FINAL REPORT

Treatment of Wastewater from Biodiesel Plant using MBR Technology

การบำบัดน้ำเสียจากโรงงานไบโอดีเซล

โดยระบบ Aerobic Respiration และเมมเบรนไบโอรีแอคเตอร์ (MBR)

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Overall Budget: 279,400 Baht

Duration of Research: 1 Year
From June, 2012 through May, 2013

Final Research Report
from
June, 2012 through December, 2013

EXECUTIVE SUMMARY

In this research, the membrane bioreactor (MBR) technology was proposed as an alternative technology for wastewater treatment of biodiesel plant. The whole research was divided in two parts: (1) Pretreatment of biodiesel wastewater and (2) MBR treatment. In the pretreatment step, H_2SO_4 with different pH of 2, 2.5 and 3 was used to treat the wastewater of biodiesel plant. Significant reduction in organic pollutants was obtained at pH of 2.5 due to strong protonation effect of H_2SO_4. COD (Chemical Oxygen Demand) and O&G (Oil and Grease) were found to be74-84% and 84-92.6%, respectively. However, a slight increase in % removal of organic pollutants was observed at a lower pH of 2. To improve the treatment efficiency of the process, MBR was incorporated as a secondary treatment procedure. Fouling mechanism in MBR was investigated by varying the HRT (Hydraulic Retention Time) and OLR (Organic Loading Rate). The following conclusions were reported from the results obtained during the experiments.

1) COD and O&G removal efficiency in the bioreactor slightly decreased with decreasing HRT, while the overall efficiency of COD and O&G remained in the range of 92.8-98.6 mg/L and 95.7-98.7 mg/L, respectively because shorter HRT induced more MLSS concentration in the reactor.

2) HRT was correlated with dissolved oxygen (DO), particle size distribution (PDS) and soluble microbial product (SMP) in order to investigate their impact on membrane fouling mechanism. The trans-membrane pressure (TMP) of about 50 kPa was reached within 4 days at HRT of 6 hrs. The TMP represents the maximum allowable pressure for efficient membrane function without causing membrane damage. The effect of low HRT on increase fouling can be explained by the back transport velocity of smaller particles at low DO concentration. Because at lower DO concentration, effluent particles had poor settling properties and higher turbidities than higher DO concentrations leading to faster foulant accumulations.

3) SMP_p (soluble microbial product as protein) and SMP_c (soluble microbial protein as polysaccharide) concentrations increased simultaneously with a decrease in HRT. However, SMP_p was found to be slightly higher than SMP_c in our research. Therefore, it was

concluded that both played active roles in membrane fouling contradictory to previous research, where only SMP_c was the only major fouling indicator.

ABSTRACT

The objective of this research was to introduce the MBR (Membrane Bioreactor) technology to the wastewater treatment of biodiesel plant and find out the key factors which are involved in membrane fouling. The research was carried out in two steps. In first step, H_2SO_4 with different pH of 2, 2.5 and 3 was added to biodiesel wastewater. A significant reduction in organic pollutants was observed at pH of 2.5, including a COD (Chemical Oxygen Demand) and O&G (Oil and Grease) reduction of 74-84% and 84.2-92.6%, respectively. In the second step, the MBR was operated at different hydraulic residence times (HRTs) of 15, 12, 9 and 6 hrs along with an increased in organic loading rates (OLRs) ranging from 1-3 g/L·day at each HRT. However, overall COD and O&G removal efficiency remained in the range of 91.7-97.20% and 95.5-97.9% throughout the experiment, respectively, while severe membrane fouling was observed with decreasing HRT due to a decrease in DO concentration and an increase in mixed-liquid-suspended-solids (MLSS), soluble microbial particles as proteins (SMP_p) and soluble microbial particles as polysaccharides SMP_c) concentrations. At lower HRT of 6 hrs, an increase in particle size was reported from 27.9 to 62.7 μm, while SMP_p and SMP_c were reported to have increased from 20 to 60 mg/L and 19 to 59 mg/L, respectively. The higher SMP level caused an increase in the particle size and irregularity in shapes which led to severe membrane fouling.

ACKNOWLEDGEMENTS

The researcher would like to acknowledge the Prince of Songkla University for funding this research project. Without its generosity, this project would not have been possible. Furthermore, the researcher would like to thank the Department of Chemical Engineering and the Faculty of Engineering for providing the space, supporting materials and equipment necessary for the completion of this project.

First and foremost, I would like to thank my outstanding graduate student and research assistant, Mr. Yasir Ali Khan, for his tireless work in conducting his research topic of the same title. Mr. Yasir showed great enthusiasm and self-motivation is studying this technology, helping to design the experiments, setting up the experiments, and conducting the experiments. Even though this research required long hours of experimentation and analytical analysis, Mr.Yasir was able to complete the experiments in a timely manner.

In addition, special thank goes out to my co-researcher, Dr. Watsa Khongnakorn, for helping to advise and guide Mr.Yasir Ali Khan. Dr. Watsa not only gave insightful comments on research setups and experimental procedures, but she also provided essential encouragements throughout the difficulties that came up during this research work. Moreover, I would like to thank Associate Professor Dr. Pakamas Chetpattananondh for serving as a co-advisor for Mr. Yasir at the Department of Chemical Engineering. Without Dr. Watsa and Dr. Pakamas’s expertise in environmental technology, none of this research would have been possible.

Furthermore, A multitude of appreciations also goes out to Mr. Nuttaporn, Mr. Sohn, and Mr. Somkid, the departmental PhD student and technicians for helping to put together entire unit and making sure that they work properly. If I have left out any names, please accept my apologies and may kindness and generosities be rewarded in your future endeavors.

FOREWORDS

With the increasing investment in biodiesel technology, the treatment of its wastewater has become an important issue. With an eager and capable graduate student arriving from Pakistan interested in this field, the research topic seems like a perfect match. The membrane bioreactor has gained numerous applications in the petroleum industry for its high efficiency and was considered a viable option for the biodiesel wastewater. With PSU having its own biodiesel pilot-plant, this research was able to apply live wastewater directly into the membrane bioreactor that was setup at the Department of Chemical Engineering. Because of the high COD (chemical oxygen demand) and oil and grease (O&G) values, the wastewater had to undergo a pretreatment step. A lab-scale test run was followed by an pilot-scale setup that was able to handle 50 L of pretreated wastewater. The latter setup was used for the main experiments yielding conclusions on the effect of HRT and OLR on MBR efficiencies in reducing COD and O&G.

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CHAPTER I

INTRODUCTION

Background and Rationale

Fossil fuels, such as petroleum, natural gas and coal are limited, non-renewable energy sources, while there is a continuous increase in energy demand today. Consequently, there is an increasing urgency to search for new sustainable and renewable sources that can produce a sufficient quantity of energy with acceptable safety (environmental and human) and reliability. Biodiesel fuel is found to be a great alternative fuel produced from the trans-esterification reaction of triglycerides from vegetable oils or fats with alcohols like methanol and ethanol in the presence of a homogenous base catalyst like NaOH or KOH. Biodiesel is biodegradable, nontoxic, burns with low sulphur, carbon monoxide and aromatic-free emission profile and it is environmentally beneficial in terms of recycling of spent oils and fats (Siles et al., 2011). It was estimated that biodiesel consumption will increase from 1 to 6.6 million gallons a year in the USA from 2006 to 2012, and from 0.36 to 8.5 million liters a day in Thailand. At present, the existing capacity of biodiesel production is approximately 1.5 million litres per day with 43 biodiesel plants registered with the Department of Industrial Work (Department of Alternative Energy Development and Efficiency) (Chavalparit et al., 2009). Currently, greater than 350,000 L/day of biodiesel is produced in Thailand causing the formation of at least 70,000 L/day biodiesel contaminated wastewater (Jaruwat et al., 2010). It is also found that factories discharging wastewater exceeding the BOD limit (500 mg/L) then they have to pay around 128.45-160 USD/m^3 (Ngamlerdpokin et al., 2011).

Several processes have been developed to find out the suitable treatment procedure for managing biodiesel wastewater for both environmental and economic reasons, such as the use of microbiological process (Suehara et al., 2005; Kato et al., 2005), and anaerobic digestion (Nishiro et al., 2007). Although, these processes are the most efficient and economical way of reducing the environmental impacts of biodiesel wastewater, they also generate large amounts of low density sludge with low decomposition efficiency (Suehara et al., 2005). Chemical coagulation and electrocoagulation processes are also proposed for the treatment of wastewater of biodiesel plant (Chavalparit et al., 2009). However, the principle drawbacks of the coagulation process, the requirement of a large treatment area and the contamination of chemical coagulants in the treated wastewater, remained (Ngamlerdpokin et al., 2011; Feng et al., 2004), and electrocoagulation process is possibly suitable for a primary treatment for biodiesel wastewater but it still requires a further biological treatment process (Emamjomeh et al., 2009; Calvo et al., 2003; Bolzonella et al., 2006; Chavalparit et al., 2006).

Therefore, there is a need to develop a more efficient treatment technique for the wastewater treatment of biodiesel plant. MBR has emerged as the water treatment and reclamation technology of choice among both municipal and industrial end users. Membrane bioreactor (MBR) technology, which combines biological-activated sludge process and membrane filtration has become more popular, abundant, and accepted in recent years for the treatment of many types of wastewaters, whereas the conventional activated sludge (CAS) process cannot cope with either composition of wastewater or fluctuations of wastewater flow rate. MBR technology is also used in cases where demand on the quality of effluent exceeds the capability of conventional activated sludge (CAS) and also considering the increasingly stringent wastewater discharge standards for various industrial sectors, MBR wastewater treatment technology is definitely the way forward. Although, MBR capital and operational costs exceed the costs of conventional processes, it seems that the upgrade of conventional process occurs even in cases, when conventional treatment works well. It can be related to an increase in water prices and needs for water reuse as well as with more stringent regulations on the effluent quality. Along with better understanding of emerging contaminants in wastewater, their biodegradability and with their inclusion in new regulations, MBR may become a necessary upgrade of existing technology in order to fulfill the legal requirements in wastewater treatment plants (WWTPs).

MBR process has been proved to have many advantages in comparison with conventional biological processes. The main advantages are high quality of treated water, small size of treatment unit, less sludge production and flexibility of operation (Visvanathan et al., 2000).

1) Treated water quality: In conventional activated sludge process, effluent quality strongly depends on the settling of sludge in sedimentation tank. In MBR process, solid/liquid separation is conducted by membrane filtration. Therefore, the final effluent does not contain suspended matter, this enables the direct discharge of the final effluent into the surface water and the reuse of the effluent for cooling, toilet flushing, lawn watering, or with further polishing, as process water.

2) Flexibility in operation: Solid retention time (SRT) can be controlled completely independent from hydraulic retention time (HRT). Therefore, the system can be run at very long SRT providing favourable conditions for the growth of slow-growing microorganisms which are able to degrade biorefractory compounds.

3) Compact plant size: Because the MBR process is independent upon sludge settling quality, high biomass concentration can be maintained up to 30 g/L in the system. Therefore, the system can stand for high volumetric loading rate resulting in the reduced size of the bioreactor. In addition, secondary settling tank, sludge thickener or post treatment for further BOD and suspended solids (SS) removal are not necessary in MBR process, thus the plant becomes more compact.

4) Low rate sludge production: Studies on MBR show that the sludge production rate is very low. Excess sludge from MBR process is much lower than conventional activated sludge process. Low feed to mass ratio (F/M) ratio and longer sludge age in the reactor may be the reason for this low sludge production rate.

Major factors, driving the growth of MBR market include rapid industrialization, high water stress levels, growing emphasis on reuse and recycling of water and increasing legislations. Other factors fuelling market growth include technological developments, the need to replace traditional equipment and increasing application across various end use markets (Global Industry Analysts Inc. (GIA), 2012). Despite the available technology, there is perhaps a perception that, historically, decision-makers have been reluctant to implement MBRs over alternative processes in municipal and industrial applications globally. Beside the presence of significant demand drivers in this market, there are several associated restraints such as cost of the system, replacement of membranes and operation and maintenance cost are the common restraints (Frost and Sullivan, 2010), which inhibits the application of MBR. These restraints can be overcome by understanding the market drivers such as regulatory norms by pollution control board, demand & awareness and investments & growth in end users segments.

Therefore, it is concluded that given the wide-ranging application potentials and advanced treatment capability of membrane filtration, it has become one of the fastest growing water filtration solutions in Southeast Asia despite the various challenges and concerns. Membrane filtration will continue to play a pivotal role in the provision and supply of clean water across end-user segments, and in wastewater treatment for recycling and reuse for both municipal and industrial functions (Frost and Sullivan, 2012). The small footprint of current technologies makes the technology suitable to renovate old plants. The latest MBRs are also capable of purifying water as per the stringent requirements in terms of water reuse and nutrient removal. Therefore, MBRs are expected to find increasing use in industrial applications over the coming years, especially for water reuse, predicts the study. The revival of economic growth is expected to result in the widespread adoption of the technology, with declining capital costs providing additional impetus. Therefore, in this research, MBR is selected for the treatment of wastewater generated from biodiesel plant. The objectives, scopes and expected benefits of this research are mentioned in next section.

CHAPTER II

LITERATURE REVIEW

2.1 Previous Research

Water, being one of the most valuable natural resources we possess, is becoming increasingly scarce due to the unsustainable anthropogenic use, and exacerbated with the impact of global climatic change. The growing demand for water in agriculture, industrial sectors, and local domestic use, with its associated pollution have led to depletion of freshwater resources and also decline in water quality. Depleting water reserves in the world, calls for effective water regeneration technologies. MBR has emerged as the water treatment and reclamation technology of choice among both municipal and industrial end users.

The main objective of this research is to introduce MBR technology for wastewater treatment of biodiesel plant and addressed the problems, which are associated with MBR technology. In Thailand, the government has promoted the production and the use of biodiesel as a substitute diesel fuel to reduce the importation of oil, enhance the energy security, and promote the use of alternative energy made from domestic crops. In the government projects of Thailand that the quantity of biodiesel sold in the market in 2012 will account for 10% of the total diesel sold (Gonsalves et al., 2006). With the likely expansion of biodiesel production by plants using the conventional method, at least in the short to near future, is the inherent need to treat the wastewater. Under the conventional process for every 100 L biodiesel produced some 20 L of raw biodiesel wastewater is discharged (Suehara et al., 2005).

Biodiesel can be produced from the trans-esterification of triglycerides (from vegetable oils or animal fats) and alcohol, such as methanol or ethanol, in the presence of a basic or acidic catalyst. It is found that the untreated biodiesel contains several impurities, such as free glycerol, soap, metals, methanol, free fatty acids (FFA), catalyst, water and glycerides. Therefore, purification method is employed to reduce the traces of these pollutants. The more traditional purification method is wet washing, which involves using water or a weak acid to remove some of the excess contaminants and leftover production chemicals from the biodiesel production. However, the inclusion of additional water to the process offers many disadvantages, including an increased cost and production time, the generation of a highly polluting effluent (wastewater) that needs to be treated prior to environmental discharge and the significant loss of biodiesel into the wastewater phase (Ngamlerdpokin et al., 2011).

In recent researches, different methodologies are employed for treatment of wastewater derived from biodiesel plant along with the pre-treatment of H_2SO_4, which are summarized below:

1) Electro-chemical treatment with the combination of chemical recovery processes: This method is carried out in two steps. In the first step, biodiesel is chemically recovered from the wastewater using sulphuric acid as a proton donor with subsequent natural phase separation. Biodiesel is recovered from the raw biodiesel wastewater, in this case at 6–7% (w/w). In the second step, the aqueous phase discharged from the first stage is supplemented with sodium chloride to 0.061 M and subject to electro-oxidation using a Ti/RuO_2 electrode. The combined treatment completely removed COD and oil and grease, and reduced BOD levels by more than 95%. In contrast, with respect to BOD removal, the electro-oxidation is not found to be effective (Jaruwat et al., 2010).

2) Comparative study between chemical and electro-coagulation processes: The remediation of biodiesel wastewater by using chemical and electrochemical techniques, are also divided into two steps. In the first step, the fatty acid methyl esters (FAME or biodiesel) and free fatty acids (FFA) are chemically removed from the wastewater, when using H_2SO_4 to set a final pH of 2.5 for 7 min. All pollutant levels are markedly reduced during this step. That is, approximately 38.94%, 76.32% and 99.36% of COD, BOD_5 and oil & grease are , respectively removed. In the second step, the acidic aqueous phase left after the removal of the FAME/FFA phase is treated by chemical- and electro-coagulation processes. The results show that both investigated treatment processes are effective for treating wastewater from a biodiesel production plant. The chemical coagulation provided a lower operating cost (1.11 USD/m^3) compared with the electro-coagulation process (1.78 USD/m^3). However, the principle drawbacks of the coagulation process, the requirement of a large treatment area and the contamination of chemical coagulants in the treated wastewater, remained (Ngamlerdpokin et al., 2011).

3) Anaerobic co-digestion of glycerol & wastewater derived from biodiesel manufacturing: This method is also divided into two steps. In the first step, glycerol is acidified with H_3PO_4 in order to recover the alkaline catalyst employed in the transesterification reaction (KOH) as agricultural fertilizer (potassium phosphates). In the second step, wastewater is subjected to an electrocoagulation process in order to reduce its oil content. After mixing, the anaerobic revalorisation of the wastewater is studied employing inoculum–substrate ratios ranging from 5.02 to 1.48 g VSS/g COD and organic loading rates of 0.27–0.36 g COD/g.VSS.d. Biodegradability is found to be around 100%, while the methane yield coefficient is 310 mL CH_4/g COD removed (1 atm, 25 °C). Although, these processes are the most efficient and economical way for reducing the environmental impacts of biodiesel wastewater, they also generate large amounts of low-density sludge with low decomposition efficiency (Siles et al., 2010).

4) A physical–chemical & biomethanization treatments of wastewater from biodiesel manufacturing: This method is also carried out into two steps. Firstly, wastewater is acidified to recover its free fatty acid content. The resulting aqueous phase is then neutralized and subjected to coagulation–flocculation and electrocoagulation to demulsify the remnant organic matter. A 45% and 63% reduction in overall COD total is observed with the acidification–electrocoagulation and acidification–coagulation–flocculation pre-treatments, respectively. In the second step, anaerobic digestion is carried out with acidification–electrocoagulation and acidification–coagulation–flocculation wastewaters. The biodegradability of electrocoagulation and coagulation- flocculation wastewaters is found to be 98% and 84%, respectively, in terms of COD removal (Siles et al., 2011).

5) Biological treatment of wastewater discharged from biodiesel fuel production plant: Biological treatment of wastewater discharged from biodiesel fuel production plant with alkali-catalyzed transesterification is found to be significant with some limitations. Biodiesel fuel (BDF) wastewater has a high pH and high hexane-extracted oil and low nitrogen concentrations, which inhibits the growth of micro-organisms. To apply the micro-biological treatment of biodiesel fuel (BDF) wastewater using an oil degradable yeast, *Rhodotorula mucilaginosa*, the pH is adjusted to 6.8 and several nutrients such as a nitrogen source (ammonium sulfate, ammonium chloride or urea), yeast extract, KH_2PO_4 and $MgSO_4.7H_2O$ are added to the wastewater. The optimal carbon to nitrogen (C/N) ratio is between 17 and 68, when using urea as a nitrogen source. These results suggest that the biological treatment system developed for biodiesel fuel (BDF) wastewater is useful for small-scale biodiesel fuel (BDF) production plants (Suehara et al., 2005).

6) Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology: In this method, electrocoagulation (EC) is adopted to treat the biodiesel wastewater. The effects of initial pH, applied voltage, and reaction time on the EC process for the removal of COD, O&G, and suspended solids (SS) are investigated using one factor at a time experiment. Furthermore, the Box-Behnken design, an experimental design for response surface methodology (RSM), is used to create a set of 15 experimental runs needed for optimizing of the operating conditions. Quadratic regression models with estimated coefficients are developed to describe the pollutant removals. The experimental results show that EC could effectively reduce COD, O&G, and SS by 55.43%, 98.42%, and 96.59%, respectively, at the optimum conditions of pH 6.06, applied voltage 18.2 V, and reaction time 23.5 min. In contrast, biological treatment is recommended after electro-coagulation process (Chavalparit et al., 2009).

In order to meet the stringent conditions of EPA, and improve the traditional wastewater treatment of biodiesel plant, one of the vital solution is available i.e. MBR. Membrane treatment is an advanced process that has become increasing popular over the past ten years. Membrane processes have been understood but unutilized since the 1960’s due to high capital costs. Combined with increasing conventional water treatment costs, membrane treatment is now considered economically viable for municipal and industrial treatment. Portions of Africa, Asia, India, China, Australia, Europe, Mexico, the Middle East, and southwest United States are identified as having a water scarcity. In areas with greater water scarcity, such as Singapore, the acceptance of recycled water is much greater. The additional treatment required for reuse comes at an increased cost, which may not be justified in areas with sufficient water supplies. Although once considered uneconomical, membrane technology costs have decreased by 80% over the past 15 years, making the use of membranes and MBR a viable option for the first time (Scott et al., 2007).

The membrane bioreactor (MBR) is based on the combination of a suspended biomass reactor and a separation step on porous membrane filtration. It presents several advantages in terms of water resource protection because of the great quality of the treated water that can be reused as well for irrigation, cleaning or cooling water on industrial site, domestic purposes (e.g. toilet flushing). The quality of the water, notably the absence of solids in suspension and turbidity, allows considering the MBR as a perfect tool for pre-treatment before desalination or preparation of water of very high quality. Moreover, because of its modular property, the MBR may also be favourable for developing a new wastewater network configuration in an urban area (Scott et al., 2007). Following are the other advantages of MBR, which intends to use it for wide applications of wastewater treatment areas. MBR has a high solid retention time (SRT) in comparison with old activated sludge process. This will create favorable conditions for the growth of slow growing microorganisms, which can degrade recalcitrant and toxic compounds such as petroleum hydrocarbons. Other advantages include stability against shock loading, low rate sludge production, compact size and high effluent quality which are attractive for water reuse (Tri et al., 2002).

However, there are some drawbacks of MBR which inhibits the wide applications of MBR for wastewater treatment areas. At present, different researchers are working on them to get ride from these problems. The main drawback of the membrane bioreactor technology still remains the capital and operation costs due to use of the membrane filtration aggregates. Quick membrane fouling and inefficient membrane cleaning after fouling impact also significantly operation and membrane replacement costs through reduced life span of membrane modules, and loss of permeate during filtration breaks and back flush. Continuous endeavour of suppliers to reduce the operation costs, minimize energy, labour and chemical requirements (Wang et al., 2008). The limiting factor remains the membrane fouling that reduces the membrane permeability during the MBR operation. This membrane fouling is dependent on various parameters concerning the suspension characteristics, the membrane characteristics and the operating conditions. Three families of compounds (particular compounds, colloidal and soluble compounds) take part in membrane fouling that can be considered to be either reversible or irreversible (Wisniewski et al., 2007). Membrane fouling is the largest concern in the design of membrane and MBR systems. As the layer builds up the membrane pores can be blocked reducing the flux through the membrane and increasing the TMP. Particulate matter can foul membranes by either plugging or narrowing the pores or through the formation of a cake layer on the surface. Membrane fouling can be controlled through the use of periodic maintenance back-flushing and chemical cleans in place (CIP). Back-flushing is completed by reversing the flow of air or water through the membrane to unclog the pores (Scott et al., 2007).

