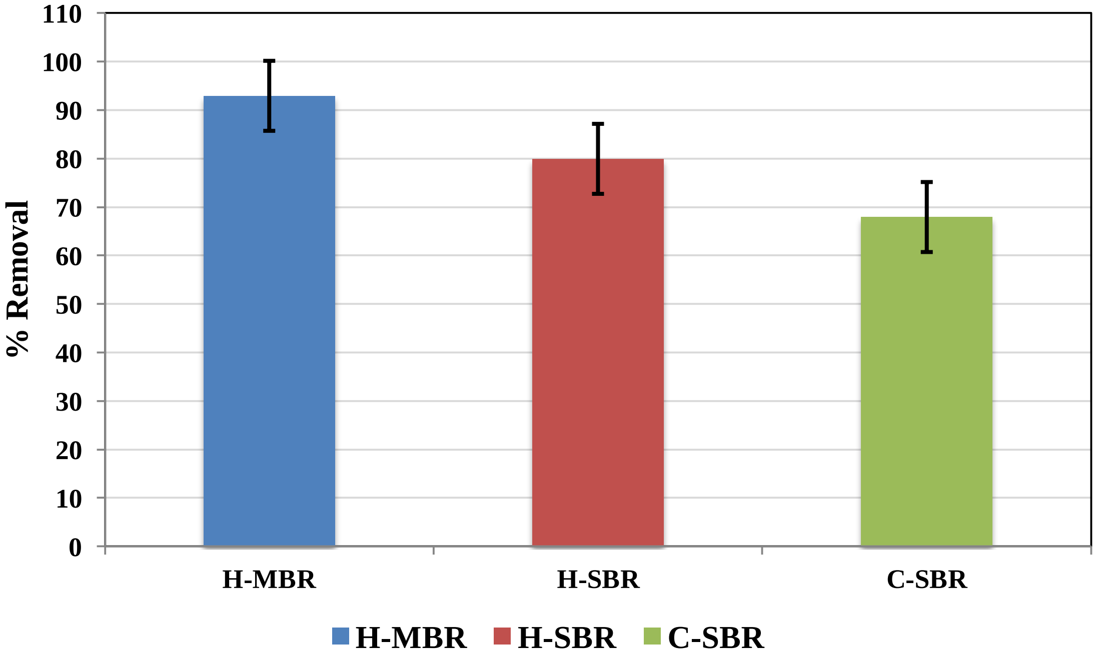


Figure 4.10 Effluent % removal from H-MBR, H-SBR and C-SBR

Discussion

H-MBR is more efficient than H-SBR and C-SBR. MBR technology does not require tertiary filtration, polymer addition, or any further treatment processes to meet standards for suspended solids and turbidity. This reduction in the number of unit processes further improves system reliability and reduces process oversight by the operator. Comparison of H-MBR and H-SBR and C-SBR is given below.

Table 4.1 Comparison of H-MBR, H-SBR and C-SBR

Analysis	**H-MBR (%)**	**H-SBR (%)**	**SBR**
COD	92	80	66
COLOR	96	91	64
TOTAL NITROGEN	73	67	61
PHOSPHATES	93	80	68

Conclusions and recommendations

Treatment of textile waste water can be formed by variety of methods but a Hybrid Membrane Bioreactor (H-MBR), a combination process of biological reactor which includes the microbial activated sludge in addition with powered activated carbon (PAC) coupled with membrane separation device, is commonly regarded as innovation technology for wastewater treatment and reclamation. In this study the compare the efficiency of H-MBR an experimental study with conventional activated sludge process using Hybrid sequential batch reactor (H-SBR) was also performed and there have seen a remarkable difference between these two techniques in term of pollutant and color removal efficiency. The membrane bioreactor process operates in a considerable same range of parameters with the conventional activates sludge process. The following specific concluding remarks can be made from the study;

5.1 Conclusions

1. PAC applied in even small amount (100-200mg/L) can remove color and COD from high strength textile waste water and can biodegrade dyes to a

major extent the amount of PAC applied will decide the total cost of MBR operation and MBRs efficiency can be improved further by using PAC

2. The application of PAC increases the chances of sludge filterability and settleability by making major flocs with the sludge solute particles which results in high flux rate.