7) Membrane fouling reduction: To enhance the filterability of mixed liquors: Powdered and porous materials such as powdered activated carbon (PAC) and zeolite were added into MBRs to modify the filterability of mixed liquors. It was found that membrane fouling was reduced after PAC addition among many studies (Kim et al., 1998; Pirbazari, et al., 1996; Zhao, 2006; Zhang et al., 2005; Li et al., 2005; Liu et al., 2005), mainly due to the decrease the content of EPS in microbial cells, the reduction of cake resistance, the increase of floc size distribution and the mitigation of apparent viscosity of mixed liquors. Similar effects are achieved with zeolite addition in MBRs by other researchers (He and Xue, 2006; Jin and Wu, 2005). Some kinds of coagulants including $Al_2(SO_4)_3$, $FeCl_3$, polymeric aluminum chloride and polymeric ferric sulfate (PFS) can also be used in MBRs for membrane fouling control (Wu et al. 2006; Wang et al., 2006).

Back-flushing is an effective way for high-pressure-resistance membranes (Yang, 2005), such as hollow fiber and ceramic membranes, to remove the particles and biofouling substances clogged in membrane pores and/or adhered onto membrane surfaces. In general, back-flushing consists of reversing the filtration direction for 5–30 s every 30–60 min. It is summarized that in order to control the fouling in MBR, operational parameters including DO concentration in MBR, aeration intensity, the ratio of suction and non-suction time (intermittent filtration), sludge retention time (SRT) and hydraulic retention time (HRT) and filtration modes, sludge concentration and temperature, etc. were investigated in order to reach better understanding of the operational characteristics and to optimize these factors for reducing membrane fouling (Wang et al., 2008).

However, popularity of MBR is increasing day by day, it is observed that total of 722 scientific papers published in peer-reviewed journals (600 Chinese papers and 122 English papers) written by Chinese authors from 1991 to 2006 and 254 full-scale MBR plants constructed in China were used as the analysis database. For commercial applications in China, a total of 254 MBR plants for municipal and industrial wastewater treatment were constructed. Eight online databases including Web of Science, Elsevier, Kluwer Online, Taylor & Francis, Proquest, American Chemical Society (ACS) and John Wiley were searched for English papers written by Chinese researchers and two Chinese online databases. In China, 1991 to 1995, it is an entry-level stage during which few papers, mostly review papers, were published to introduce the MBR concept. The intermediate level stage, from 1996 to 2000, was featured by an increase in the paper outputs and by the emergence of original research papers probably attributed to Research and Development Project on MBR initiated by China MOST under the national 9th "5-year-plan". In the year of 2005, the number of Chinese articles surprisingly reached 141, as shown in including 111 research papers and 30 review papers. In China, water resources are rich in the south and east and poor in the north and west, and 400 cities out of 669 are suffering the shortage of water due to the extremely uneven regional distribution. 1999 a number of companies and institutes, such as Tianjin Motimo Membrane Technology Co., Ltd., Tianjin Tsinghua Daring Co., Ltd., Beijing Origin Water Technology Co., Ltd., Chinese Academy of Sciences and Hangzhou Development Center of Water Treatment Technology, etc. joined in the research and dedicated their efforts to the development of MBR technology. China's research on MBR technology started in 1991. Chen published the first paper on MBR technology in Chinese journals and introduced the application of MBR for the treatment of wastewater in other countries. They include the Research and Development Project on MBR from 1996 under the national 9th "5-year-plan" and from 2002 under the national high-tech development plan ("863" project) (Wang et al., 2008).

To date, England, Germany, France, Belgium and the Netherlands are the European countries with the highest numbers of full-scale plants for municipal or industrial wastewater treatment. In France, over 22 MBR plants designed and built by the group Veolia Water, 19 of them are implemented for industries. Industrial effluents are characterised by relatively low daily volumes and high pollutants loads in comparison with municipal wastewater. In 1989, the Japanese Government launched a 6-year R&D project with many large Japanese companies, in order to develop low cost treatment processes utilising MBR to produce reusable water from industrial, municipal and domestic wastewater (Lesjeanet al., 2002).

Globally, membrane bioreactor (MBR) market is persistently increasing. According to US based Global Industry Analysts Inc (GIA) recently announced the release of a report on the membrane bioreactor (MBR) market worldwide. The global market for this technology is forecast to reach $ 888 million by the year 2017. Asia Pacific also represents the fastest growing regional MBR market, displaying a compound annual growth rate (CAGR) of about 20.2% over the analysis period (Global Industry Analysts Inc. (GIA), 2012). On the other hand, current MBR market in China is $ 228.1 million, which is expected to reach $ 1.35 billion in 2017 at an impressive compound annual growth rate (CAGR) of 28.9 Per cent (Frost and Sullivan, 2011). While the Middle East and North Africa membrane bioreactor market to grow at a compound annual growth rate (CAGR) of 17.77 per cent by 2015 (Frost and Sullivan, 2012).

Southeast Asia is predominantly a net importer of water filtration equipment. Thailand for instance remains a net exporter with a trade value of $ 367.3 million in 2011 due to its manufacturing activities of such equipment for export purposes. In the same year, the largest trading nation is Singapore which recorded a trade value of $ 490.6 million. Of the total water filtration equipment revenue in Southeast Asia, membrane filtration equipment for water and wastewater treatment accounted $ 249.0 million in 2011 and is expected to reach $ 398.0 million by 2017 with a compound annual growth rate (CAGR) of 7.0% from 2012 to 2017. Out of the four major membrane types commercially used for both water and wastewater treatment, Microfiltration (MF) led with 35% of the total membrane market size, followed by Ultrafiltration (UF) at 25%, Reverse Osmosis (RO) at 22% and lastly Nano-filtration (NF) at 18%. The market size for membrane technologies such as MF and UF are slowly being overtaken by the RO and NF due to its increasing viability (Frost and Sullivan, 2012).

The future for the MBR market is thus generally perceived to be optimistic with, it is argued, substantial potential for growth. This level of optimism is reinforced by an understanding of the key influences driving the MBR market today and those which are expected to exert an even greater influence in the future. These key market drivers include greater legislative requirements regarding water quality, increased funding and incentives allied with decreasing costs and a growing confidence in the performance of the technology.

2.2 Research Objectives

1. To investigate the effects of pre-treatment of wastewater from a biodiesel plant with alkali-catalyzed trans-esterification process using H_2SO_4 at different pH range (2.4-6) on the removal efficiencies of BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand) and Oil & Grease .
2. To investigate the performance of MBR at different HRTs (hydraulic retention times) for the removal efficiencies of COD, BOD and Oil & Grease in wastewater from a biodiesel plant.

2.3 Scopes of Research Work

2.3.1 Original Scope in Proposal

1. To investigate the performance of MBR process when treating biodiesel wastewater at different MLSS concentration (3000 to 9000 mg/L)
2. To measure the performance of MBR in terms of hydraulic retention time (HRT) of 3-15 hours on the basis of COD removal efficiency.
3. To find out the effect of HRT on the performance of MBR in relations to membrane fouling and develop solutions in terms of cleaning mechanism.

2.3.2 Modified Scope for Research Project

1. To study the effects of pre-treatment of wastewater derived from biodiesel plant with H_2SO_4 at different pH range of 2, 2.5 and 3, and find out the removal efficiencies of BOD, COD and Oil & Grease.
2. To study the performance of MBR at different hydraulic retention times (HRTs) such as 15, 12, 9 and 6 hrs by varying the organic loading rates from 1 to 2 and 3 g/L·day on each HRT and find out the removal efficiencies of COD and Oil & Grease.
3. To find out the influence of hydraulic retention time (HRT) on membrane fouling and the relationship between HRT and biomass characteristics, including soluble microbial products (SMP), particle size distribution (PSD), and dissolved oxygen (DO) concentration.

2.4 Expected Benefits

1. Can develop an efficient MBR process for the treatment of biodiesel wastewater, which can meet the stringent environmental standards.
2. To have knowledge on MBR process as a green technology for biodiesel wastewater treatment.

CHAPTER III

MATERIALS AND METHODS

3.1 Research Methodology

A schematic diagram of microbial reactor is shown in Fig. 3.1. The reactor consisted of a cylindrical acrylic tank with the working volume of 50 L. MBR was equipped with submerged hollow fiber membrane, which was made of PVDF (Polyvinylidene fluoride) material and had the nominal pore size of 0.1 μm and effective surface of 0.23 m^2 (Table 3.1).

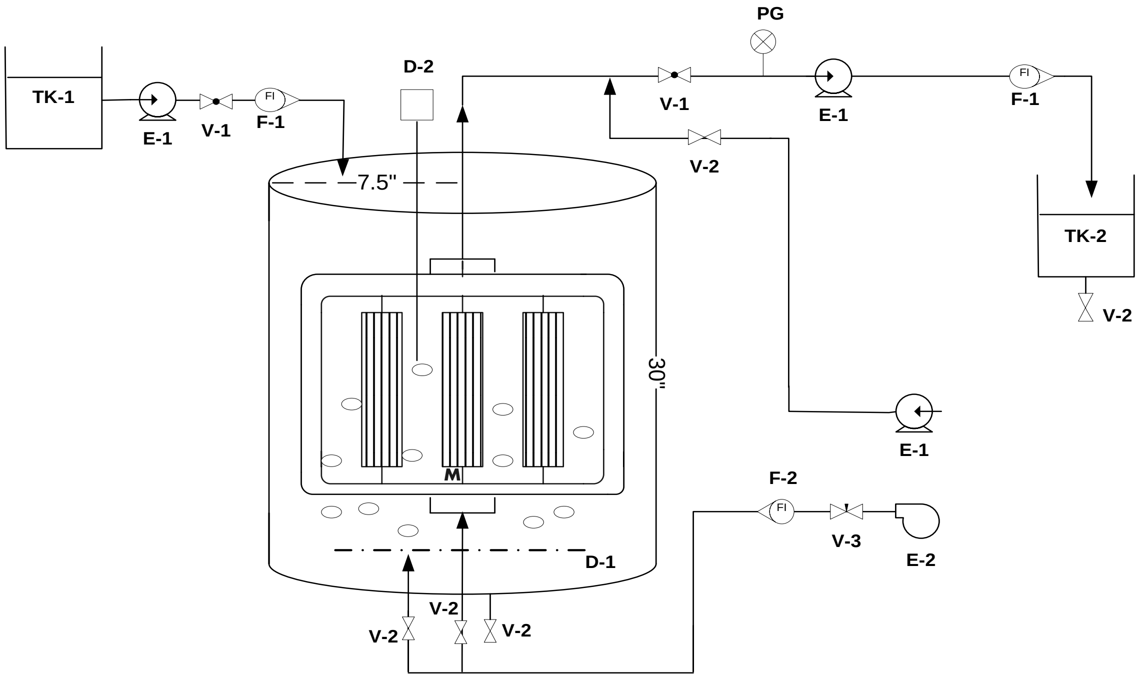

Figure 3.1 Schematic diagram of the MBR: (TK-1) feed tank, (TK-2) effluent tank, (E-1) peristaltic pump, (E-2) blower, (F-1) rotameter for liquid, (F-2) rotameter for air, (V-1) globe valve, (V-2) gate valve, (V-3) needle valve, (M) membrane, (PG) vacuum gauge, (D-1) diffuser) and (D-2) dipstick.

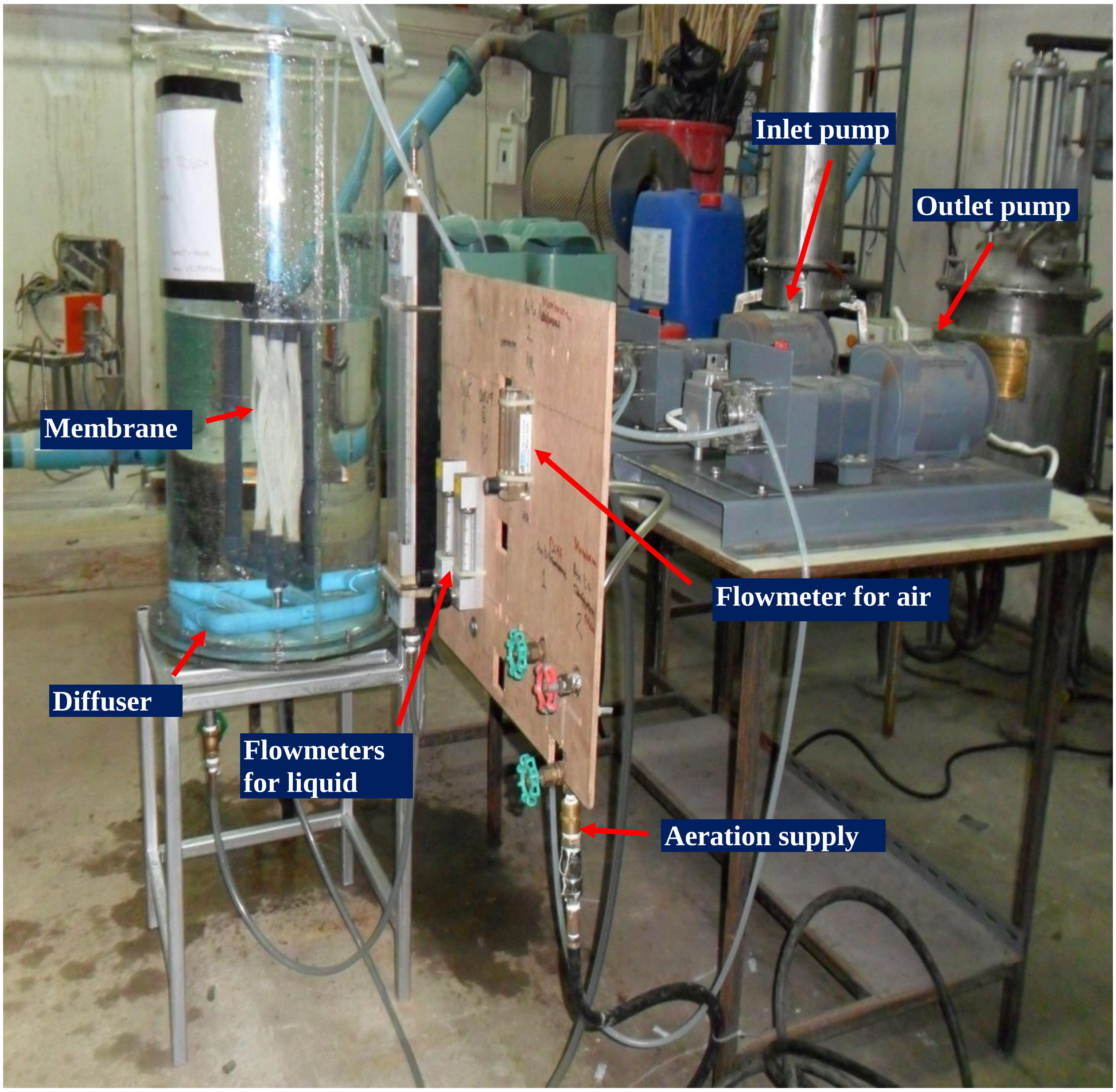

Figure 3.2 Laboratory setup of MBR.

Table 3.1 Characteristic of membrane module.

Membrane Type	Material	Pore size	Cross sectional area	Filtration area
Micro filtration (MF)	PVDF	0.1 µm	0.012 m^2	0.23 m^2

For the start-up of experiment, pretreatment of biodiesel wastewater was carried out. The characteristics of biodiesel wastewater are mentioned in Table 4.1. Raw biodiesel wastewater was acidified by addition of 1 M H_2SO_4 as a proton donor to the indicated final pH (range from 2-3), and mixed by shaking in separatory funnel at different retention times (range from 5 to 15 min).

After pretreatment of biodiesel wastewater with H_2SO_4, MBR operation was initiated by adjusting the OLRs from 1 to 2, 3 g/L·day as shown in Table 3.3. COD input values to MBR was calculated on the basis of OLRs as described in Appendix A. The lab scale set up comprises of the feed tank, submerged MBR and MBR effluent tank as (Fig. 3.2). The experiments were carried out under aerobic condition. Compressed air was supplied through diffuser, aligned at the bottom of membrane at the flow rate of 14.15 L/min providing the O_2 for the biological processes and simultaneously generated a cross flow shearing effect over the membrane surfaces. Dissolved oxygen (DO) was monitored by titration method and changed in the range of (1-4 mg/L). The operation conditions are listed in Table 3.2. Parameters being monitored included removal of COD (%), removal of O&G (%), MLSS (mg/L), MLVSS/MLSS ratio, DO (mg/L), particle size (µm), protein concentration (mg/L), polysaccharide concentration (mg/L), and number of days before membrane clogging (TMP > 290 mmHg). Data were collected at HRT's of 6, 9, 12, and 15 hours. Measurements of each parameter were done in triplicates. Statistical analysis of these results is discussed in Section 3.3 later in this Chapter.

A pH was monitored by pH meter and maintained in the range of 6.00-8.00 by dosing the 1 N H_2SO_4 or 1 N NaOH. During the utilization of membrane, no biomass was wasted with the effluent and solid retention time (SRT) controlled by volume of MLSS (Mixed liquid suspended solids) wasted daily from reactor.

Table 3.2 Operating conditions of MBR.

Parameters	**Value**
Working Volume of reactor (L)	50
HRT (hrs)	15, 12, 9, 6
pH	6-8
OLR (g/L·day)	1, 2, 3
SRT (days)	28
Aeration intensity L/min)	14.15
Working pressure (Kpa)	10-30

Table 3.3 Values of COD input to MBR at different OLRs.

OLR (g/L.day)	**HRT (hrs)**			
	15	12	9	6
1	625	500	375	250
2	1250	1000	750	500
3	1875	1500	1125	750

* COD values = mg/L

Wastewater was fed from the feed tank to the MBR by peristaltic pump, while constant level and hydraulic retention time (HRT) in bioreactor were maintained by discharging the membrane filtered effluent from the reactor. Membrane filtered effluent was intermittently discharged at a constant flux by peristaltic pump (controlled with timer), installed at the outlet of membrane. Each intermittent cycle consisted of 8 min suction followed by 2 min non-suction period. Non-suction periods facilitated back transport of membrane foulants under pressure relaxation. During the filtration, suction pressure of effluent pump was determined by vacuum guage positioned at the outlet of membrane to indicate the pressure difference between outside and inside of membrane. The observed increase or the need for a higher suction pressure to maintain a constant permeating flux gave an indirect indication of fouling. Hence, membrane cleaning was initiated once suction pressure exceeded 50 kPa.

The fouled membrane was withdrawn from the reactor, washed with tap water to remove accumulated biomass and thin layer of cake from the surface of membrane and allowed the operation at the initial trans-membrane pressure (TMP) of 10 kPa. When mechanical cleaning was unable to recover the initial trans-membrane pressure (TMP) of 10 kPa then chemical cleaning was applied with NaOCl (300-500 mg/L) to recover the initial trans-membrane pressure (TMP).

3.2 Analytical Methods

Fouling is usually attributed to organic accumulation on or in the membrane in the form of extracellular polymeric substances (EPS) or soluble microbial products (SMP). The former refers to a complex mixture of polysaccharides, proteins, lipids and nucleic acids, which form a highly hydrated gel matrix. Whereas, soluble microbial products (SMP) are defined as soluble cellular components that are released during cell lysis and then diffuse through the cell membrane, are lost during synthesis or are extracted for some purpose. According to the unified theory for EPS, SMP, and biomass proposed by (Laspidou and Rittman, 2002) that SMP represents the same fraction as soluble EPS. It has been now widely accepted that the concepts of soluble EPS and SMP are identical (Rosenberger and Evenblij, 2005). As with EPS, the SMP solution can be characterized with respect to its relative protein and carbohydrate content (Evenblij and Van, 2004).

To find out the contents of SMP such as protein (SMP_p) and carbohydrate (SMP_c), the sample was withdrawn from the bottom of reactor and pre-filtration was carried out through filter paper (1.2 µm) to separate the water phase from the biomass, so as to isolate the SMP. After pre-filtration, the protein (SMP_p) and polysaccharide (SMP_c) were analyzed by following the methods of Lowery and Anthrone as proposed by (Raunkjaer et al., 1994). In this research, carbohydrate was referred as polysaccharide.

Table 3.4 Standard for wastewater analysis (APHA, 1995).

S No.	Analysis	Standards/Metods
1	COD	SM 5520B
2	BOD	SM 5510B
3	Oil & Grease	SM 5520D
4	MLSS	SM 2540 D
5	MLVSS	SM 2540 E
5	Particle size	Mastersizer 2000 ver.5.1
6	Protein analysis	Lowry method
7	Polysaccharide analysis	Anthrone Method

MLSS, COD, BOD and oil and grease (O&G) were measured according to analytical methods as described in Standard methods (APHA, 1995) and dissolved oxygen (DO) concentration was analyzed by titration method as shown in Table 3.4, while particle size of flocs was analyzed by using the Mastersizer (Malvern ver. 5.1).

3.3 Statistical Analysis

One way ANOVA (analysis of variance) with post-hoc corrected t-test was used for statistical analysis of data to find out the significant difference between the mean values, obtained at different process conditions. Statistical analysis was carried out by considering the two conditions such as if the F-statistics computed in the ANOVA table was less than the F-table statistics or the P-value (α), if greater than the alpha level of significance, then null hypothesis was accepted, which showed that all means were same and there was no significant differences exited between different process conditions, while if the F-statistics computed in the ANOVA table was greater than the F-table statistics or the P-value (α), if less than the alpha level of significance, then null hypothesis was rejected, which showed that all means were significantly different at different process conditions. Therefore, t-test (assuming two equal variances) with Bonferroni correction was used to find out significant difference between each process conditions. Bonferroni correction is defined as:

$$\text{Bonferroni correction} = \frac{\alpha}{n} \tag{3.1}$$

where α represents the probability with the defined value of 0.05, and n represents the number of comparisons between the process conditions. Bonferroni correction was compared with the P (T < = t) two-tail, which was obtained by t-test analysis. If P (T < = t) < $\frac{\alpha}{n}$ then there was significant difference existed between each process conditions and it was defined as true, while if P (T < = t) > $\frac{\alpha}{n}$ then there was no significant difference existed between each process conditions and it was defined as false. Description of ANOVA table is given in Table 3.5.

Table 3.5 Description of ANOVA table.

Source	Sum of Squares (SS)	Degree of Freedom (df)	Mean Square MS=SS/df	F-Statistics	P-value /F-Table
Between Samples	SSB	k-1	MSB=SSB/k-1	F=MSB/MSE	
Within Samples	SSE	n-k	MSE=SSE/n-k		
Total	SSTO	n-1			

*SSB= Sum of squares between, SSE= Sum of squares within, SSTO= Total sum of squares, k= Number of population, n= Number of data values for all samples, MSB= Mean square between, MSE= Mean square within.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Pretreatment of Biodiesel Wastewater with H_2SO_4

When 1 M H_2SO_4 was added directly to the raw biodiesel wastewater then the mixture automatically separated into two phases, the lower phase was the aqueous phase having low turbidity and transparent color, whereas the upper phase was oil rich and yellow in color similar to biodiesel (Fig. 4.1). For the aqueous phase attained after protonation and extraction of raw biodiesel, it was found that BOD, COD and oil and grease (O&G) were significantly reduced to approximately 27-34%, 74-84% and 84-92.6%, respectively as shown in the Table 4.1.

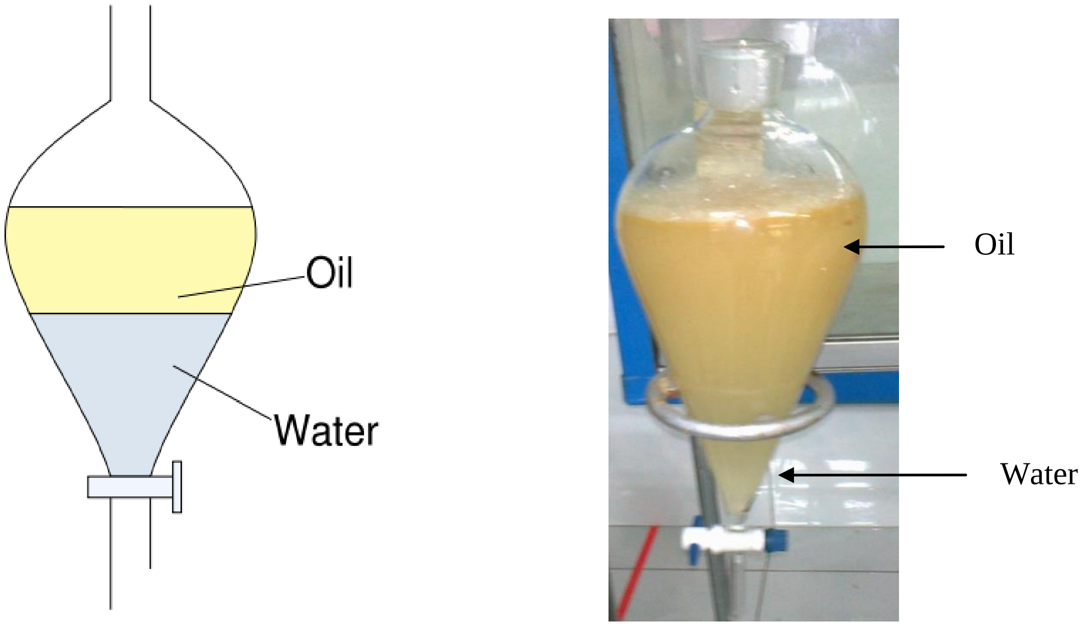

Figure 4.1 Separation of oil phase after acid treatment (H_2SO_4).

Table 4.1 Characteristics of raw biodiesel wastewater.

Parameters	**PCD standards (Thai)**	**EPA standards**	**Avg values of raw biodiesel wastewater**
pH	5.5-9	6-9	10
COD (mg/L)	400	150	64,625
BOD (mg/L)	≤ 60	130	34,000
O&G (mg/L)	≤ 5	10	20,500

*Biodiesel wastewater sample was taken from R&D Center for Alternative Energy, Prince of Songkla University.

Table 4.2 Mean value of organic pollutants after pretreatment with H_2SO_4.

pH	**COD value after treatment (mg/L)**	**Removal (%) of COD**	**O&G value after treatment (mg/L)**	**Removal (%) of O&G**	**BOD value after treatment (mg/L)**	**Removal (%) of BOD**
2	10,273 (±74)	84.1	1,521 (±9)	92.6	22,597 (±62)	33.5
2.5	10,618 (±67)	83.6	2,411 (±11)	88.2	23,605 (±67)	30.6
3	16,742 (±63)	74.1	3,247 (±14)	84.2	24,702 (±63)	27.3

To find out the significant difference for the mean values of COD, BOD and O&G obtained after the pretreatment with H_2SO_4 at different pH of 2, 2.5 and 3, one way Anova with post hoc correct t-test was performed to ensure whether mean values of organic pollutants at different pH were significantly different or not. When one way Anova was performed for pretreatment results, it was found that F-statistics values < F-critical value for the mean value of COD and oil and grease (O&G), which shows that mean value of organic pollutants were significantly at different pH as shown in Appendix B. Therefore, t-test (assuming equal variances) along with Bonferroni correction was used to compare the effect of pH of 2 with pH of 2.5 and 3 for COD and O&G values. When pH of 2 was compared with pH of 2.5 and 3 then it was found that P (T < = t) two-tail < α/n, which shows that mean values of COD and O&G were significantly different at each pH. However, there was large significant difference existed for COD and O&G values at pH of 3. Therefore, it was concluded that pH of 2.5 was optimum, which reduced the organic pollutants from wastewater significantly, while there was small significant difference in organic pollutants was observed at pH of 2 as compared with pH of 2.5 (Table 4.2).

Ngamlerdpokin et al. (2011) observed that removal of raw biodiesel (contained FFA and FAME) in the presence of a strong proton donor may be speculated that H^+ from H_2SO_4 would quickly neutralize any residual alkali catalyst in the biodiesel wastewater and substitute the Na atom in the soap molecule, arising from the reaction between triglyceride and base catalyst (NaOH) in the presence of water in the initial feedstock or by esterification of FFA in the feedstock with alcohol, leading to the formation of uncharged FFA. In addition, it can also substitute the H_2O molecule combining biodiesel leading to the formation of the free FAME (Jaruwat et al., 2010). A significantly higher removal efficiency of all pollutants were observed under strong acidic conditions (pH of 2.5 especially 2). This is attributed to the fact that large amount of raw biodiesel was separated under these acidic conditions leading to lower amount of organic substances particularly oil and grease in the residual wastewater. From the point of view of the efficiency further treatment would be required to deal with the aqueous phase obtained after pre-treatment. Therefore, MBR was incorporated with pre-treatment to reduce the pollutants further as per stringent environmental conditions.

4.2 Effect of HRT on Biomass Concentration and TMP

The reactor was run at HRTs of 15, 12, 9 and 6 hrs and at each HRT, organic loading rate (OLR) was varied from 1 to 2 and 3 g/L·day. When the reactor was operated at HRT of 15 hrs then the mean MLSS concentration was reported as 2550, 4190 and 5812 mg/L at OLRs of 1, 2 and 3 g/L·day, respectively (Table 4.3), increased in MLSS concentration at HRT of 15hrs occurred due to varying the OLR, similar trend was observed for HRT of 12, 9 and 6 hrs (Table 4.3). However, significantly increased in MLSS concentration was observed while decreasing the HRT from 15 to 12, 9 and 6 hrs because shorter HRT provides more nutrients to the biomass, and leads to a greater biological growth and so a higher MLSS (Dufresne et al., 1998). According to Nagaoka et al., 1998, MLSS is also directly influenced by OLR, therefore, when OLR was varied from 1 to 2 and 3 g/L·day on each HRT then increased in MLSS concentration was also reported. Due to increased in MLSS concentration at lower HRT, membrane fouled more quickly as compared to higher HRT because membrane exposed with more concentrated culture and higher non Newtonian viscosity at lower HRT, which caused the membrane fouling more faster. Similar results were derived by Drews and Kraume, (2005) and Drews and Evenblij, (2005) that higher MLSS concentrations give rise to high and non-Newtonian viscosities, which impeded oxygen transfer and require more energy for pumping. Overall mean values of MLSS concentration at HRTs of 15, 12, 9 and 6 hrs are shown in Table 4.5.

Table 4.3 Mean value of MLSS (mg/L) at different OLRs.

HRT (hrs)	MLSS (mg/L)								
	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
	Min. Value	Max. Value	Mean Value	Min. Value	Max. Value	Mean Value	Min. Value	Max. Value	Mean Value
15	2,239	2,862	2,550	3,656	4,725	4,190	5,333	6,290	5,812
12	2,231	3,071	2,651	2,970	5,052	4,011	5,536	7,527	6,532
9	2,041	4,533	3,287	6,005	9,160	7,583	10,236	14,310	12,273
6	3,639	8,697	6,168	10,408	15,114	12,761	15,071	17,413	16,242

Figures 4.2, 4.3 and 4.4 illustrate that at OLR of 1 g/L·day, membrane operation was terminated around 17, 12, 8 and 6 days with the corresponding HRTs of 15, 12, 9 and 6 hrs , respectively, while severe fouling was observed at OLR of 2 and 3 g/L·day as shown in Table 4.4. It was observed that tendency of membrane fouling was more severe at shorter HRT of 6 hrs due to higher interaction of MLSS concentration with membrane. Different authors correlated the MLSS concentration with membrane fouling on the basis of derived results, some authors correlated impact of MLSS concentration on viscosity of sludge, while other authors discussed the positive and negative impact of MLSS concentration on TMP. Tanaka et al., 1994 defined the critical value of MLSS concentration that critical MLSS concentration exists under which the viscosity remains low and rises only slowly with the concentration. Above this critical value, suspension viscosity tends to increase exponentially with the solids concentration. This critical value was observed to change from 10 to 17 g MLSS/L for different operating conditions.

Table 4.4 Membrane clogging with respect to OLRs at different HRTs.

HRT (hrs)	Flux (L/m^2. hr)	TMP (KPa)	Membrane clogging (days)		
			1	2	3
15	12	≤50	17	15	12
12	14	≤50	12	9	6
9	19	≤50	8	7	5
6	29	≤50	6	4	3

* 1, 2 and 3 represents the OLR (g/L·day).

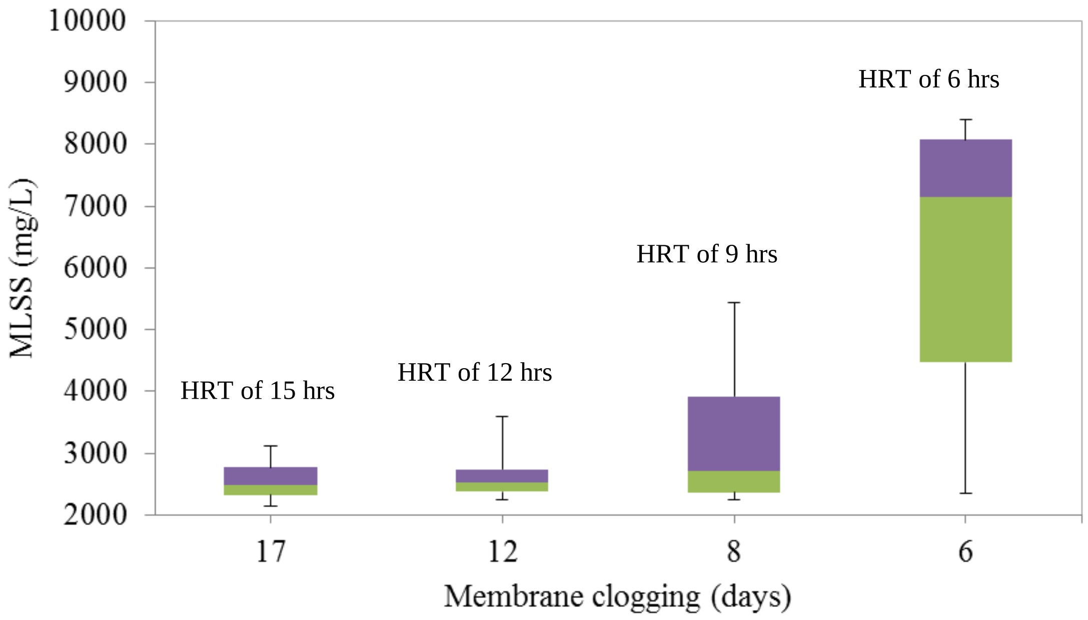

Figure 4.2 Effects of MLSS (mg/L) on TMP at OLR of 1 g/L·day.

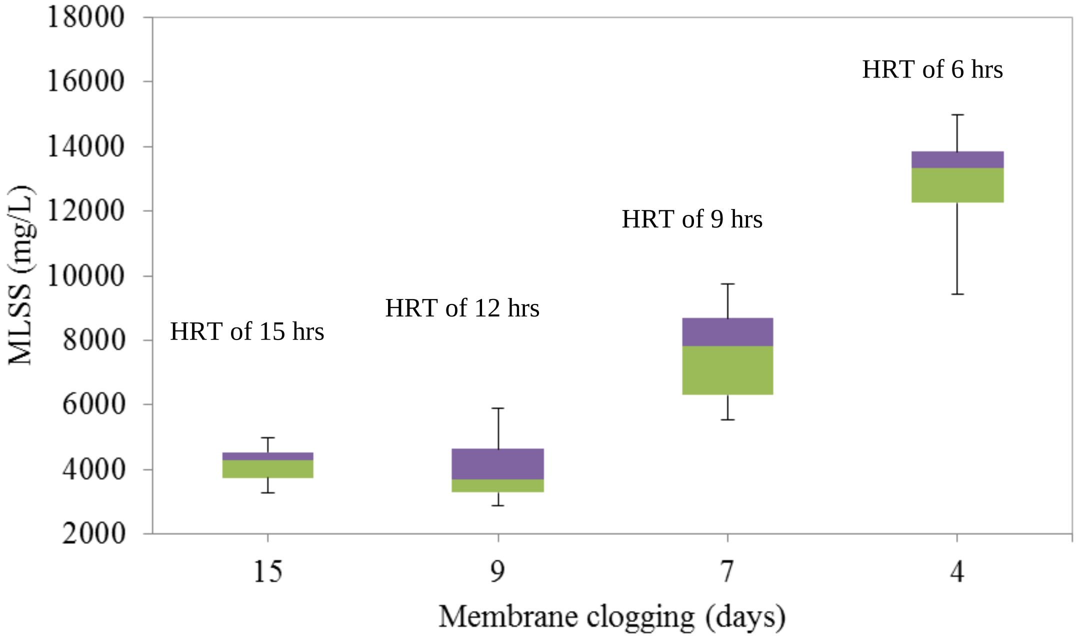

Figure 4.3 Effects of MLSS (mg/L) on TMP at OLR of 2 g/L·day.

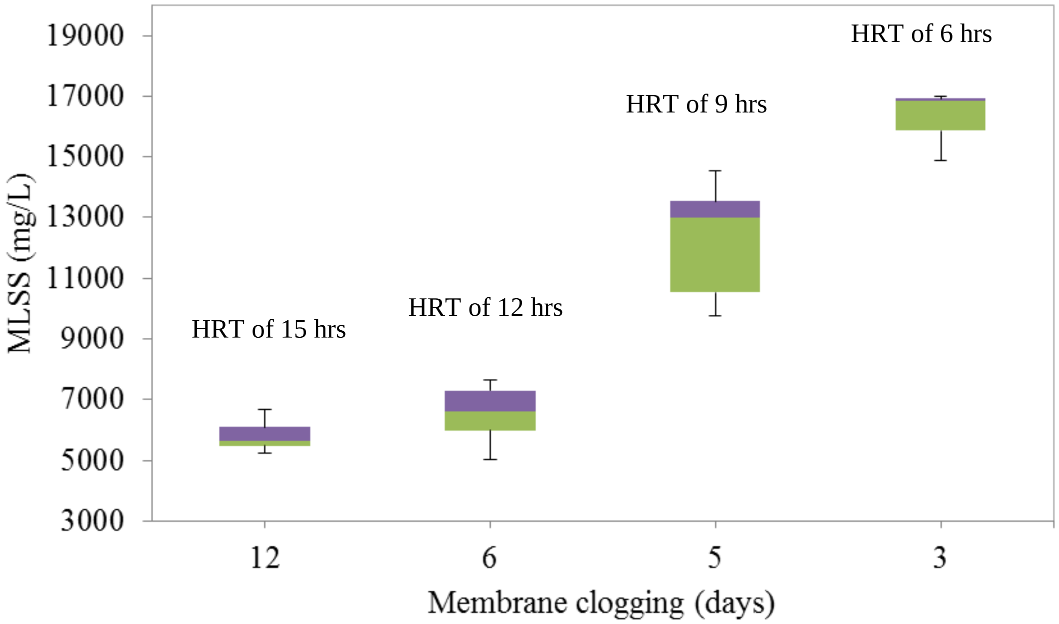

Figure 4.4 Effects of MLSS (mg/L) on TMP at OLR of 3 g/L·day.

Table 4.5 Mean values of monitoring parameters of MBR at different HRTs.

Parameters	HRT (hrs)							
	15		12		9		6	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Removal (%) of COD (after 10 days)	97	97.9	94.7	96.4	92.9	93.3	90.8	91.2
Removal (%) of COD (after 15 days)	97.7	98.6	95.8	97	94	95.2	91.7	92.8
Removal (%) of O&G (after 10 days)	97.5	98.4	97.1	97.4	96.1	96.4	95.2	95.3
Removal (%) of O&G (after 15 days)	97.9	98.7	97.2	97.9	96.6	97	95.5	96
MLSS (g/L)	2.5	5.8	2.6	6.5	3.2	12.2	6.1	16.2
MLVSS/MLSS	0.52	0.61	0.57	0.67	0.57	0.71	0.56	0.82
DO (mg/L)	2.2	3.2	1.9	3.3	1.2	2.5	1.1	2.6
Particle size (µm)	12.5	29.6	15.2	36.2	14.6	49.8	27.9	62.7
Protein (mg/L)	8	26	14	38	21	50	20	60
Polysaccharide(mg/L)	7	25	12	37	20	49	19	59
Membrane clogging (days)	12	17	6	12	5	8	3	6

Chang and Kim, (2005) observed that the increase in MLSS concentration seems to have a mostly negative impact (higher TMP or lower flux) on the MBR hydraulic performances. However, some authors have reported positive impact (Defrance et al., 1999; Brookes and Jefferson, 2006), and some observed insignificant impact (Hong et al., 2002; Lesjean et al., 2005). The existence of a threshold above which the MLSS concentration has a negative influence was also reported at 30 g/L (Lubbecke et al., 1995).

Jefferson and Brookes, (2004) observed that there is a lack of a clear correlation between MLSS concentration and any other foulant characteristics indicates that the MLSS concentration (alone) is a poor indicator of biomass fouling propensity. Therefore, in the present work, the influence of HRT on membrane fouling is analyzed, and the relationship between

HRT and biomass characteristics, including soluble microbial product (SMP), particle size distribution (PSD) and dissolved oxygen (DO) concentration are studied systematically to specify how the HRT affects membrane fouling.

MLVSS/MLSS ratio was also analyzed to find out the effect of organic content on membrane fouling. MLVSS/MLSS was also found in increasing trend, when HRT was decreased due to increase in MLSS concentration Mean value of MLVSS/MLSS ratio at HRT of 15, 12, 9 and 6 hrs are reported in Table 4.6.

Figures 4.5, 4.6 and 4.7 illustrate that at lower HRT, MLVSS/MLSS ratio increased due to an increase in MLSS concentration while increasing the MLVSS/MLSS ratio found have severe impact on membrane operation. It was observed that at the lower HRT of 6 hrs, membrane operation was terminated 3-11 times faster than higher HRTs as described in Table 4.4. Increased in TMP at lower HRT was occurred due to increase in ratio of MLVSS/MLSS. Increased in MLVSS/MLSS ratio were reported as 0.52-0.61, 0.57-0.670, 0.57-0.718 and 0.56-0.829 at HRT of 15, 12, 9 and 6 hrs, respectively as shown in Table 4.5.

Table 4.6 Mean value of MLVSS/MLSS at different OLRs.

HRT (hrs)	MLVSS/MLSS								
	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
	Min. Value	Max. Value	Mean Value	Min. Value	Max. Value	Mean Value	Min. Value	Max. Value	Mean Value
15	0.52	0.54	0.527	0.56	0.57	0.563	0.61	0.62	0.615
12	0.56	0.59	0.573	0.61	0.64	0.624	0.67	0.67	0.670
9	0.56	0.59	0.577	0.64	0.70	0.670	0.71	0.73	0.718
6	0.54	0.59	0.566	0.67	0.78	0.723	0.81	0.84	0.829

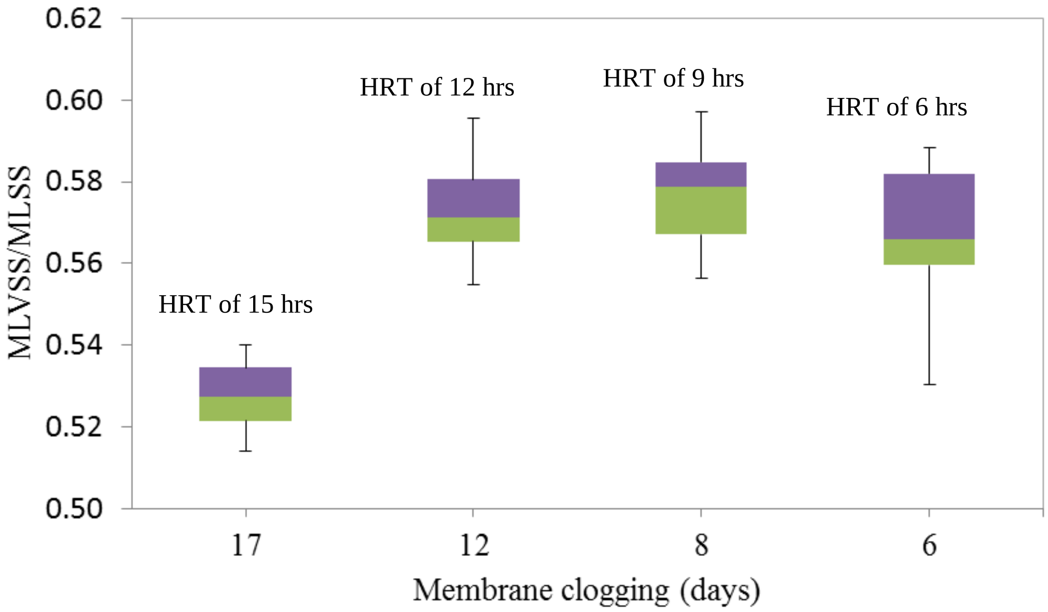

Figure 4.5 Effects of MLVSS/MLSS on TMP at OLR of 1 g/L·day.