5.2 Recommendations

1. The efficiency can be improved for total nitrogen and nutrients removal if DO is controlled in the MBRs. This can be made possible by installing DO controllers in the reactors.
2. The efficiency can be enhanced by applying PAC in a separate compartment (portion) so that PAC can absorb the particles from the waste water and installing membrane in the next one for highly improved quality effluent.
3. The effluent from the SBR can further be polished by passing it through the dead end filtration unit.

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APPENDIX –A

A/O- MBR DESIGN

Design Parameters of A/O-MBR

Hydraulic Retention Time (HRT) Design

Volume of reactor = 16 liters

Flow rate of reactor = 25 ml/min

As reactor was operated under 10 minutes ON and 2 minutes OFF condition for peristaltic pump to suck permeate through membranes. So, actual running time is 50 minutes per hour.

Flow rate = 25 x 50 ml

= 1.25 Liters/hr

HRT = V / Q

= 16 liters / 1.25 liters/hr

= 12 hours

Sludge Retention Time (SRT) Design

Volume of reactor = 16 liters

Sludge wasted per day = 530 ml

= 0.53 Liters

SRT = Volume / Volume wasted per day = 16 liters / 0.53 liters

= 30 days

APPENDIX –B

PROTOCOLS

Mixed Liquor Suspended Solids (MLSS)/Mixed Liquor Volatile Suspended Solids (MLVSS)

Procedure

Preparation of filter paper

- Warm-up muffle furnace and adjust the temperature to 550 ^{o}C.
- Heat GF/C filter paper (Whatman, USA) in a clean evaporating dish in the oven for 15 min at 550^{0} C.
- Place the dish in a desiccator to cool.
- Weigh the dish on balance and note the weight.

Determination of MLSS

- Assemble filtering apparatus
- Wet filter with a small volume of reagent-grade water to seat it
- Pipette a measured volume onto the seated glass-fiber filter.
- Wash filter with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete.
- Carefully remove filter from filtration apparatus and transfer to china dish and put it in an oven and dry for at least 1 h at 103 to 105°C, cool in a desiccator to balance temperature, and weigh.

- Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less.

Calculations

$$MLSS\,\frac{mg}{L} = \frac{(A - B) * 1000}{Sample\ Volume, mL}$$

Where:

A = weight of filter + dried residue, mg, and

B = weight of filter, mg.

Determination of MLVSS

- Place the above GF/C filter paper (Whatman, USA) in a muffle furnace already set at 550°C for 15 min.
- Cool in a desiccator and weigh.

$$MLSS\,\frac{mg}{L} = \frac{(A - B) * 1000}{Sample\ Volume, mL}$$

Where:

A = weight of residue + filter before ignition, mg,

B = weight of residue + filter after ignition, mg

Attached MLSS/MLVSS (Sponge)

- Take out certain volume of sponge (30mL) in a 250mL beaker or 15mL sponge in 100mL beaker (according to reactor sponge fill volume%).
- Stir at 300rpm for 60 minutes.
- Squeeze the sponge and return them back to the reactor.
- Take 50mL of the mixture and perform the MLSS/MLVSS protocol as per standard methods.
- Report results in mg/L.

Chemical Oxygen Demand (COD) Method

Closed Reflux, Titrimetric Method

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence.

Chemicals Required

1) Potassium dichromate ($K2Cr2O_7$) 0.01667*M*
2) Sulphuric acid ($H2SO_4$)
3) Mercuric sulphate (HgSO4) crystals
4) Ferrous ammonium sulphate (FAS) [$Fe(NH4)_2(SO_4)_2$], approximately 0.01N
5) Ferroin indicator (1, 10-phenanthroline and ferrous ammonium sulphate)

Reagents Preparation

Standard potassium dichromate digestion solution, 0.01667M:

- Add to about 500 mL distilled water 4.903 g $K2Cr2O_7$, primary standard grade, previously dried at 150°C for 2 h, 167 mL conc $H2SO_4$, and 33.3 g $HgSO_4$.
- Dissolve, cool to room temperature, and dilute to 1000 mL.

Sulfuric acid reagent:

- Add Ag_2SO_4 , reagent or technical grade, crystals or powder, to concentrated H2SO4 at the rate of 5.5 g Ag_2SO_4/kg H_2SO4.
- Let stand 1 to 2 d to dissolve.

Ferroin indicator solution:

- Dissolve 1.485 g 1,10-phenanthroline monohydrate and 695 mg $FeSO_4.7H_2O$ in distilled water and dilute to 100 mL. This indicator solution may be purchased already prepared.
- Dilute this reagent by a factor of 5 (1+4).

Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10N:

- Dissolve 39.2 g $Fe\ (NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 mL concentrated H_2SO_4, cool, and dilute to 1000 mL.

Standardize solution daily against standard $K_2Cr_2O_7$ digestion solution as follows:

- Pipette 3 mL digestion solution into a small beaker.
- Add 5 mL reagent water to substitute for sample and 7mL $H_2\ SO_4$.
- Cool to room temperature.
- Add 1 to 2 drops diluted ferroin indicator and titrate with FAS titrant.

Normality of FAS solution

$$Volume\ 0.01667M\ \ K_2Cr_2O_7 = \frac{soltuion\ titrated,mL}{Volume\ FAS\ used\ in\ titration,mL} * 0.1$$

Procedure

- Wash culture tubes and caps with 20% H_2SO_4 before first use to prevent contamination.
- Oven dry the tubes in pre-heated oven at 150^{o} C for 1 hr.
- Take tubes out of oven and let them stay to cool.
- Refer to Table 5220:I from Standard Methods (APHA, 2005) for proper sample and reagent volumes.
- Place sample in culture tube or ampule and add digestion solution.
- Carefully run sulfuric acid reagent down inside of vessel so an acid layer is formed under the sample-digestion solution layer.
- Tightly cap tubes or seal ampules, and invert each several times to mix completely.
- Place tubes or ampules in block digester (or oven) preheated to
- 150°C and reflux for 2 hour behind a protective shield.
- Cool to room temperature and place vessels in test tube rack.
- Remove culture tube caps and transfer contents to a larger container (flask) for titration and add small TFE-covered magnetic stirring bar.
- Add 0.05 to 0.10 mL (1 to 2 drops) ferroin indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.10N FAS.

- The end point is a sharp color change from blue-green to reddish brown, although the blue-green may reappear within minutes.
- In the same manner reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of the sample.

Calculations

$$COD\ as\frac{mg}{L}=\frac{(A-B)*M*8000}{mL\ sample}$$

Where:

A = mL FAS used for blank

B= mL FAS used for sample

M= molarity of FAS

8000= milliequivalent weight of oxygen *1000 mL/L

Ammonium, Nitrite, Nitrate-Nitrogen and Phosphorous Determination

In water and wastewater, the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen. All these forms of nitrogen, as well as nitrogen gas (N), are biochemically inter convertible and are components of the nitrogen cycle. They are of interest for many reasons. Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen.

$NH4^{+1}$-N Determination

Ammonia was determined by Hach method.

- Switch on the Hach Spectrophotometer DR2010. Adjust the wavelength to 655nm by rotating the knob. Touch Hach Program 343. Press Enter.
- Add 0.1 mL sample in TNT vial.
- Add Ammonia Salicylate Reagent and Ammonia Cynurate Reagent in each vial.
- For blank add 0.1 mL distilled water in a vial and then add Ammonia Salicylate Reagent and Ammonia Cynurate Reagent.
- Shake well both blank and sample vial.
- Press Shift, and then press timer. A 20-min reaction period will begin.
- After 20-min wipe the blank vial and place in the holder and press
- Zero. The display willl show: 0.0 mg/L $NH_4{}^{1+}$
- Wipe the prepared sample vial and place it into the cell holder.
- Touch Read. Results will appear in mg/L $NH_4{}^{1+}$

NO_3^{-1}-N Determination

Determination of nitrate (NO_3^{-1}-N) is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges of various techniques. For determination of nitrate Hach method was used.

- Select Program 355 N, Nitarte HR
- Switch on the Hach Spectrophotometer. Touch Hach Program 355 N, Nitrate HR and then Touch Start.
- Fill a round sample cell with 10 mL of sample.
- Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow.
- Cap (this is prepared sample).
- Touch the Timer icon. Touch OK. A one-minute reaction period will begin. Shake the cell vigorously until the timer beeps.
- When the timer beeps, touch the timer icon. Touch OK. Five-minute reaction periods will begin. An amber color will develop if nitrate is present.
- When the timer beeps, fill a second round sample cell with 10 mL of sample (this is the blank).
- Wipe the blank and place it into the cell holder.
- Touch Zero. The display will show: 0.0 mg/L NO_3^{-1}-N.
- Within one minute after the timer beeps, wipe the prepared sample and place it into the cell holder.
- Touch Read. Results will appear in mg/L NO_3^{-1}-N.