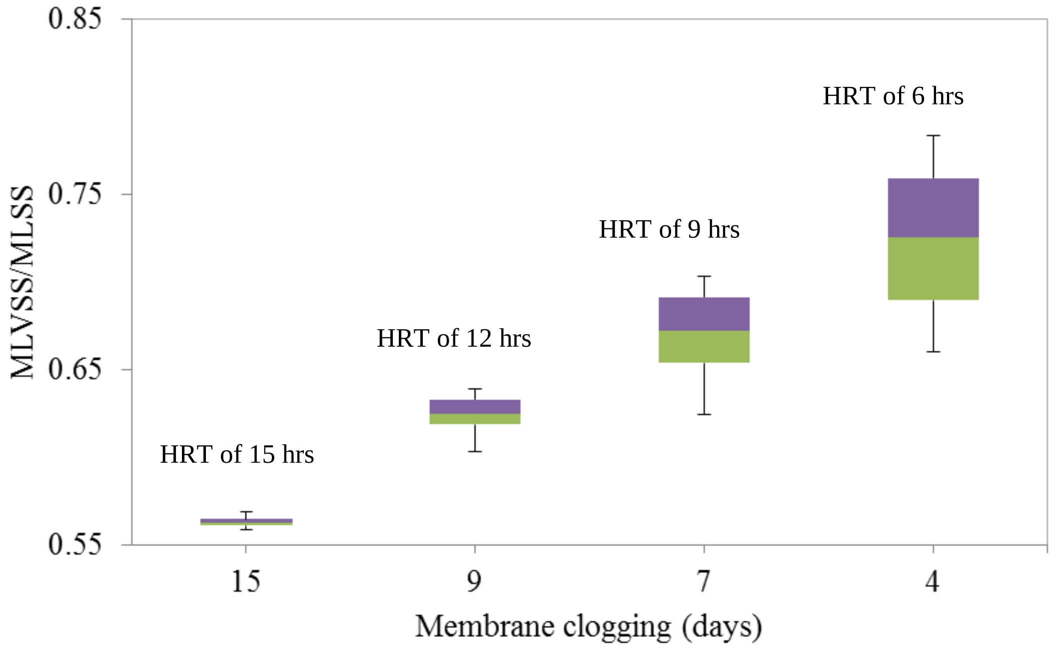

Figure 4.6 Effects of MLVSS/MLSS on TMP at OLR of 2 g/L·day.

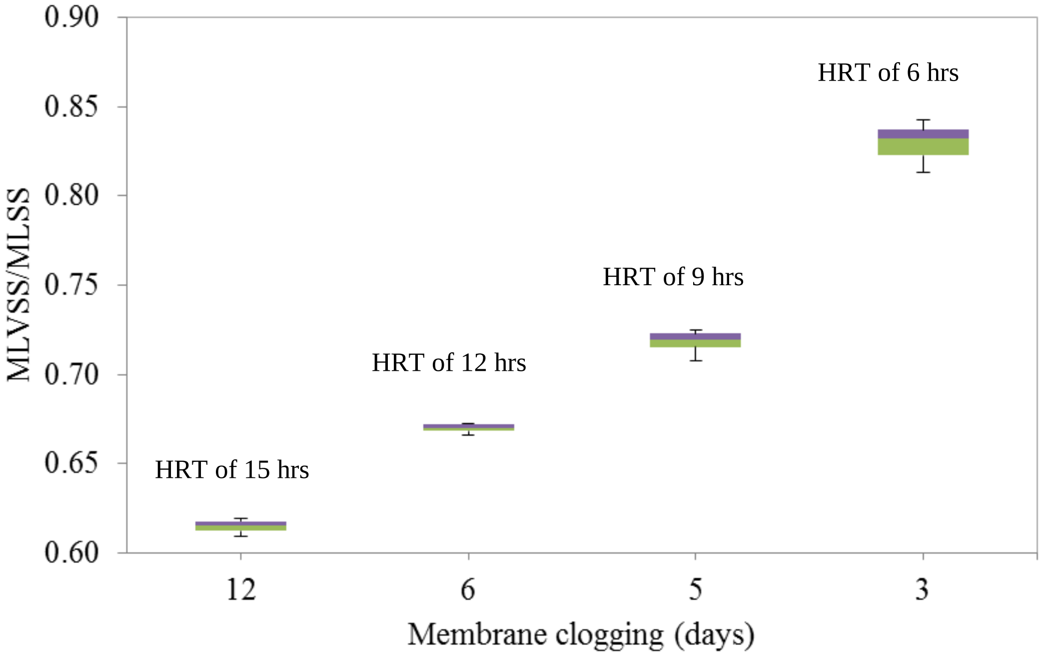

Figure 4.7 Effects of MLVSS/MLSS on TMP at OLR of 3 g/L·day.

4.3 Removal Efficiency of COD and O&G

Removal efficiency of COD and O&G were also examined at different HRTs and increased in COD removal efficiency was observed by varying the operating time for each HRT from 10 to 15 days. At 10 days of operation, COD removal efficiency was reported as 97-97.9%, 94.7-96.4%, 92.9-93.3% and 90.8-91.2% with the corresponding HRT of 15, 12, 9 and 6 hrs, respectively as shown in Table 4.7, while at 15 days of operation, COD removal efficiency was reported as 97.7-98.6%, 95.8-97%, 94-95.2% and 91.7-92.8% at HRT of 15, 12, 9 and 6 hrs, respectively as shown in Table 4.8. When operating time was increased from 10 to 15 days, it increased the efficiency of MBR because at longer operating time, organic pollutants degrade more efficiently as compared to the shorter operating time

Table 4.7 Removal (%) of COD after 10 days operation.

HRT (hrs)	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
	Input COD (mg/L)	Output COD (mg/L)	(%)	Input COD (mg/L)	Output COD (mg/L)	(%)	Input COD (mg/L)	Output COD (mg/L)	(%)
15	625	13 (±0.29)	97.9	1250	26 (±0.16)	97.9	1875	57 (±0.08)	97.0
12	500	18 (±0.08)	96.4	1000	51 (±0.15)	94.9	1500	80 (±0.08)	94.7
9	375	25 (±0.20)	93.3	750	48 (±0.06)	93.6	1125	80 (±0.09)	92.9
6	250	22 (±0.13)	91.2	500	46 (± 0.13)	90.8	750	69 (±0.16)	90.8

Table 4.8 Removal (%) of COD after 15days of operation.

HRT (hrs)	**OLR of 1 g/L·day**			**OLR of 2 g/L.day**			**OLR of 3 g/L.day**		
	Input COD (mg/L)	Output COD (mg/L)	(%)	Input COD (mg/L)	Output COD (mg/L)	(%)	Input COD (mg/L)	Output COD (mg/L)	(%)
15	625	9 (±0.09)	98.6	1250	21 (±0.14)	98.3	1875	43 (±0.10)	97.7
12	500	15 (±0.11)	97.0	1000	41 (±0.13)	95.9	1500	63 (±0.08)	95.8
9	375	18 (±0.41)	95.2	750	38 (±0.10)	94.9	1125	68 (±0.09)	94.0
6	250	18 (±0.11)	92.8	500	38 (±0.04)	92.4	750	62 (±0.07)	91.7

Figures 4.8 and 4.9 illustrate that when reactor was run at HRT of 15 hrs, COD removal efficiency decreased due to an increase in OLR because higher OLR induced more nutrients to biomass, which increased the MLSS concentration in MBR and decreased biomass activity, similar trend was observed by Meng et al., 2007 that increase of MLSS concentration and sludge viscosity would lead to an increase of oxygen and substrate diffusion limitation in the sludge suspension, so the activities of biomass decreased, while Holler et al., 2001 observed that the COD removal efficiency slightly increased as HRT increased due to the lower OLR. It can be seen that the membrane showed a significant contribution (4–10%) to COD removal due to the complete retention of all particulate COD and macromolecular COD components by the membrane. Similar trend for COD removal efficiency was also observed at HRT of 12 , 9 and 6 hrs, it was found that decreased in HRT had a greater influence on COD removal efficiency due to increasing trend in MLSS concentration was observed .

To find out the significant effect of HRT on COD and O&G removal efficiency, when OLRs was changed from 1 to 2, 3 g/L·day, one way Anova with post hoc corrected t-test was used (Appendix C). At OLR of 1 g/L·day, when each HRT was run 10 days, it was found that $P < \alpha/n$, which shows that COD removal efficiency were significantly at different HRT. Similar, significant difference was observed at OLR of 2 and 3 g/L·day but when HRT of 12 hrs compared with HRT of 9 hrs at OLR of 3 g/L·day, it was found that $P > \alpha/n$, which indicates that COD removal efficiency decreased, when OLR was increased with decreasing HRT. However, removal efficiency of COD was found significantly higher at 15 days operation of each HRT as compared with the 10 days operation. At 15 days of operation, when HRT of 9 hrs compared with HRT of 6 hrs at OLR 1 and 2 g/L·day then it was observed that $P > \alpha/n$, which indicates the removal efficiency of COD was not significantly different. Therefore, it was concluded that higher OLR and shorter HRT can reduce the removal efficiency of COD. For O&G, when one way Anova with post hoc corrected t-test was performed then it was found that $P < \alpha/n$ for all OLRs (1, 2 and 3 g/L·day) at each HRT, which indicates that removal efficiency of O&G were significantly different when OLR was decreased while HRT increased.

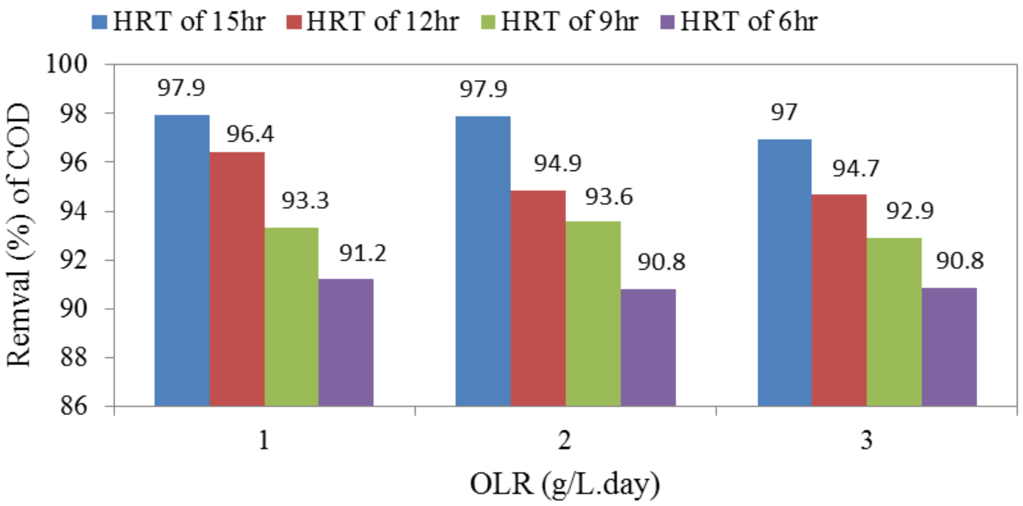

Figure 4.8 Removal (%) of COD after 10 days.

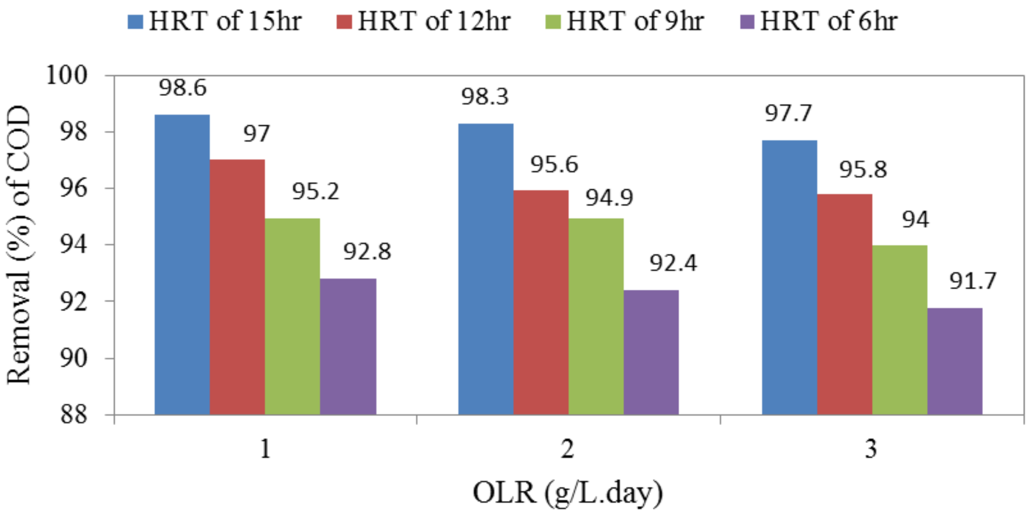

Figure 4.9 Removal (%) of COD after 15 days.

From Figures 4.10 and 4.11 illustrate that O&G removal efficiency followed the same pattern as COD removal efficiency and O&G removal efficiency was reported as 97.5-98.4%, 97.1-97.4%, 96.1-96.4% and 95.2-95.3% at HRT of 15, 12, 9 and 6 hrs, respectively with the corresponding operating time of 10 days as described in Table 4.9, while at operating time of 15days, O&G removal efficiency reported as 97.9-98.7%, 97.2-97.9%, 96.6-97% and 95.5-96% at HRTs of 15, 12, 9 and 6 hrs, respectively as mentioned in Table 4.10.

Table 4.9 Removal (%) of O&G after 10 days operation.

HRT (hrs)	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
	Input O&G (mg/L)	Output O&G (mg/L)	(%)	Input O&G (mg/L)	Output O&G (mg/L)	(%)	Input O&G (mg/L)	Output O&G (mg/L)	(%)
15	690	11 (±0.12)	98.4	720	16 (±0.12)	97.8	865	22 (±0.11)	97.5
12	923	24 (±0.11)	97.4	976	29 (±0.11)	97.0	1054	31 (±0.17)	97.1
9	1089	39 (±0.17)	96.4	1154	43 (±0.12)	96.3	1254	49 (±0.10)	96.1
6	1287	60 (±0.08)	95.3	1323	62 (±0.03)	95.3	1423	69 (±0.15)	95.2

Table 4.10 Removal (%) of O&G after 15 days of operation.

HRT (hrs)	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
	Input O&G (mg/L)	Output O&G (mg/L)	(%)	Input O&G (mg/L)	Output O&G (mg/L)	(%)	Input O&G (mg/L)	Output O&G (mg/L)	(%)
15	690	9 (±0.20)	98.7	720	14 (±0.16)	98.1	865	18 (±0.11)	97.9
12	923	19 (±0.08)	97.9	976	25 (±0.08)	97.4	1054	30 (±0.10)	97.2
9	1089	33 (±0.07)	97.0	1154	40 (±0.11)	96.5	1254	43 (±0.11)	96.6
6	1287	52 (±0.16)	96.0	1323	55 (±0.11)	95.8	1423	64 (±0.08)	95.5

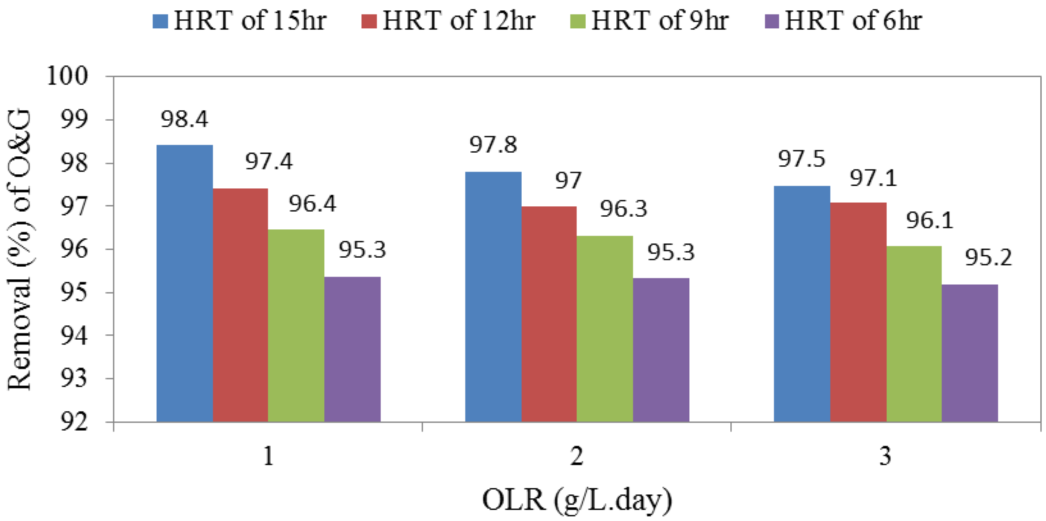

Figure 4.10 Removal (%) of O&G after 10 days.

It was observed that oil and grease (O&G) was removed efficiently, when oil and grease (O&G) concentration was kept less than 700 mg/L in feed at HRT of 15 hrs as described in Table 4.9 and 4.10 but when it was increased more than 700 mg/L, it reduced the efficiency of MBR and violet the EPA standards (O&G < 10 mg/L).

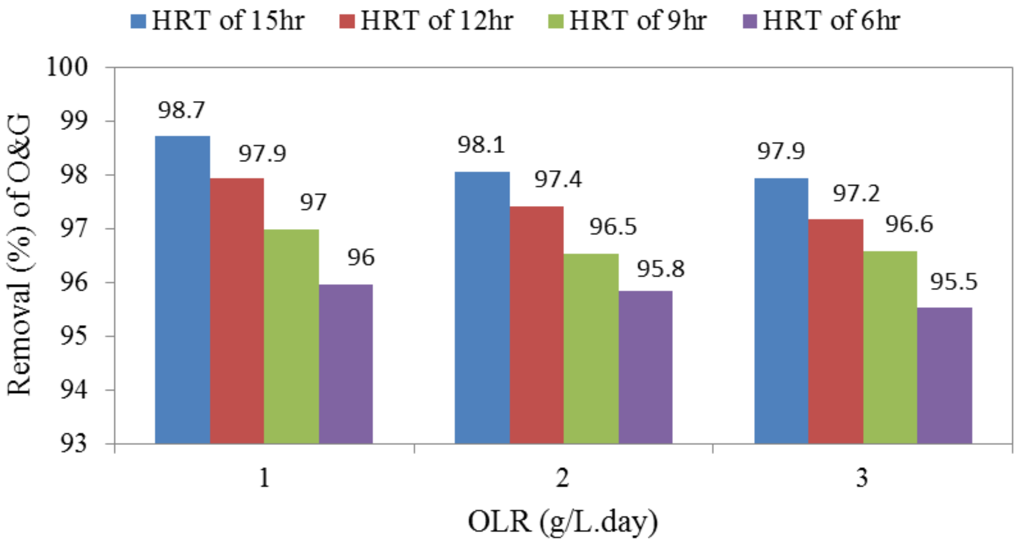

Figure 4.11 Removal (%) of O&G after 15 days.

4.4 Effect of DO Concentration on TMP

The impact of HRT on DO concentration was analyzed and it was found that decreased in HRT had a greater impact on DO concentration When the reactor was run at HRT of 15 hrs then the mean DO concentration was reported as 3.2, 2.7 and 2.2 mg/L with the corresponding OLR of 1, 2 and 3 g/L·day, respectively as shown in Table 4.11.

Table 4.11 Mean value of DO (mg/L) at different OLRs.

HRT (hrs)	**DO (mg/L)**		
	OLR of 1 g/L·day	OLR of 2 g/L·day	OLR of 3 g/L·day
15	3.2 (±0.24)	2.7 (±0.06)	2.2 (±0.10)
12	3.3 (±0.33)	2.1 (±0.04)	1.9 (±0.08)
9	2.5 (±0.24)	1.7 (±0.04)	1.2 (±0.09)
6	2.6 (±0.33)	1.8 (±0.23)	1.1 (±0.22)

Decreased in DO concentration was observed due to an increase in OLR at HRT of 15 hrs because at higher OLR, MLSS concentration was increased which utilized more oxygen for biodegradation while similar trends were observed at HRT of 12, 9 and 6 hrs but it was observed that DO concentration decreased tremendously, when HRT was decreased from 15 to 12, 9 and 6 hrs. It was explained by Meng et al., 2007, that this might be an impeded transfer rate of both substrate and oxygen due to an increase of the sludge viscosity and MLSS concentration at short HRT or high OLR. Therefore, it was concluded that shorter induced more MLSS concentration in bioreactor, which caused the higher utilization of DO concentration in bioreactor. Mean value of DO concentrations are summarized in Table 4.5.

From Figures 4.12, 4.13 and 4.14 illustrate that at OLR of 1 g/L·day, membrane operation was terminated around 17, 12, 8 and 6 days with the corresponding HRTs of 15, 12, 9 and 6 hrs as described in Table 4.4.

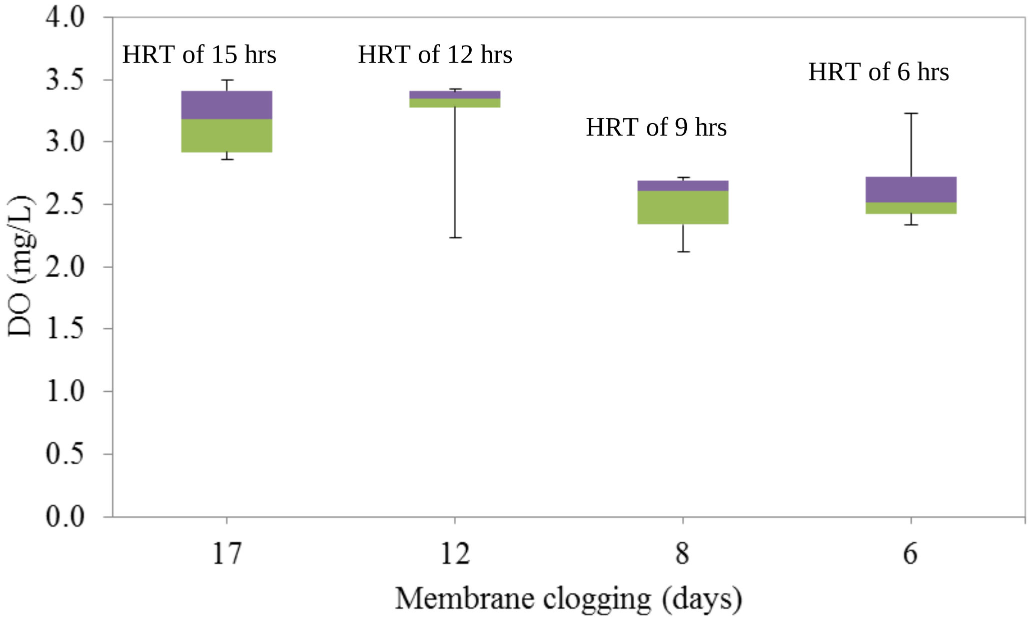

Figure 4.12 Effect of DO (mg/L) on TMP at OLR of 1 g/L·day.

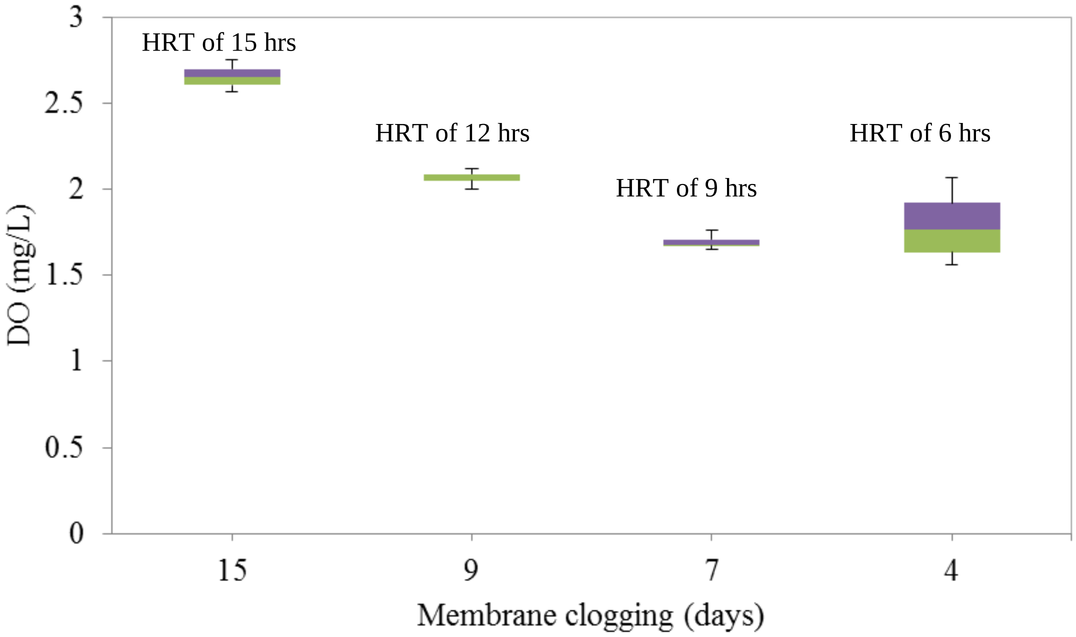

Figure 4.13 Effect of DO (mg/L) on TMP at OLR of 2 g/L·day.

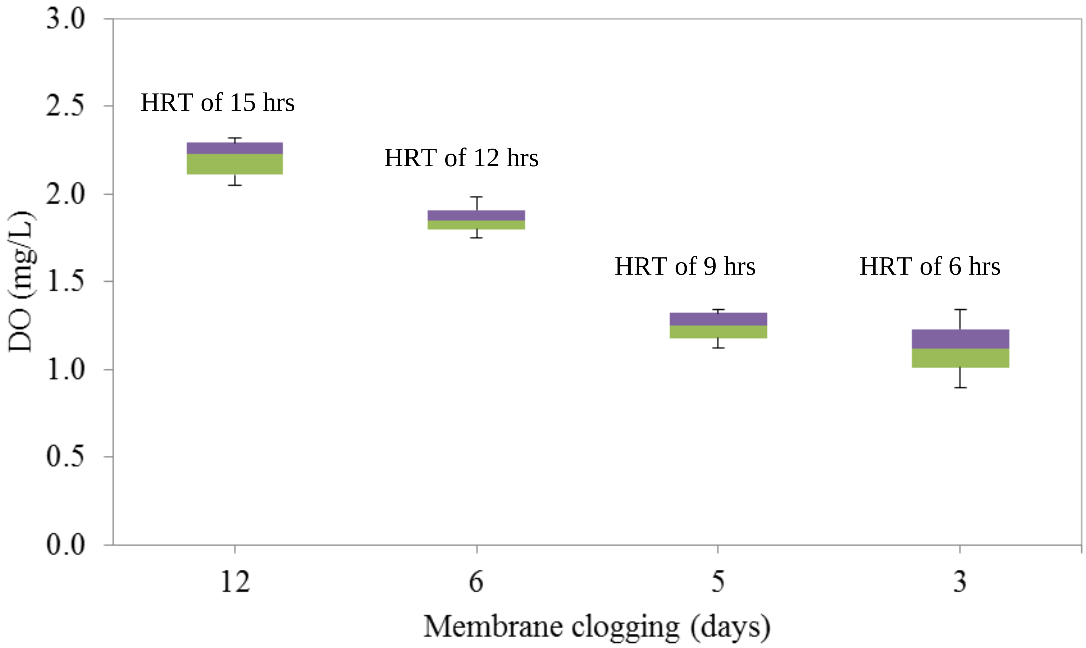

Figure 4.14 Effect of DO (mg/L) on TMP at OLR of 3 g/L·day.

This phenomenon was explained by Martinez et al., 2006 that membrane fouling was more severe at lower HRT. This can be explained by the high velocity of blocking materials towards the membrane surface at low HRTs, while similar patterns were observed at OLRs of 2 and 3 g/L·day as explained in Table 4.4.

Chae et al., 2006 explained that to reduce membrane fouling, HRT was found to be a key parameter, while Huang and Ong, (2010) reported that when HRT decreases, membrane fouling happens faster at constant membrane surface area. Rate of membrane fouling at lower DO concentration was explained by Jin and Lee, (2006) that the rate of membrane fouling for the low DO (LDO) reactor was 7.5 times faster than that for the high DO (HDO) reactor. Even though the biofilm deposited on the membrane surface in the HDO was thicker than in the LDO at the operating terminated (TMP reached 30 Kpa). Difference in biofilm characteristics as a result of different DO level was main factor affecting biofouling for both MBRs. It was concluded the shorter HRT or high OLR and high flux condition resulted in the acceleration of membrane fouling.

4.5 Particle Size Distribution

The particle size distributions of flocs were also analyzed by varying the HRTs. It was observed that particle size was increased, while HRT decreased. When the reactor was run at HRT of 15 hrs, increased in particle size observed as 12.52, 20.75 and 29.59 µm with the corresponding OLRs of 1, 2 and 3 g/L.day, respectively as shown in Table 4.12, increased in particle size was observed due to an increase in MLSS concentration at higher OLR which caused severe membrane fouling due to over growth of filamentous bacteria as explained by Sezgin et al., 1978, because the excessive growth of filamentous bacteria would produce an abundance of filaments extending from the flocs into the bulk solution, producing a bridging lattice, which prevents the agglomeration of floc particles. Therefore, as filamentous microorganisms started to grow, the sludge flocs became more irregularly shaped and porous (Wilen et al., 1999). Thus, it was concluded that the overgrowth of filamentous bacteria and the low shear stress were the main reasons which led to irregular particle shape at lower HRT, which caused severe membrane fouling. Similar trends for particle size growth were obtained for HRTs of 12, 9 and 6 hrs as mentioned in Table 4.12.

Table 4.12 Mean particle size distribution at different OLRs.

HRT (hrs)	**Particle size (µm)**		
	OLR of 1 g/L·day	OLR of 2 g/L·day	OLR of 3 g/L·day
15	12.5 (±2)	20.7 (±2)	29.6 (±1)
12	15.2 (±3)	28.2 (±2)	36.2 (±1)
9	14.6 (±6)	31.3 (±2)	49.8 (±6)
6	27.9 (±11)	46.6 (±4)	62.7 (±7)

Figures 4.15, 4.16 and 4.17 illustrate the impact of particle size on membrane fouling and it was revealed that at HRTs of 15, 12, 9 and 6 hrs, membrane operation was terminated around 12-17, 6-12, 5-8 and 3-6 days, respectively as shown in Table 4.5, because shorter HRT led to decrease in DO concentration continuously, which caused the severe membrane fouling.

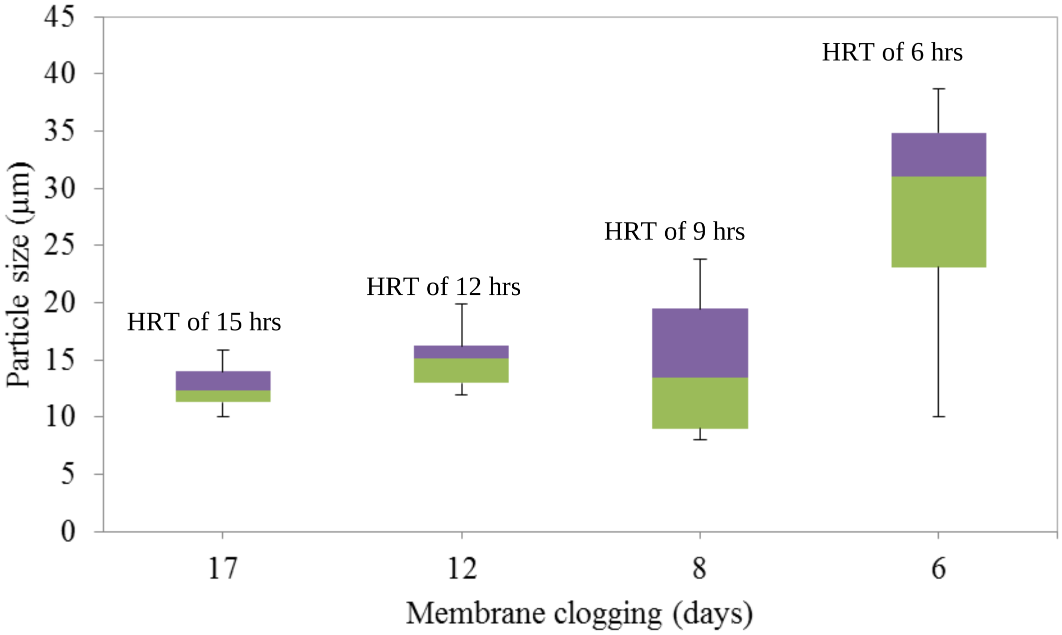

Figure 4.15 Effect of particle size on TMP at OLR of 1 g/L·day.

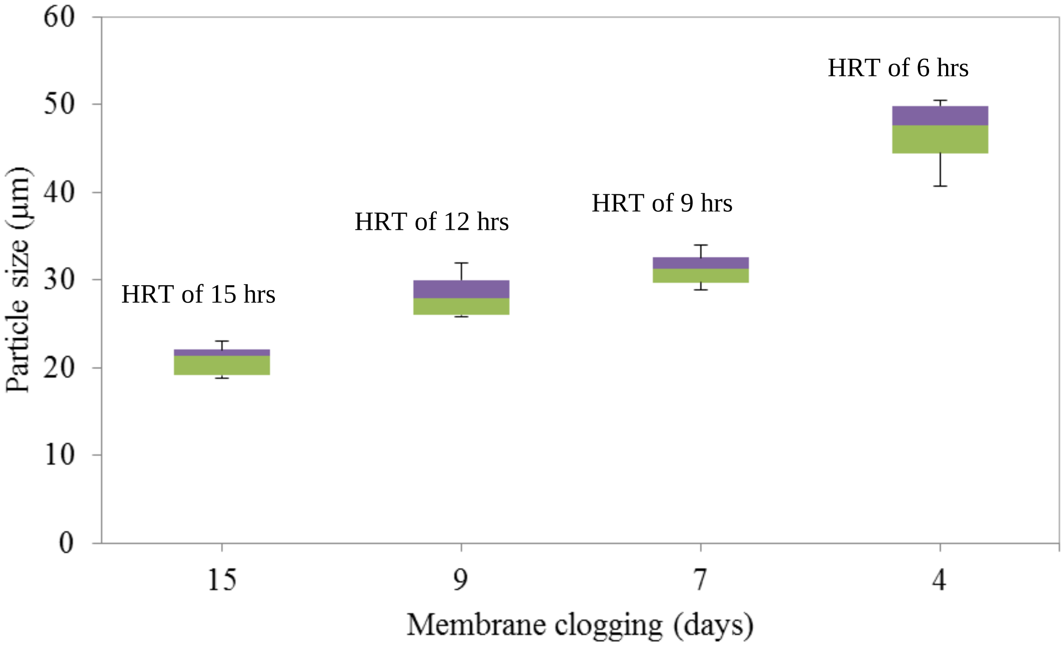

Figure 4.16 Effect of particle size on TMP at OLR of 2 g/L·day.

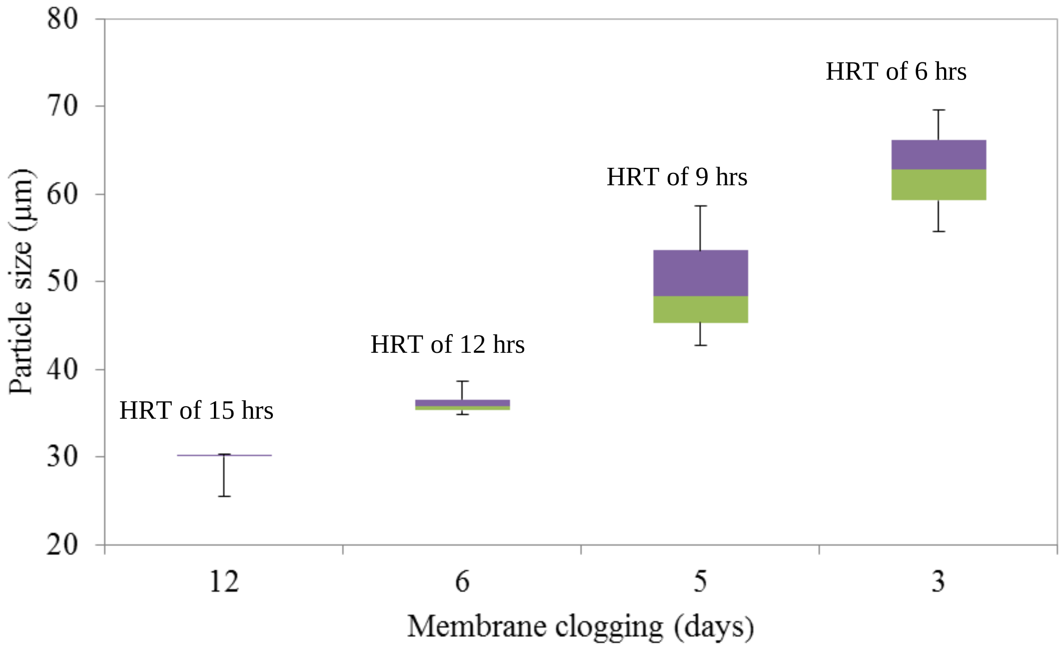

Figure 4.17 Effect of particle size on TMP at OLR of 3 g/L·day.

4.6 Evolution of SMP in Sludge Suspension

Although the influence of dissolved matter has been studied for a decade, the concept of SMP fouling in the MBR is relatively new as no report on SMP levels existed for MBRs prior to 2001 (Chang and Le-Clech, 2002). In order to reveal the feasibility and relevance of liquid phase analyses on MBR filterability and potentially standardize the method, therefore SMP analysis was carried out. In this research, SMP categorized as SMP_p (protein) and SMP_c (polysaccharide) to evaluate their impact on membrane fouling.

When reactor was run at HRT of 15 hrs, then mean SMP_p was reported as 8.37, 22.82 and 26.07 mg/L with the corresponding OLRs of 1, 2 and 3 g/L·day, respectively (Table 4.13), while SMP_c concentration was reported as 7.07, 22.2 and 24.81 mg/L with the corresponding OLRs of 1, 2 and 3 g/L·day (Table 4.14). Increased in SMP_p and SMP_c concentrations were resulted due to increase in MLSS concentration at shorter HRT and higher OLRs. Similar trends were also observed for HRT of 12, 9 and 6 hrs.

Table 4.13 Mean protein concentration at different OLRs.

HRT (hrs)	Protein (mg/L)		
	OLR of 1 g/L·day	OLR of 2 g/L·day	OLR of 3 g/L·day
15	8 (±2)	23 (±1)	26 (±2)
12	14 (±6)	31 (±2)	38 (±1)
9	21 (±5)	41 (±2)	50 (±2)
6	20 (±12)	56 (±3)	60 (±1)

Table 4.14 Mean polysaccharide concentration at different OLRs.

HRT (hrs)	**Polysaccharide (mg/L)**		
	OLR of 1 g/L·day	OLR of 2 g/L·day	OLR of 3 g/L·day
15	7 (±2)	22 (±1)	25 (±2)
12	12 (±6)	29 (±2)	37 (±2)
9	20 (±5)	40 (±2)	49 (±2)
6	19 (±12)	55 (±3)	59 (±2)

From Figures 4.18, 4.19 and 4.20 illustrate that membrane operation was terminated around 12-17, 6-12, 5-8 and 3-6 days with the corresponding HRT of 15, 12, 9 and 6 hrs, respectively as shown in Table 4.5.

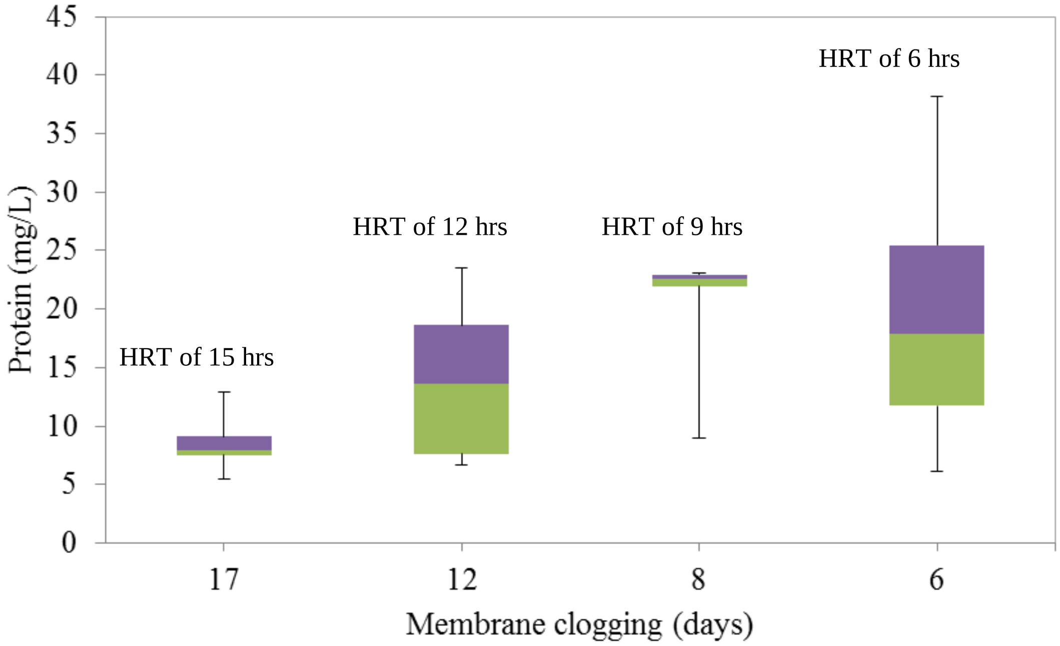

Figure 4.18 Effect of protein on TMP at OLR of 1 g/L·day.

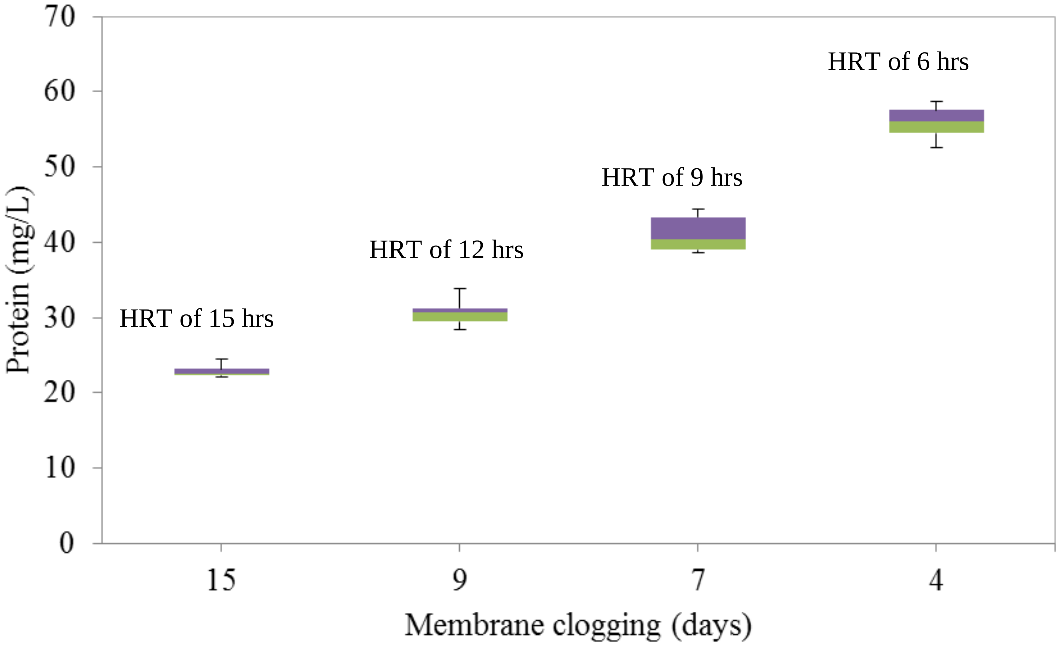

Figure 4.19 Effect of protein on TMP at OLR of 2 g/L·day.

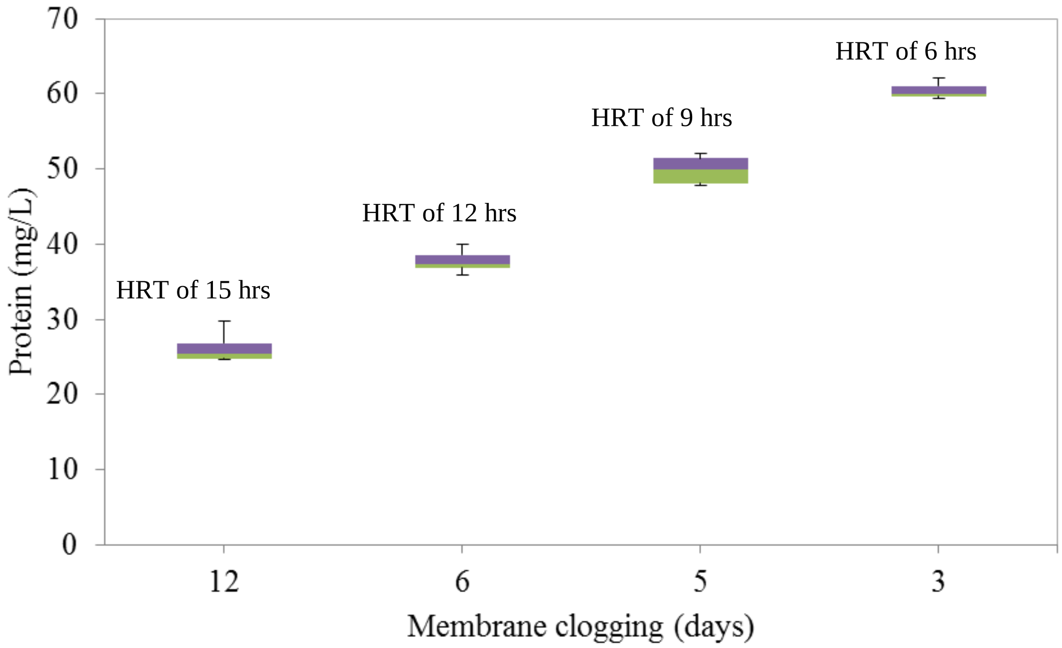

Figure 4.20 Effect of protein on TMP at OLR of 3 g/L·day.