NO_2^{-1} -N determination

Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. For determination of nitrite Hach method was used.

- Selected Program 373 N, Nitrite LR
- Switch on the Hach Spectrophotometer. Touch Hach Program 371 N, Nitrite LR and then Touch Start.
- Fill a round sample cell with 10 mL of sample.
- Add the contents of one NitraVer 3 Nitrite Reagent Powder Pillow.
- Cap (this is prepared sample) and shake to dissolve. A pink color will develop if nitrite is present.
- Touch the Timer icon. Touch OK. A twenty-minute reaction period will begin.
- When the timer beeps, fill a second round sample cell with 10 mL of sample (this is the blank). Wipe the blank and place it into the cell holder.
- Touch Zero. The display will show: 0.000 mg/L NO_2^{-1}-N.
- Wipe the prepared sample and place it into the cell holder.
- Touch Read. Results will appear in mg/L NO_2^{-1}-N.

TN Determination

Total nitrogen (TN) in influent contains no other forms of nitrogen (organic-N, NO_2^{-1}-N or NO_3^{-1}-N) but only NH_4^{+1}–N. Effluent TN was not determined separately and was considered as a sum of NH_4^{+1}–N, NO_2^{-1}-N and NO_3^{-1}-N in effluent. Ammonia nitrogen (NH_4^{+1}–N), nitrite nitrogen (NO_2^{-1}-N), nitrate nitrogen (NO_3^{-1}-N) and phosphate phosphorous (PO_4^{-3}--P) were determined by spectrophotometric method with DR 2400 (HACH, USA).

$$TN_{\text{influent}} = NH_4^{+1} - N_{\text{influent}}$$

$$TN_{\text{effluent}} = NH_4^{+1} - N_{\text{effluent}} + NO_2^{-1}\text{-}N + NO_3^{-1}\text{-}N$$

Phosphorus Determination

- Enter the stored program number 480 for reactive phosphorus, molybdo-vanadate method.
- Rotate the wavelength dial until the small display shows: 430 nm.
- When the correct wavelength is dialed in, the display will quickly show: Zero Sample then: mg/L PO_4^{3-} MV.
- Use a 25-mL graduated cylinder to fill a sample cell with 25 mL of deionized water (the blank).
- Use another 25-mL graduated cylinder to fill a second sample cell with 25 mL of sample (the prepared sample).
- Add 1.0 mL of Molybdo-vanadate Reagent to each sample cell.
- Swirl to mix. Note: A yellow color will form if phosphate is present. A light yellow color will appear in the blank, because of the reagent.
- Press: SHIFT TIMER; A three-minute reaction period will begin.

- When the timer beeps, the display will show: mg/L PO_4^{3-}MV.
- Place the blank into the cell holder. Close the light shield.
- Press: ZERO. The display will show: Zeroing. . . then: 0.0 mg/L PO_4^{3-}MV
- Place the prepared sample into the cell holder. Close the light shield.
- Press: READ. The display will show: Reading . . . then the result in mg/L PO_4^{3-} - P will be displayed.

Membrane Cleaning

- The Hollow fiber membrane (Mitsubishi Rayon, 2004) module cleaning process

  termed as =out-of-system immersion cleaning‘ was applied that involved two main stages.
- First, membrane unit was physically cleaned to remove all visible cake layer deposited on the membrane fibers and within adjacent fibers. In the second stage, the membrane was chemically cleaned to decompose organic matter deposited on the membrane surface and inside pores restoring the intrinsic TMP. Detailed procedure is as given:
- Membrane unit was removed from the aeration tank by disconnecting the suction line.
- Biofilm deposited on membrane fibers were washed with tap water for physical cleaning.

- Aqueous solution of 4 % wt/vol. aqueous sodium hydroxide and sodium hypochlorite (effective chlorine concentration= 3,000 mg/L) was prepared and membrane unit was completely immersed in a chemical cleaning tank.
- The membrane was immersed in the solution for about 6–10 hours.
- After immersion, chemical solution was filtered from the membrane for 30 minutes.
- The membrane was rinsed thoroughly with tap water to remove chemicals.
- Distilled water was then filtered through the membrane for next 30 minutes.
- The membrane was returned to aeration tank.
- For first 30 minutes, system was operated at a half flux of standard.
- After that returned to the standard flux and operation was resumed.