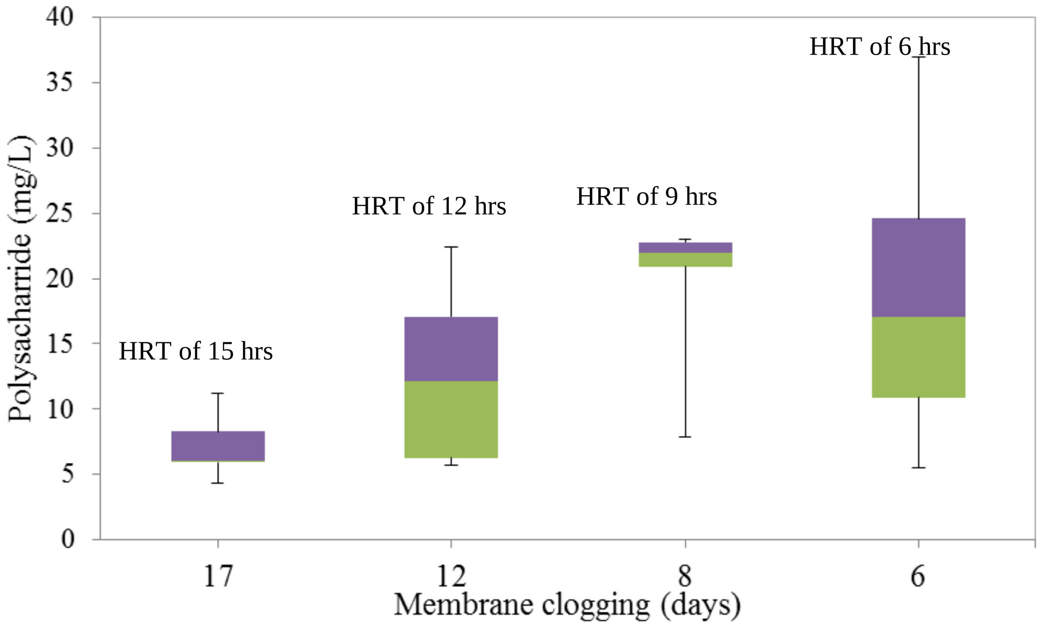

Figure 4.21 Effect of polysaccharide on TMP at OLR of 1 g/L·day.

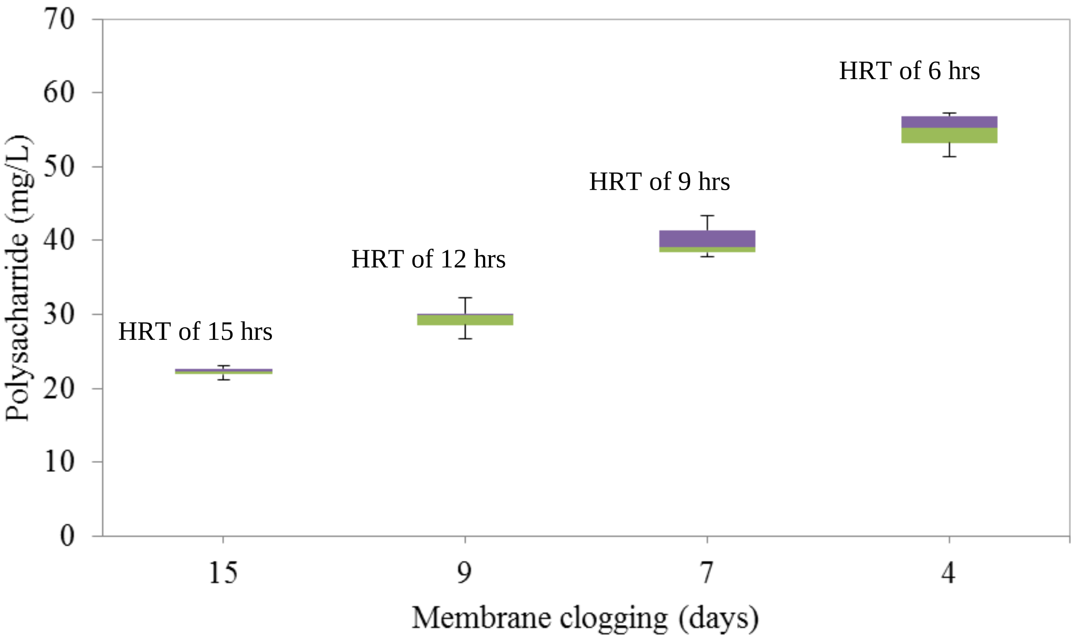

Figure 4.22 Effect of polysaccharide on TMP at OLR of 2 g/L·day.

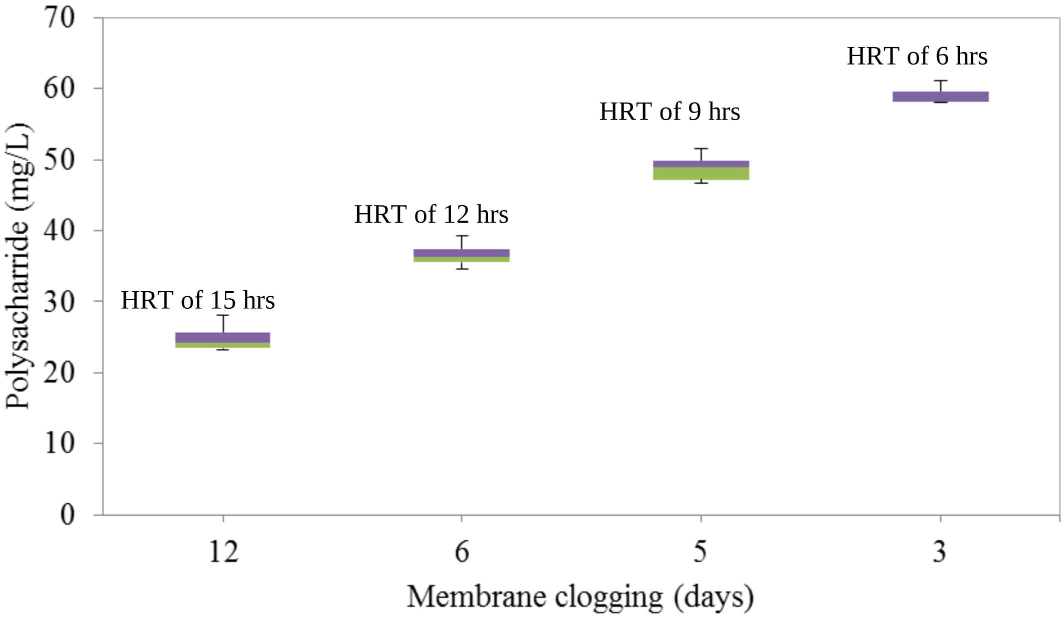

Figure 4.23 Effect of polysaccharide on TMP at OLR of 3 g/L·day.

It was also concluded that increased in SMP production, caused to increase membrane fouling. It was explained by Rosenberger et al., 2005 observed that during filtration, SMP adsorb on the membrane surface, block membrane pores and/or form a gel structure on the membrane surface where they provide a possible nutrient source for biofilm formation and a hydraulic resistance to permeate flow. In our research, SMP_p was found to be higher than SMP_c. However in some research, it revealed that SMP_c as the major foulant indicator in MBR systems. However, the nature and fouling propensity of SMP_c were observed to change during the study of unsteady MBR operation (Drews and Vocks, 2005).

However, it was not possible to correlate SMP_c to fouling. Evenblij et al. (2004) and Drews & Vocks (2005) observed that the effect of the protein fraction contained in the SMP solution on MBR fouling has been rarely reported. Since a significant amount of proteins is retained by the membrane (from 15% to 90%), it is expected that this plays a role in MBR fouling. This was recently confirmed by the value of specific resistance increasing by a factor of 10 as the SMP_p increased from 30 to 100 mg/L (Hernandez et al., 2005).Therefore, it was concluded that both SMP_p and SMP_c played a significant role in membrane fouling.

CHAPTER V

ECONOMIC ANALYSIS

5.1 Blower Power Consumption

Blower power consumption was directly obtained by multiplication of conversion factor with the aeration rate (Grady et al., 1999) as shown in Eq. 5.1.

$$P = 0.7\ Q_{air} \qquad (5.1)$$

Where Q_{air} is aeration requirement (m^3/min)

P is power demand (kWh)

* Q_{air} = 0.01415 m^3/hr (calculated).

P = 0.7 x 0.01415 = 0.009905 kWh

5.2 Power Consumption of Permeate Pump

Power consumption of permeate pump can be calculated by:

$$HP = \frac{Q \text{ x } P}{1713 \text{ x efficiency of pump}} \qquad (5.2)$$

Where Q is permeate flowrate (m^3/min)

P is outlet pressure of peristaltic pump (PSI)

* Efficiency of pump is 90 % (assumed).

Values of Q at HRT of 15, 12, 9 and 6 hrs can be calculated by dividing the volume of reactor with HRT.

$$\text{HRT} = \frac{V}{Q} \qquad (5.3)$$

Or

$$Q = \frac{V}{\text{HRT}}$$

Where V is volume of reactor (50 L)

* Q = A x J

Where J is permeate flux (L/m^2.hr)
A is filtration area (0.23 m^2)

At HRT of 15 hrs, $Q_1 = \frac{50}{15}$ = 3 L/hr, J = 3 x 0.23 = 14 L/m^2.hr

At HRT of 12 hrs, $Q_2 = \frac{50}{12}$ = 4 L/hr, J = 4 x 0.23 = 18 L/m^2.hr

At HRT of 9 hrs, $Q_3 = \frac{50}{9}$ = 6 L/ hr, J = 6 x 0.23 = 24 L/m^2.hr

At HRT of 15 hrs, $Q_4 = \frac{50}{6}$ = 8 L/hr, J = 8 x 0.23 = 36 L/m^2.hr

To calculate the power consumption of permeate pump, put the values of Q_1, Q_2, Q_3 and Q_4 in Eq. 5.2.

HP at HRT of 15 hrs, $\text{HP} = \frac{3 \text{ x } 0.0044 \text{ x } 20}{1713 \text{ x } 0.90}$ = 0.000171 HP or 0.000128 kWh

HP at HRT of 12 hrs, $\text{HP} = \frac{4 \text{ x } 0.0044 \text{ x } 20}{1713 \text{ x } 0.90}$ = 0.000228 HP or 0.00017 kWh

HP at HRT of 9 hrs, $HP = \frac{6 \times 0.0044 \times 20}{1713 \times 0.90} = 0.000343$ HP or 0.000256 kWh

HP at HRT of 6 hrs, $HP = \frac{8 \times 0.0044 \times 20}{1713 \times 0.90} = 0.000457$ HP or 0.000341 kWh

* 1 L/hr = 0.0044 GPM, 1 HP = 0.746 kW

Total power consumption for operation of MBR can be determined by:

kWh = Blower consumption power + Power consumption of permeate pump

At HRT of 15 hrs, kWh = 0.009905 + 0.000128 = 0.010033 kWh
At HRT of 12 hrs, kWh = 0.009905 + 0.000128 = 0.010075 kWh
At HRT of 9 hrs, kWh = 0.009905 + 0.000128 = 0.010161 kWh
At HRT of 6 hrs, kWh = 0.009905 + 0.000128 = 0.010246 kWh

5.3 Cost Analysis of Overall Power Consumption for MBR

It was observed that the power consumption in MBR at shorter HRT was less than the higher HRT, but shorter HRT was unfavorable for MBR operation because at shorter HRT, severe membrane fouling occurred. Therefore, further optimizations are required at higher HRT. According to Yoon et al. (2004), the oxygen requirement is a function of HRT and target MLSS concentration; however, small changes in the target MLSS may cause a more significant change of oxygen requirement then when HRT is longer. In order to control the aeration rate, MLSS concentration must be optimized to reduce the aeration demand for MBR. However, operating cost of MBR for wastewater treatment was found to be less than chemical coagulation and electro-coagulation processes. Operating cost of chemical and electro-coagulation processes in Thailand were reported as 1.11 USD/m^3 and 1.78 USD/m^3 , respectively (Ngamlerdpokin et al., 2011), which was found to be much higher than operating cost of MBR as illustrated in Table 5.1.

CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this research, MBR was proposed an alternative technology for wastewater treatment of biodiesel plant. The whole research was divided in two parts: (1) Pretreatment of biodiesel wastewater and (2) MBR treatment.

1) In pretreatment step, H_2SO_4 with different pH (2, 2.5 and 3) was used to treat the wastewater of biodiesel plant. Significant reduction in organic pollutants was obtained at pH of 2.5 of due to strong protonation effect of H_2SO_4. COD and O&G were found to be 74.1-84.1% and 84.2-92.6%, respectively. To find out the significant difference for the removal efficiency of COD and O&G values at different pH, t-test (assuming equal variances) was performed with Anova results for the group comparison of pH of 2 with pH of 2.5 and 3. It was observed that P (T < =t) two-tail < α/n (Bonferroni correction), which shows that mean values of COD and O&G were significantly different at each pH. However, there was large significant difference existed for COD and O&G values at pH of 3, when compared with pH of 2. Therefore, it was concluded that pH of 2.5 was optimum, which reduced the organic pollutants from wastewater significantly, while there was small significant difference in organic pollutants were observed when pH of 2.5 was compared with pH of 2 (Appendix B).

2) To improve the treatment efficiency of the process, MBR was incorporated as secondary treatment. It was observed that COD and O&G removal efficiency in the bioreactor slightly decreased with decreasing HRT, while the overall efficiency of COD and O&G after 15 days of operation remained in the range of 91.7-97.7% and 95.5-97.9%, respectively, because shorter HRT induced more MLSS concentration in reactor which caused to decrease the biomass activity because higher MLSS concentration would lead to an increase of oxygen and substrate diffusion limitation in the sludge suspension (Meng et al. 2007). When t-test (assuming equal variances) was performed for Anova results, then significance difference for COD and O&G values was observed at different HRT, it was found that P (T < = t) two-tail > α/n (Bonferroni correction) for COD values, when HRT of 9 hrs compared with HRT of 6 hrs

which shows that there was no significant difference existed for removal efficiency of COD values. However, P (T < = t) two-tail > α/n (Bonferroni correction), when HRT of 15 hrs compared with 12, 9 and 6 hrs which shows that removal efficiency of COD decreased with decreasing HRT. When t-test was performed for O&G values then it was found that P (T < = t) two-tail > α/n (Bonferroni correction), when HRT of 15 hrs was compared with HRT of 12, 9 and 6 hrs, which shows that O&G removal efficiency significantly reduced with decreasing HRT.

3) COD and O&G values in MBR effluent was compared with EPA standards, it was found that COD values < 150 mg/L at all HRTs while O&G values found to be greater than 10 mg/L (EPA standard) at different HRTs. Increased in O&G concentration in MBR effluent was resulted due to an increase of O&G conc. in feed water. It was observed that when O&G concentration increased more than 690 mg/L in feed which caused a decrease in efficiency of the MBR.

4) HRT was correlated with dissolved oxygen (DO), particle size distribution (PDS) and protein and polysaccharide contents of soluble microbial product (SMP) in order to investigate their impact on membrane fouling mechanism. Trans-membrane pressure (TMP) about 50 kPa achieved within 3-6 days at HRT of 6 hrs. This can be explained by low back transport of velocity of smaller particles at low DO concentration of 1.1-2.6 mg/L with HRT of 6 hrs because at lower DO concentration, particles had poor settling properties and higher turbidities of the effluent than higher DO concentration. This could be the reason why there was severe membrane fouling at low DO concentration (Jin et al. 2006).

5) SMP_p and SMP_c were increased simultaneously with decreased in HRT. However, SMP_p was found slightly higher than SMP_c in our research. Therefore, it was concluded that both played active role in membrane fouling with the contradiction of previous research, in which SMP_c was major fouling indicator.

6.2 Recommendations for Future Work

After performing a set of experiments using this unit, several suggestions were made regarding the operability of this unit as well as its advantages and disadvantages. Here are some suggestions for future work.

1. Several sets of experiments using the high HRT could be considered to substantiate the results from this work.
2. A comparison between the suggested operation using a pretreatment step followed by MBR and a treatment using just anaerobic MBR should be made, since the latter could be conducted to produce beneficial biogas.
3. The kinetics of the operation could be considered in order to develop predictive model for fouling of membranes and when it is necessary to clean or replace them.
4. The control system could be utilized to monitor the flow rate, the pressure drop, and even the pH changes continuously.
5. A scale-up of this unit (200-500 L) could be constructed and operated to study the economics of industrial scale operation compared to current treatment method.
6. The pilot-scale unit could be installed at a small biodiesel factory in order to study its efficiency and cost effectiveness after prolonged operation.

REFERENCES

APHA. 1995. Standard methods for the examination of water and wastewater. 19th edn. American Public Health Association, Baltimore, MD.

Bolzonella, D. Pavan, P. Battistoni, P and Cecchi, F. 2006. Anaerobic co-digestion of sludge with other organic wastes and phosphorus reclamation in wastewater treatment plants for biological nutrients removal. Water Sci. and Tech. 53, 177–186.

Bowen, R. Calvo, I and Hernandez, A. 1995. Steps of membrane blocking in flux decline during protein microfiltration. J. Membrane Sci. 101, 153–165.

Brookes, A. Jefferson, B. Guglielmi, G and Judd, J. 2006. Sustainable flux fouling in a membrane bioreactor: Impact of flux and MLSS. Sep. Sci. Technol. 41, 1279–1291.

Calvo, L. Leclerc, J. Tanguy, G. Cames, M. Patemotte, G. Valentin, G. Rostan, A and Lapicque, F. 2003. An electrocoagulation unit for the purification of soluble oil wastes of high COD. Environ. Prog. 22, 57–65.

Chae, R. Ahn, T. Kang, T and Shin, S. 2006. Mitigated membrane fouling in a vertical submerged membrane bioreactor (VSMBR). J. Membrane Sci. 280, 572-581.

Chang, S and Kim, N. 2005. Wastewater treatment using membrane filtration-effect of biosolids concentration on cake resistance. Process Biochem. 40, 1307–1314.

Chang, S. Bag, O and Lee, H. 2001. Effects of membrane fouling on solute rejection during membrane filtration of activated sludge. Proc. Biochem. 36, 855–860.

Chang, S. Le Clech, P. Jefferson, B and Judd, S. 2002. Membrane fouling in membrane bioreactors for wastewater treatment. J. Env. Eng. ASCE. 128, 1018–1029.

Chavalparit, O and Meanseta, P. 2006. Treatment of agro-industrial wastewater by means of electro-coagulation: crude palm oil mill in Thailand. In: Proceedings of the 12th Thailand-Korea Conference Environmental Engineering, Korea Advanced Institute of Science and Technology (KAIST), Soul, Korea, 21-25 April.

Chavalparit, O and Ongwandee, M. 2009. Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology (RSM). J. Environ. Sci. 21, 1491-1496.

Cho, D and Fane, G. 2002. Fouling transients in nominally sub-critical flux operation of a membrane bioreactor. J. Membrane Sci. 209, 391–403.

Choi, H. Zhang, K. Dionysiou, D. Oerther, B and Sorial, A. 2005a. Effect of permeate flux and tangential flow on membrane fouling for wastewater treatment. Sep. Purif. Technol. 45, 68–78.

Choi, H. Zhang, K. Dionysiou, D. Oerther, B and Sorial, A. 2005b. Influence of cross-flow velocity on membrane performance during filtration of biological suspension. J. Membrane Sci. 248, 189–199.

Choo, H and Lee, H. 1996. Membrane fouling mechanisms in the membrane coupled anaerobic bioreactor. J. Water Res. 30, 1771-1780.

Cote, P. 2002. Inverted air box aerator and aeration method for immersed membrane, US Patent. 6, 863-823.

Defrance, L and Jaffrin, Y. 1999. Reversibility of fouling formed in activated sludge filtration. J. Membr. Sci. 157, 73–84.

Drews, A and Kraume, M. 2005. Process improvement by application of membrane bioreactors. Chem. Eng. Res. Des. 83, 276–284.

Drews, A. Vocks, M. Iversen, V. Lesjean, B and Kraume, M. 2005. Influence of unsteady membrane bioreactor operation on EPS formation and filtration resistance, in: Proceedings of the International Congress on Membranes and Membrane Processes (ICOM), Seoul, Korea.

Drews, A. Evenblij, H and Roenberger, S. 2005. Potential and drawbacks of microbiology-membrane interaction in membrane bioreactors. Environ. Prog. 24, 426–433.

Dufresne, R. Lavallee, C. Lebrun, E and Lo, N. 1998. Comparison of performance between membrane bioreactor and activated sludge system for the treatment of pulping process wastewaters. Tappi J. 81, 131–135.

Emamjomeh, M and Sivakumar, M. 2009. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. J. Environ. Manage. 90, 1663–167.

Evenblij, H and Van, J. 2004. Occurrence of EPS in activated sludge from a membrane bioreactor treating municipal wastewater. Water Sci. Technol. 50, 293–300.

Fane, G and Chang, S. 2002. Filtration of biomass with laboratory-scale submerged hollow fibre modules – effect of operating conditions and module configuration. J. Chem. Technol. Biotechnol. 77, 1030–1038.

Fang, P and Shi, X. 2005. Pore fouling of microfiltration membranes by activated sludge. J. Membrane Sci. 264, 161–166.

Feng, C. Sugiura, N and Maekawa, T. 2004. Performance of two new electrochemical treatment system for wastewaters. J. Environ. Sci. and Health. 39, 2533–2543.

Frost and Sullivan (2010), Growing opportunities for membrane systems in Indian water and wastewater treatment market, Report, Sep 2010.

Frost and Sullivan (2011), China membrane bioreactor (MBR) market outlook, Report, Aug 2011.

Frost and Sullivan (2012), Membrane filtration in Southeast Asia water and wastewater treatment, Report, August 2012.

Fuchs, W. Braun, R and Theiss, M. 2005. Influence of various wastewater parameters on the fouling capacity during membrane filtration, Proceedings of International Congress on Membranes and Membrane Processes (ICOM), Seoul, Korea.

Gander, A. Jefferson, B and Judd, J. 2000. Membrane bioreactors for use in small wastewater treatment plants: Membrane materials and effluent quality. Water Sci. Technol. 41, 205–211.

Global Industry Analysts Inc (2012), Global MBR market forecast, Report, Jan 2012.

Gonsalves, B. 2006. An assessment of the biofuels industry in Thailand. United Nations Conference on Trade and Development, Geneva, Switzerland.

Grace, P. 1956. Resistance and compressibility of filter cakes. Chem. Eng. Prog. 49, 303–318.

Grady, C. Daigger, T and Lim, H. 1999. Biological wastewater treatment. New York, Marcel Dekker. 61-125.

Gunder, B and Krauth, K. 1998. Replacement of secondary clarification by membrane separation – results with plate and hollow fibre modules. Water Sci. Technol. 38, 383–393.

Hai, I. Yamamoto, K and Fukushi, K. 2005. Different fouling modes of submerged hollow-fiber and FS membranes induced by high strength wastewater with concurrent biofouling. Desalination. 180, 89–97.

He, G. and Xue, K. 2006. Zeolite powder addition to improve the performance of submerged gravitation-filtration membrane bioreactor. Journal of Environmental Science. 18, 242–247.

He, Y. Xu, P. Li, C and Zhang, B. 2005. High-concentration food wastewater treatment by an anaerobic membrane bioreactor. Water Res. 39, 4110–4118.

Hernandez, E. Van, R. Schetrite, S and Albasi, C. 2005. Role and variations of supernatant compounds in submerged membrane bioreactor fouling. Desalination. 179, 95–107.

Holbrook, D. Higgins, J. Murthy, N. Fonseca, D. Fleischer, J. Daigger, T. Grizzard, J. Love, G and Novak, T. 2004. Effect of alum addition on the performance of submerged membranes for wastewater treatment. Water Env. Res. 76, 2699–2702.

Holler, S and Trosch, W. 2001. Treatment of urban wastewater in a membrane bioreactor at high organic loading rates. J. Biotechnol. 92, 95–101.

Hong, P. Bae, H. Tak, M and Hong, A. 2002. Randall, Fouling control in activated sludge submerged hollow fiber membrane bioreactors. Desalination. 143, 219–228.

Huang, X. Gui, P and Qian, Y. 2001. Effect of sludge retention time on microbial behaviour in a submerged membrane bioreactor. Process Biochem. 36, 1001–1006.

Huang, Z. Ong, L and Ng, Y. 2010. Submerged anaerobic membrane bioreactor for low-strength wastewater treatment: Effect of HRT and SRT on treatment performance and membrane fouling. J. Water Res. 45, 1543-1554.

IUPAC. 1985. Reporting physisorption data. Pure Appl. Chem. 57, 603.

Jang, J. Trussell, S. Merlo, P. Jenkins, D. Hermanowicz, W and Kim, S. 2005. Exocellular polymeric substances molecular weight distribution and filtration resistance as a function of food to microorganism ratio in the submerged membrane bioreactor, In: Proceedings of the International Congress on Membranes and Membrane Processes (ICOM), Seoul, Korea.

Jang, N. Ren, X. Choi, K and Kim, S. 2005. Comparison of membrane biofouling in nitrification and denitrification for the membrane bio-reactor (MBR), In: Proceedings of the IWA on Aspire, Singapore.

Jaruwat, P. Kongiao, S and Hunsom, M. 2010. Management of biodiesel wastewater by the combined processes of chemical recovery and electrochemical treatment. Energy Conver. Manage. 51, 531–537.

Jefferson, B. Brookes, A. Le-Clech, P and Judd, J. 2004. Methods for understanding organic fouling in MBRs. Water Sci. Technol. 49, 237–244.

Jefferson, B. Fawehinmi, F. Lens, P. Stephenson, T and Rogalla, F. 2004. The influence of operating conditions on extracellullar polymeric substances (EPS), soluble microbial products (SMP) and bio-fouling in anaerobic membrane bioreactors, Proceedings of Water Environment – Membrane Technology Conference, Seoul, Korea.

Jin, L. Lee, N. Lee, H. Chang, S. Huang, X and Swaminathand, T. 2006. Effect of DO concentration on biofilm structure and membrane filterability in submerged membrane bioreactor. J. Water Res. 40, 2829-2836.

Jeong, Y. Cha, C. Yoo, K and Kim, J. 2007. Characteristics of bio-fouling in a submerged MBR. Desalination. 207, 107-113.

Judd, S and Jefferson, B. 2003. Membranes for industrial wastewater recovery and re-use, Elsevier, Oxford.

Judd, S. 2005. Fouling control in submerged membrane bioreactors. Water Sci. Technol. 51, 27–34.

Kato, S. Yoshimura, H. Hirose, K. Amornkitbamurung, M. Sakka, M and Sugahara, I. 2005. Application of microbial consortium system to wastewater from biodiesel fuel generator. IEA-Waterqual, Singapore, CD-ROM.

Kim, J. Lee, H and Kang, J. 2003. Characteristics of microfiltration membranes in a membrane coupled sequencing batch reactor system. Water Res. 37, 1192–1197.

Kim, S. Lee, H. and Chun, D. 1998. Comparison of ultrafiltration characteristics between activated sludge and BAC sludge. Water Research. 32, 3443- 3451.

Laspidou, S and Rittmann, E. 2002. A unified theory for extracellular polymeric substances, soluble microbial products and active and inert biomass. Water esearch. 36, 2711-2720.

Le-Clech, P. Jefferson, B and Judd, J. 2003. Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor. J. Membrane Sci. 218, 117–129.

Le-Clech, P. Jefferson, B and Judd, J. 2005. A comparison of submerged and sidestream tubular membrane bioreactor configurations. Desalination. 173, 113–122.

Lee, H. Ahn, T. Kang, T. Chae, R. Lim, L and Shin, S. 2005. Effect of internal recycle rate on the high-strength nitrogen wastewater treatment in the combined UBF/MBR system. Water Sci. Technol. 51, 241–247.

Lee, M. Jung, Y and Chung, C. 2001. Novel method for enhancing permeate flux of submerged membrane system in two phase anaerobic reactor. J. Water Res. 35, 471–477.

Lesjean, B and Luck, F. Assessment of the membrane bioreactor technology and european market outlook, IDS Water - White Paper, KWB Ggmbh Co. http://www.idswater.com

Lesjean, B. Rosenberge, S. Laabs, C. Jekel, M. Gnirss, R and Amy, G. 2005. Correlation between membrane fouling and soluble/colloidal organic substances in membrane bioreactors for municipal wastewater treatment. Water Sci. Technol. 51, 1–8.

Li, Y. He, Y. Liu, S. and Yang, Z. 2005. Comparison of the filtration characteristics between biological powdered activated carbon sludge and activated sludge in submerged membrane bioreactors. Desalination. 174, 305–314.

Lim, R. Ahn, H. Song, G and Ji, C. 2004. Microbial community in biofilm on membrane surface of submerged MBR: Effect of in-line cleaning chemical agent, Proceedings of Water Environment, Membrane Technology Conference, Seoul, Korea.

Liu, L. Wang, B. Wang, H. and Cui, Z. 2005. Performance improvement of hybrid membrane bioreactor with PAC addition for water reuse. Water Science and Technology. 52, 383–391.

Lubbecke, S. Vogelpohl, A and Dewjanin, W. 1995. Wastewater treatment in a biological high-performance system with high biomass concentration. Water Res. 29, 793–802.

Martinez, B. Barbot, E. Marrot, B. Moulin, P and Roche, N. 2006. Degradation of synthetic phenol-containing wastewaters by MBR. J. Membrane Sci. 281 288-296.

Meng, F. Shi, B. Yang, F and Zhang, H. 2007. Effect of hydraulic retention time on membrane fouling and biomass characteristics in submerged membrane bioreactors. Bioprocess Biosyst. Eng. 30, 359–367.

Metcalf and Eddy. 2003. Wastewater engineering: Treatment and reuse (3rd edn). McGraw-Hill, New York.

Nagaoka, H. Yamanishi, S and Miya, A. 1998. Modeling of biofouling by extracelluar polymers in a membrane separation activated sludge. Water Sci. Technol. 38, 497–504.

Ngamlerdpokin, K. Kumjadpai, S. Chatanon, P. Tungmanee, U. Chuenchuanchom, S. Jaruwat, P. Lertsathitphongs, P and Hunsom, M. 2011. Remediation of biodiesel wastewater by chemical and electro-coagulation. J. Environ. Manage. 92, 2454-2460.

Nishiro, N and Nakashimada, Y. 2007. Recent development of anaerobic digestion processes for energy recovery from wastes. J. Biosci. Bioeng.103, 105–112.

Pirbazari, M. Ravindran, V. Badriyha, N. and Kim, H. 1996. Hydrid membrane filtration process for leachate treatment. Water Research. 30, 2691-2706.

Rabie, R and Cote, P. Singh, M and Janson, A. 2003. Cyclic aeration system for submerged membrane modules, US Patent 6, 881, 343.

Raunkjaer, K. Hvitved, T and Nielsen, H. 1994. Measurement of pools of protein, carbohydrate and lipid in domestic wastewater. J. Wat. Res. 28, 251-262.

Romero, A and Davis, H. 1991. Experimental verification of the shear induced hydrodynamic diffusion model of crossflow microfiltration. J. Membrane Sci. 62, 249–273.

Rosenberger, S. Evenblij, H. Te, S. Wintgens, T and Laabs, C. 2005. The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes-six case studies of different European research groups. J. Membr. Sci. 263, 113–126.

Rosenburger, S. Kraume, M and Szewzyk, U. 1999. Operation of different membrane bioreactors experimental results and physiological state of the microorganisms, Proceedings IWA Conference Membrane Technology in Environmental Management, Tokyo. 310–316.

Schoeberl, P. Brik, M. Bertoni, M. Braun, R and Fuchs, W. 2005. Optimization of operational parameters for a submerged membrane bioreactor treating dyehouse wastewater. Sep. Purif. Technol. 44, 61–68.

Schrader, A. Zwijnenburg, A and Wessling, M. 2005. The effect of WWTP effluent zeta-potential on direct nanofiltration performance. J. Membrane Sci. 266, 80–93.

Scott, S. 2007. Application of MBR to wastewater treatment and reuse. URL:http://home.eng.iastate.edu/~tge/ce421-521/scott.pdf.

Sezgin, M. Jenkins, D and Parker, S. 1978. A unified theory of filamentous activated sludge bulking. J. Water Pollut. Control Fed. 50, 362-381.

Sven, L. Djamila, H and Thomas, W. 2007. Polymeric compounds in activated sludge supernatant-Characterisation and retention mechanisms at a full-scale municipal membrane bioreactor. J. Water Res. 41, 3894-3902.

Siles, J. Gutiérrez, M. Martin, M and Martin, A. 2011. Physical–chemical and biomethanization treatments of wastewater from biodiesel manufacturing. Bioresource Technol. 102, 6348–6351.

Siles, J. Martin, M. Chica, A and Martin, A. 2010. Anaerobic co-digestion of glycerol and wastewater derived from biodiesel manufacturing. J. Biores. Tech. 101, 6315–6321.

Smith, J. Vigneswaran, S. Ngo, H. Ben-Aim, R and Nguyen, H. 2005. Design of a generic control system for optimising back flush durations in a submerged membrane hybrid reactor. J. Membrane Sci. 255, 99–106.

Stephenson, T. Judd, S. Jefferson, B and Brindle, K. 2000. Membrane bioreactors for wastewater treatment, IWA Publishing, London.

Suehara, K. Kawamoto, Y. Fujii, E. Kohda, J. Nakano, Y and Yano, T. 2005. Biological treatment of wastewater discharged from biodiesel fuel production plant with alkali-catalyzed trans-esterification. J. Biosci. Bioeng. 100, 437–442.

Tanaka, T. Abe, I. Asakawa, H. Yoshida, H and Nakanishi, K. 1994. Filtration characteristics and structure of cake in crossflow filtration of bacterial suspension. J. Ferment. Bioeng. 78, 455–461.

Tardieu, E. Grasmick, A. Geaugey, V and Manem, J. 1999. Influence of hydrodynamics on fouling velocity in a recirculated MBR for wastewater treatment. J. Membrane Sci. 156, 131–140.

Tri, P. 2002. Oily wastewater treatment by membrane bioreactor process coupled with biological activated carbon process. Thesis: AIT, Bangkok, Thailand.

Trussell, T. Merlo, P. Hermanowicz, W and Jenkins, D. 2006. The effect of organic loading on process performance and membrane fouling in a submerged membrane bioreactor treating municipal wastewater. J. Wat. Res. 40, 2675-2684.

Visvanathan, C. Ben, R and Parameshwaran, K. 2000. Membrane separation bioreactors for wastewater treatment. Enviro. Sci. and Tech. 30, 1-48.

Wang, Z. Wu, Z. Mai, S. Yang, C. Wang, X . An, Y and Zhou, Z. 2008. Research and applications of membrane bioreactors in China. Journal of Separation and Purification Technology. 62, 249-263.

Wang, Z. Wu, G. and Gu, Y. 2006. Simultaneous nitrogen and phosphor removal in an aerobic submerged membrane bioreactor. Journal of Environmental Science. 18, 439–445.

Wilen, M and Balmer, P. 1999. The effect of dissolved oxygen concentration on the structure, size and size distribution of activated sludge flocs. Water Res. 33, 391–400.

Wisniewski, C and Grasmick, A. 1998. Floc size distribution in a membrane bioreactor and consequences for membrane fouling. Colloid. Surface. A Physicochem. Eng. Aspect. 138, 403–411.

Wisniewski, C. 2007. Membrane bioreactor for reuse. Desalination. 203, 15–19.

Wu, F. Chen, X. Huang, W. and Geng, W. 2006. Using inorganic coagulants to control membrane fouling in a submerged membrane bioreactor. Desalination. 197, 124–136.

Xing, H. Wu, Z and Tardieu, E. 2003. Excess sludge production in membrane bioreactors: a theoretical investigation. J. Env. Eng. 129, 291–297.

Yang, G. 2005. Membrane fouling in membrane bioreactor and its controlling measures. Membrane Science and Technology. 25, 80–84.

Yoon, S. Kim, H and Yeom, I. 2004. The optimum operational condition of membrane bioreactor (MBR): cost estimation of aeration and sludge treatment. Water Research . 38, 37–46.

Yu, Y. Hu, X. Xu, K. Wang, L and Wang, Y. 2005b. Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH_3 plasma treatment. Sep. Purif. Technol. 45, 8–15.

Yu, Y. Xie, J. Hu, X. Wang, L. Wang, Y and Xu, K. 2005a. Surface modification of polypropylene microporous membrane to improve its antifouling property in MBR: CO_2 plasma treatment. J. Membrane Sci. 254, 219–227.

Zhang, Y. Wang, L. Song, J. Hu, S. Ong, W. and Ng, L. 2005. Feasibility investigation of refinery wastewater treatment by combination of PACs and coagulant with ultrafiltration. Desalination. 174, 247–256.

Zhao, G. 2006. Effect of powdered activated carbon dosage on retarding membrane fouling in MBR. Separation and Purification Technology. 52, 154–160.

APPENDIX A

COD Input Calculations for MBR

1. Calculation of COD input

$$\mathrm{HRT} = \frac{V}{J \times A} \qquad (1)$$

Or

$$J = \frac{V}{\mathrm{HRT} \times A}$$

Where HRT is hydraulic retention time (hrs)

V is volume of reactor (L)

A is filtration area (m^2)

J is permeate flux ($L/m^2.hr$)

$$\mathrm{VOLR} = \frac{S_0 \times Q}{V} \qquad (2)$$

Or

$$S_0 = \frac{\mathrm{VOLR} \times V}{Q}$$

Where VOLR is volumetric organic loading rate (g/L·day)

V is volume of reactor (L)

Q is permeate flow rate (L/day)

S_0 is COD input (mg/L)

Table A1 Values of operation parameters used in calculations.

Parameters	Unit	Values
Filtration area (A)	m^2	0.23
Volume of reactor (V)	L	50
Hydraulic retention time (HRT)	hrs	15, 12, 9, 6
Volumetric organic loading rate (VOLR)	g/L·day	1, 2, 3

Table A2 COD input calculations for MBR.

OLR (g/L·day)	Volume of reactor (L)	HRT (hrs)	Flux rate (L/m^2·hr)	Permeate flow rate (L/hr)	Permeate flow rate (L/day)	COD input (mg/L)
1	50	6	36	8	200	250
1	50	9	24	6	133	375
1	50	12	18	4	100	500
1	50	15	14	3	80	625
2	50	6	36	8	200	500
2	50	9	24	6	133	750
2	50	12	18	4	100	1,000
2	50	15	14	3	80	1,250
3	50	6	36	8	200	750
3	50	9	24	6	133	1,125
3	50	12	18	4	100	1,500
3	50	15	14	3	80	1,875

APPENDIX B

One-way ANOVA with post-hoc corrected t-tests for pre-research data

Table B1. Single factor (Anova) for COD analysis.

pH	Count	Sum	Average	Variance	Std. Dev.	Low	High
pH 2	5	51,364	10,273	5,524	74	10,198	10,347
pH 2.5	5	53,089	10,618	4,470	67	10,551	10,685
pH 3	5	83,711	16,742	4,019	63	16,679	16,806

* COD value = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.32E+08	2	66233697	14179.67	0.0000	3.8852938
Within Groups	56052.4	12	4671.033			
Total	1.33E+08	14				

Table B2. t-test for COD analysis.

pH	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
pH 2 vs pH 2.5	5.65503E-05	0.01667	True
pH 2 vs pH 3	4.83701E-15	0.01667	True
pH 2.5 vs pH 3	4.69647E-15	0.01667	True

* α = 0.05 (fixed), n = 3 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

Table B3. Single factor (Anova) for BOD analysis.

pH	Count	Sum	Average	Variance	Std. dev.	Low	High
pH 2	5	112,983	22,597	3,814	62	22,535	22,658
pH 2.5	5	118,025	23,605	4,556	67	23,538	23,672
pH 3	5	123,509	24,702	3,911	63	24,639	24,764

* BOD value = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	11086180	2	5543090	1354.12	0.0000	3.8852938
Within Groups	49122	12	4093.5			
Total	11135302	14				

Table B4. t-test for BOD analysis.

pH	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
pH 2 vs pH 2.5	7.84468E-09	0.01667	True
pH 2 vs pH 3	1.63769E-11	0.01667	True
pH 2.5 vs pH 3	4.22343E-09	0.01667	True

* α = 0.05 (fixed), n = 3 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

Table B5. Single factor (Anova) for O&G analysis.

pH	Count	Sum	Average	Variance	Std. Dev.	Low	High
pH 2	5	7,604	1,521	72.7	9	1,512	1,529
pH 2.5	5	12,055	2,411	131	11	2,400	2,422
pH 3	5	16,234	3,247	188.7	14	3,233	3,261

* O&G value = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	7450156	2	3725078	28479.19	0.0000	3.8852938
Within Groups	1569.6	12	130.8			
Total	7451726	14				

Table B6. t-test for O&G analysis.

pH	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
pH 2 vs pH 2.5	7.81193E-15	0.01667	True
pH 2 vs pH 3	1.06173E-16	0.01667	True
pH 2.5 vs pH 3	7.84053E-14	0.01667	True

* α = 0.05 (fixed), n = 3 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

APPENDIX C

One-way Anova with post-hoc corrected t-tests for MBR data

1. COD analysis for 10days operation

Table C1. Single factor (Anova) for OLR of 1 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	37.65	13	0.084	0.29	12.26	12.84
12	3	54.1	18	0.006	0.08	17.96	18.11
9	3	75.26	25	0.042	0.20	24.88	25.29
6	3	66.41	22	0.017	0.13	22.01	22.27

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	265.8214	3	88.60712	2391.555	0.0000	4.066181
Within Groups	0.2964	8	0.03705			
Total	266.1178	11				

Table C2. t-test for COD analysis at OLR of 1 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	5.85954E-06	0.0125	True
15 hrs vs 9 hrs	4.23874E-07	0.0125	True
15 hrs vs 6 hrs	7.98965E-07	0.0125	True
12 hrs vs 9 hrs	6.05603E-07	0.0125	True
12 hrs vs 6 hrs	1.21522E-06	0.0125	True
9 hrs vs 6 hrs	2.99498E-05	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

Table C3. Single factor (Anova) for OLR of 2 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	79.48	26	0.024	0.16	26.34	26.65
12	3	153.53	51	0.021	0.15	51.03	51.32
9	3	144.17	48	0.004	0.06	48.00	48.12
6	3	138.37	46	0.016	0.13	46.00	46.25

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1123.942	3	374.6474	23257.99	0.0000	4.066181
Within Groups	0.128867	8	0.016108			
Total	1124.071	11				

Table C4. t-test for COD analysis at OLR of 2 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	3.66318E-09	0.0125	True
15 hrs vs 9 hrs	2.37703E-09	0.0125	True
15 hrs vs 6 hrs	7.0985E-09	0.0125	True
12 hrs vs 9 hrs	4.25667E-06	0.0125	True
12 hrs vs 6 hrs	1.37011E-06	0.0125	True
9 hrs vs 6 hrs	1.7512E-05	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

Table C5. Single factor (Anova) for OLR of 3 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	171.11	57	0.007	0.08	56.96	57.12
12	3	240.09	80	0.006	0.08	79.95	80.11
9	3	240.07	80	0.008	0.09	79.94	80.11
6	3	205.55	69	0.025	0.16	68.36	68.68

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1090.373	3	363.4577	31605.02	0.0000	4.066181
Within Groups	0.092	8	0.0115			
Total	1090.465	11				

Table C6. t-test for COD analysis at OLR of 3 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	3.98932E-10	0.0125	True
15 hrs vs 9 hrs	4.85986E-10	0.0125	True
15 hrs vs 6 hrs	3.9447E-08	0.0125	True
12 hrs vs 9 hrs	0.927	0.0125	False
12 hrs vs 6 hrs	3.81861E-08	0.0125	True
9 hrs vs 6 hrs	4.15576E-08	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

2. COD analysis for 15days operation

Table C7. Single factor (Anova) for OLR of 1 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	26.19	9	0.007	0.09	8.64	8.82
12	3	44.61	15	0.012	0.11	14.76	14.98
9	3	55.27	18	0.172	0.41	18.01	18.84
6	3	54.36	18	0.012	0.11	18.01	18.23

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	182.3348	3	60.77828	1199.177	0.0000	4.066181
Within Groups	0.405467	8	0.050683			
Total	182.7403	11				

Table C8. t-test for COD analysis at OLR of 1 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	1.76337E-07	0.0125	True
15 hrs vs 9 hrs	2.40748E-06	0.0125	True
15 hrs vs 6 hrs	3.09418E-08	0.0125	True
12 hrs vs 9 hrs	0.000136718	0.0125	True
12 hrs vs 6 hrs	3.36789E-06	0.0125	True
9 hrs vs 6 hrs	0.287087414	0.0125	False

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

Table C9. Single factor (Anova) for OLR of 2 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	63.59	21	0.019	0.14	21.06	21.33
12	3	122.57	41	0.017	0.13	40.73	40.99
9	3	114.04	38	0.010	0.10	37.91	38.11
6	3	113.48	38	0.002	0.04	37.79	37.87

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	722.3798	3	240.7933	20305.83	0.0000	4.066181
Within Groups	0.094867	8	0.011858			
Total	722.4747	11				

Table C10. t-test for COD analysis at OLR of 2 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	5.67559E-09	0.0125	True
15 hrs vs 9 hrs	6.89652E-09	0.0125	True
15 hrs vs 6 hrs	3.57959E-09	0.0125	True
12 hrs vs 9 hrs	7.47195E-06	0.0125	True
12 hrs vs 6 hrs	2.74354E-06	0.0125	True
9 hrs vs 6 hrs	0.040715535	0.0125	False

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

Table C11. Single factor (Anova) for OLR of 3 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	129.7	43	0.011	0.10	43.13	43.34
12	3	189.1	63	0.006	0.08	62.96	63.11
9	3	203.54	68	0.008	0.09	67.76	67.94
6	3	184.93	62	0.005	0.07	61.57	61.71

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1050.274	3	350.0915	46939.64	0.0000	4.066181
Within Groups	0.059667	8	0.007458			
Total	1050.334	11				

Table C12. t-test for COD analysis at OLR of 3 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	1.19036E-09	0.0125	True
15 hrs vs 9 hrs	6.60307E-10	0.0125	True
15 hrs vs 6 hrs	1.4609E-09	0.0125	True
12 hrs vs 9 hrs	2.41952E-07	0.0125	True
12 hrs vs 6 hrs	2.04481E-05	0.0125	True
9 hrs vs 6 hrs	7.9177E-08	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No significant difference between the values.

3. O&G analysis for 10 days operation

Table C13. Single factor (Anova) for OLR of 1 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	33.38	11	0.014	0.12	11.01	11.24
12	3	71.3	24	0.012	0.11	23.66	23.88
9	3	115.88	39	0.028	0.17	38.46	38.79
6	3	179.28	60	0.006	0.08	59.68	59.84

* O&G values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3933.134	3	1311.045	87548.88	0.0000	4.066181
Within Groups	0.1198	8	0.014975			
Total	3933.253	11				

Table C14. t-test for O&G analysis at OLR of 1 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	1.74681E-08	0.0125	True
15 hrs vs 9 hrs	1.98483E-09	0.0125	True
15 hrs vs 6 hrs	4.78267E-11	0.0125	True
12 hrs vs 9 hrs	2.1721E-08	0.0125	True
12 hrs vs 6 hrs	1.37907E-10	0.0125	True
9 hrs vs 6 hrs	3.87055E-09	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No difference between the values.

Table C15. Single factor (Anova) for OLR of 2 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	46.99	16	0.014	0.12	15.54	15.78
12	3	88.37	29	0.013	0.11	29.34	29.57
9	3	127.65	43	0.013	0.12	42.43	42.67
6	3	185.69	62	0.001	0.03	61.87	61.92

* O&G values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3486.564	3	1162.188	113384.2	0.0000	4.066181
Within Groups	0.082	8	0.01025			
Total	3486.646	11				

Table C16. t-test for O&G analysis at OLR of 2 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	1.34885E-08	0.0125	True
15 hrs vs 9 hrs	9.81133E-10	0.0125	True
15 hrs vs 6 hrs	3.31219E-11	0.0125	True
12 hrs vs 9 hrs	1.52503E-08	0.0125	True
12 hrs vs 6 hrs	1.05949E-10	0.0125	True
9 hrs vs 6 hrs	9.23758E-10	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No difference between the values.

Table C17. Single factor (Anova) for OLR of 3 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	65.3	22	0.012	0.11	21.66	21.88
12	3	91.84	31	0.028	0.17	30.45	30.78
9	3	148	49	0.010	0.10	49.23	49.43
6	3	205.59	69	0.021	0.15	68.38	68.68

* O&G values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3886.213	3	1295.404	72368.97	0.0000	4.066181
Within Groups	0.1432	8	0.0179			
Total	3886.357	11				

Table C18. t-test for O&G analysis at OLR of 3 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	1.78027E-07	0.0125	True
15 hrs vs 9 hrs	5.7234E-10	0.0125	True
15 hrs vs 6 hrs	1.54892E-10	0.0125	True
12 hrs vs 9 hrs	7.94733E-09	0.0125	True
12 hrs vs 6 hrs	7.84939E-10	0.0125	True
9 hrs vs 6 hrs	4.75746E-09	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No difference between the values.

4. O&G analysis for 15days operation

Table C19. Single factor (Anova) for OLR of 1 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	26.35	9	0.038	0.20	8.59	8.98
12	3	57.1	19	0.006	0.08	18.96	19.11
9	3	98.52	33	0.005	0.07	32.77	32.91
6	3	155.43	52	0.025	0.16	51.65	51.97

* O&G values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3119.906	3	1039.969	56468.89	0.0000	4.066181
Within Groups	0.147333	8	0.018417			
Total	3120.053	11				

Table C20. t-test for O&G analysis at OLR of 1 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	1.15584E-07	0.0125	True
15 hrs vs 9 hrs	3.71991E-09	0.0125	True
15 hrs vs 6 hrs	7.65459E-10	0.0125	True
12 hrs vs 9 hrs	2.19282E-09	0.0125	True
12 hrs vs 6 hrs	5.3496E-10	0.0125	True
9 hrs vs 6 hrs	4.60152E-09	0.0125	True

* $\alpha = 0.05$ (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No difference between the values.

Table C21. Single factor (Anova) for OLR of 2 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. dev.	Low	High
15	3	41.43	14	0.0247	0.16	13.65	13.97
12	3	75.7	25	0.006533	0.08	25.15	25.31
9	3	119.61	40	0.0121	0.11	39.76	39.98
6	3	164.58	55	0.0112	0.11	54.75	54.97

* O&G values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2858.543	3	952.8475	69891.02	0.0000	4.066181
Within Groups	0.109067	8	0.013633			
Total	2858.652	11				

Table C22. t-test for O&G analysis at OLR of 2 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	3.81718E-08	0.0125	True
15 hrs vs 9 hrs	1.95729E-09	0.0125	True
15 hrs vs 6 hrs	3.02569E-10	0.0125	True
12 hrs vs 9 hrs	5.0424E-09	0.0125	True
12 hrs vs 6 hrs	2.72106E-10	0.0125	True
9 hrs vs 6 hrs	7.16661E-09	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No difference between the values.

Table C23. Single factor (Anova) for OLR of 3 g/L·day.

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.	Low	High
15	3	53.32	18	0.011	0.11	17.67	17.88
12	3	89.55	30	0.010	0.10	29.75	29.95
9	3	128.31	43	0.011	0.11	42.66	42.88
6	3	191.24	64	0.007	0.08	63.67	63.83

* O&G values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3480.118	3	1160.039	117870.2	0.0000	4.066181
Within Groups	0.078733	8	0.009842			
Total	3480.197	11				

Table C24. t-test for O&G analysis at OLR of 3 g/L·day.

HRTs	P (T<=t) two-tail	Bonferroni correction (α/n)	True/False
15 hrs vs 12 hrs	1.47989E-08	0.0125	True
15 hrs vs 9 hrs	8.66955E-10	0.0125	True
15 hrs vs 6 hrs	4.81739E-11	0.0125	True
12 hrs vs 9 hrs	1.09537E-08	0.0125	True
12 hrs vs 6 hrs	1.43089E-10	0.0125	True
9 hrs vs 6 hrs	1.07052E-09	0.0125	True

* α = 0.05 (fixed), n = 4 (number of comparison), True = Significant difference between the values, False = No difference between the values.

Table C25: Results of data collection for all parameters at HRT of 15 hours (shaded row indicates day of membrane clogging).

Days	HRT (hrs)	OLR (g/L.day)	Flux (L/m^2.hr)	TMP (mmHg)	TMP (mmbar)	MLSS (mg/L)	DO (mg/L)	Avg particle Size (µm)	Protein (mg/L)	Polysacharride (mg/L)	MLVSS (mg/L)	MLVSS/MLSS
1	15	1	12	130	173.32	2140	3.5	10.00	5.45	4.34	1100	0.514
2	15	1	12	130	173.32	2140	3.5	10.00	5.45	4.34	1100	0.514
3	15	1	12	135	179.98	2234	3.47	10.45	6.76	5.27	1154	0.517
4	15	1	12	140	186.65	2276	3.41	10.98	6.76	5.27	1185	0.521
5	15	1	12	140	186.65	2323	3.41	11.29	7.54	5.92	1212	0.522
6	15	1	12	150	199.98	2387	3.38	11.29	7.54	5.92	1245	0.522
7	15	1	12	160	213.31	2399	3.32	11.29	7.54	5.92	1257	0.524
8	15	1	12	170	226.64	2445	3.24	12.37	7.94	6.02	1283	0.525
9	15	1	12	185	246.64	2487	3.18	12.37	7.94	6.02	1312	0.528
10	15	1	12	200	266.64	2543	3.12	12.87	8.54	7.65	1344	0.529
11	15	1	12	210	279.97	2577	3.04	13.12	8.54	7.65	1364	0.529
12	15	1	12	215	286.64	2598	2.99	13.12	8.54	7.65	1379	0.531
13	15	1	12	230	306.64	2776	2.92	13.98	9.12	8.27	1484	0.535
14	15	1	12	245	326.63	2878	2.92	14.43	9.48	8.75	1540	0.535
15	15	1	12	260	346.63	2987	2.9	14.40	10.34	9.02	1599	0.535
16	15	1	12	280	373.30	3045	2.89	14.98	11.87	10.98	1645	0.540
17	15	1	12	300	399.96	3120	2.86	15.90	12.87	11.24	1684	0.540
18	15	2	12	150	199.98	3300	2.75	18.76	22.15	21.17	1844	0.559
19	15	2	12	155	206.65	3465	2.75	18.76	22.15	21.17	1939	0.560
20	15	2	12	160	213.31	3676	2.74	19.12	22.15	21.67	2058	0.560
21	15	2	12	170	226.64	3687	2.71	19.12	22.35	21.72	2068	0.561
22	15	2	12	180	239.98	3798	2.69	19.12	22.38	21.98	2132	0.561
23	15	2	12	190	253.31	3876	2.69	19.34	22.45	22.02	2178	0.562

24	15	2	12	205	273.31	4112	2.67	20.12	22.55	22.1	2317	0.563
25	15	2	12	220	293.30	4312	2.65	21.34	22.58	22.25	2427	0.563
26	15	2	12	230	306.64	4387	2.62	21.34	22.58	22.25	2468	0.563
27	15	2	12	240	319.97	4465	2.62	21.98	22.78	22.38	2520	0.564
28	15	2	12	245	326.63	4498	2.62	21.98	23.12	22.57	2537	0.564
29	15	2	12	250	333.30	4598	2.59	22.12	23.22	22.72	2598	0.565
30	15	2	12	270	359.96	4786	2.58	22.54	23.56	22.86	2714	0.567
31	15	2	12	285	379.96	4897	2.58	22.54	23.87	22.98	2787	0.569
32	15	2	12	300	399.96	5000	2.57	23	24.46	23.12	2844	0.569
33	15	3	12	160	213.31	5243	2.32	25.6	24.65	23.14	3193	0.609
34	15	3	12	170	226.64	5310	2.32	27.7	24.65	23.14	3234	0.609
35	15	3	12	180	239.98	5421	2.32	30.12	24.78	23.34	3318	0.612
36	15	3	12	190	253.31	5498	2.28	30.12	24.85	23.54	3365	0.612
37	15	3	12	200	266.64	5543	2.25	30.32	25.34	24.15	3398	0.613
38	15	3	12	215	286.64	5587	2.25	30.28	25.34	24.15	3436	0.615
39	15	3	12	230	306.64	5698	2.2	30.25	25.54	24.15	3503	0.615
40	15	3	12	245	326.63	5897	2.15	30.20	26.12	25.21	3639	0.617
41	15	3	12	260	346.63	6012	2.12	30.18	26.78	25.45	3712	0.617
42	15	3	12	275	366.63	6354	2.08	30.18	27.12	26.53	3927	0.618
43	15	3	12	290	386.63	6523	2.08	30.13	27.87	26.78	4033	0.618
44	15	3	12	300	399.96	6654	2.05	30.10	29.76	28.12	4121	0.619
Mean Value						**3999**	**2.73**	**19.98**	**18.12**	**17.07**	**2299.93**	**0.56**

Table C26: Results of data collection for all parameters at HRT of 12 hours (shaded row indicates day of membrane clogging).

Days	HRT (hrs)	OLR (g/L.day)	Flux (L/m^2.hr)	TMP (mmHg)	TMP (mmbar)	MLSS (mg/L)	Do (mg/L)	Avg particle Size (μm)	Protein (mg/L)	Polysacharride (mg/L)	MLVSS (mg/L)	MLVSS/MLSS
1	12	1	14	145	193.31	2240	3.42	12.0	6.65	5.78	1243	0.555
2	12	1	14	155	206.65	2240	3.42	12.0	6.65	5.78	1243	0.555
3	12	1	14	170	226.64	2300	3.42	13.0	6.95	5.68	1294	0.563
4	12	1	14	185	246.64	2398	3.4	13.0	7.87	6.42	1358	0.566
5	12	1	14	205	273.31	2487	3.38	14.7	9.44	8.34	1411	0.567
6	12	1	14	220	293.30	2498	3.38	14.7	12.76	11.21	1424	0.570
7	12	1	14	235	313.30	2576	3.32	15.6	14.54	13.17	1475	0.573
8	12	1	14	250	333.30	2624	3.3	15.6	16.87	15.22	1511	0.576
9	12	1	14	265	353.30	2698	3.28	16.0	18.47	16.87	1563	0.579
10	12	1	14	280	373.30	2853	3.26	16.9	18.98	17.72	1667	0.584
11	12	1	14	295	393.29	3298	3.25	18.8	21.43	20.65	1958	0.594
12	12	1	14	300	399.96	3599	2.23	19.9	23.54	22.41	2143	0.595
13	12	2	14	140	186.65	2900	2.12	25.8	28.45	26.78	1750	0.603
14	12	2	14	150	199.98	3043	2.11	25.8	28.65	26.91	1849	0.608
15	12	2	14	155	206.65	3287	2.09	26.0	29.45	28.57	2034	0.619
16	12	2	14	170	226.64	3486	2.09	27.5	30.23	29.76	2174	0.624
17	12	2	14	190	253.31	3687	2.09	28.0	30.67	29.85	2303	0.625
18	12	2	14	215	286.64	3874	2.08	28.8	30.98	29.92	2437	0.629
19	12	2	14	235	313.30	4638	2.05	30.0	31.24	30.15	2935	0.633
20	12	2	14	260	346.63	5287	2.03	30.5	31.98	30.87	3375	0.638
21	12	2	14	290	386.63	5897	2	32	33.87	32.32	3770	0.639
22	12	3	14	150	199.98	5012	1.98	34.9	35.98	34.68	3338	0.666
23	12	3	14	170	226.64	5890	1.92	35.8	36.76	35.32	3937	0.668
24	12	3	14	190	253.31	6308	1.87	35.2	37.12	36.21	4214	0.668

25	12	3	14	230	306.64	6905	1.83	35.9	37.48	36.42	4631	0.671
26	12	3	14	276	367.96	7432	1.79	36.9	38.98	37.78	4999	0.673
27	12	3	14	300	399.96	7643	1.75	38.7	40.02	39.23	5141	0.673
Mean value						**3967**	**2.55**	**24.20**	**24.67**	**23.48**	**2488.04**	**0.61**

Table C27: Results of data collection for all parameters at HRT of 9 hours (shaded row indicates day of membrane clogging).

Days	**HRT (hrs)**	**OLR (g/L.day)**	**Flux (L/m^2.hr)**	**TMP (mmHg)**	**TMP (mmbar)**	**MLSS (mg/L)**	**DO (mg/L)**	**Avg particle Size (μm)**	**Protein (mg/L)**	**Polysacharride (mg/L)**	**MLVSS (mg/L)**	**MLVSS/MLSS**
1	9	1	19	160	213.31	2254	2.72	8.0	8.98	7.87	1254	0.556
2	9	1	19	175	233.31	2300	2.69	9.0	20.45	19.97	1298	0.564
3	9	1	19	190	253.31	2387	2.69	9.0	22.43	21.22	1356	0.568
4	9	1	19	205	273.31	2539	2.69	11.2	22.53	21.87	1465	0.577
5	9	1	19	215	286.64	2887	2.53	15.8	22.73	22.12	1676	0.581
6	9	1	19	240	319.97	3598	2.38	18.9	22.93	22.76	2096	0.583
7	9	1	19	270	359.96	4898	2.22	21.3	23.03	22.87	2897	0.591
8	9	1	19	290	386.63	5432	2.12	23.8	23.13	22.98	3243	0.597
9	9	2	19	160	213.31	5534	1.76	28.9	38.65	37.74	3456	0.625
10	9	2	19	170	226.64	6000	1.71	29.1	38.85	37.87	3867	0.645
11	9	2	19	190	253.31	6598	1.71	30.3	39.12	38.98	4374	0.663
12	9	2	19	220	293.30	7834	1.68	31.3	40.43	39.12	5267	0.672
13	9	2	19	255	339.97	8457	1.67	32.3	42.65	40.15	5787	0.684
14	9	2	19	275	366.63	8912	1.67	32.9	43.99	42.78	6224	0.698
15	9	2	19	290	386.63	9743	1.65	34.0	44.43	43.44	6853	0.703
16	9	3	19	180	239.98	9759	1.34	42.8	47.87	46.77	6902	0.707
17	9	3	19	205	273.31	10537	1.32	45.3	48.12	47.21	7536	0.715
18	9	3	19	245	326.63	12984	1.25	48.4	49.98	48.87	9345	0.720
19	9	3	19	270	359.96	13545	1.18	53.6	51.43	49.87	9791	0.723

20	9	3	19	300	399.96	14540	1.12	58.7	52.12	51.65	10540	0.725
Mean value						**7037**	**1.91**	**29.23**	**35.19**	**34.31**	**4761.35**	**0.64**

Table C28: Results of data collection for all parameters at HRT of 6 hours (shaded row indicates day of membrane clogging).

Days	**HRT (hrs)**	**OLR (g/L.day)**	**Flux (L/m^2.hr)**	**TMP (mmHg)**	**TMP (mmbar)**	**MLSS (mg/L)**	**DO (mg/L)**	**Avg particle Size (µm)**	**Protein (mg/L)**	**Polysacharride (mg/L)**	**MLVSS (mg/L)**	**MLVSS/MLSS**
1	6	1	29	190	253.31	2343	3.23	10.0	6.09	5.54	1243	0.531
2	6	1	29	205	273.31	3823	2.78	21.0	10.54	9.76	2134	0.558
3	6	1	29	220	293.30	6425	2.55	29.4	15.34	14.23	3621	0.564
4	6	1	29	250	333.30	7873	2.48	32.5	20.45	19.98	4476	0.569
5	6	1	29	270	359.96	8143	2.41	35.7	27.15	26.12	4776	0.587
6	6	1	29	290	386.63	8400	2.34	38.8	38.16	36.98	4943	0.588
7	6	2	29	190	253.31	9430	2.07	40.8	52.54	51.32	7543	0.660
8	6	2	29	225	299.97	13200	1.87	45.6	55.13	53.86	9232	0.699
9	6	2	29	260	346.63	14961	1.56	50.4	57.12	56.78	11232	0.751
10	6	2	29	290	386.63	13454	1.66	49.7	58.71	57.21	10543	0.784
11	6	3	29	215	286.64	14893	1.34	55.8	59.32	58.13	12922	0.813
12	6	3	29	250	333.30	16832	1.12	62.8	59.98	58.12	14005	0.832
13	6	3	29	290	386.63	17000	0.9	69.7	62.12	61.12	14321	0.842
Mean value						**10521**	**2.02**	**41.69**	**40.20**	**39.17**	**7768.54**	**0.68**

APPENDIX D

FULFILLMENT OF OBJECTIVES AND PLANNED ACTIVITIES

D.1 Fulfillment of Objectives

Objectives	Results
1. To investigate the effects of pre-treatment of wastewater from a biodiesel plant with alkali-catalyzed trans-esterification process using H_2SO_4 at different pH range (2.4-6) on the removal efficiencies of BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand) and Oil & Grease .	1. In pretreatment step, H_2SO_4 with different pH (2, 2.5 and 3) was used to treat the wastewater of biodiesel plant. Significant reduction in organic pollutants was obtained at pH of 2.5 of due to strong protonation effect of H_2SO_4. COD and O&G were found to be 74.1-84.1% and 84.2-92.6%, respectively. It was concluded that pH of 2.5 was optimum, which reduced the organic pollutants from wastewater significantly, while there was small significant difference in organic pollutants were observed when pH of 2.5 was compared with pH of 2.
2. To investigate the performance of MBR at different HRTs (hydraulic retention times) for the removal efficiencies of COD, BOD and Oil & Grease in wastewater from a biodiesel plant.	2. It was observed that COD and O&G removal efficiency in the bioreactor slightly decreased with decreasing HRT, while the overall efficiency of COD and O&G after 15 days of operation remained in the range of 91.7-97.7% and 95.5-97.9%, respectively, and from statistical analysis, the O&G removal efficiency was significantly reduced with decreasing HRT. Moreover, the COD and O&G values in MBR effluent was compared with EPA standards, it was found that COD values < 150 mg/L at all HRTs while O&G values found to be greater than 10 mg/L (EPA standard) at different HRTs. Increased in O&G concentration in MBR effluent was resulted due to an

	increase of O&G conc. in feed water. It was observed that when O&G concentration increased more than 690 mg/L in feed which caused a decrease in efficiency of the MBR.
3. To study factors affecting the rate of membrane fouling, develop a model of the fouling mechanism and suggest prevention methods.	3. HRT was correlated with dissolved oxygen (DO), particle size distribution (PDS) and protein and polysaccharide contents of soluble microbial product (SMP) in order to investigate their impact on membrane fouling mechanism. Trans-membrane pressure (TMP) about 50 kPa achieved within 3-6 days at HRT of 6 hrs. It was concluded that both SMP_p and SMP_c played active roles in membrane fouling.

D.2 Planned (arrows) and Completed Activities (shaded region)

Activities	Month											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1. Literature Review	▨ ↔	▨ ↔										
2. Group Meetings	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔
3. Study pretreatment effect of pH on BOD, COD, and Oil & Grease removal		▨ ↔	▨ ↔									
4. Design of bioreactors and MBR tank			▨ ↔	▨								
5. Test equipment/ Cultivation of bacterial				▨ ↔	▨ ↔							
6. Study effect of HRT of the aerobic/MBR process on BOD, COD, and Oil & Grease removal				▨ ↔	▨ ↔	▨ ↔	▨ ↔	▨ ↔				
7. Study effect of HRT and COD loading on rate of fouling							▨ ↔	▨ ↔	▨ ↔	▨ ↔		
8. Statistical Analysis							↔	↔	▨ ↔	▨ ↔	▨	
9. Conference Participation					▨	▨			↔	↔		
10. Economic Analysis										▨ ↔	▨ ↔	
11. Manuscript Write-up[1]					▨ ↔	▨ ↔	▨ ↔			▨ ↔	▨ ↔	▨ ↔
12. Technology Transfer[2]											↔	↔
13. Mid-Term/Final Report[3]						↔						▨ ↔

[1] First manuscript as a review paper needs to be resubmitted, while second manuscript covering the entire research results has been accepted with major revision.

[2] No technology transfer has been conducted accept through conference participation.

[3] The mid-term and final report have been combined into a single report.

APPENDIX E

INTERNATIONAL CONFERENCES AND JOURNAL SUBMISSION

Conference Presentations:

1. Khan, Y.A., Yamsaengsung, R., and Chetpattananondh, P., and Khongnakorn, W. 2011. **Review of wastewater treatment methods and MBR technology for application in biodiesel plants.** The 21st Thai Institute of Chemical Engineering and Applied Chemistry Conference; 10-11 November 2011. Hat Yai, Thailand.

2. Khan, Y.A., Yamsaengsung, R., and Chetpattananondh, P., and Khongnakorn, W. 2012. **Designing of MBR for wastewater treatment of biodiesel plant.** The 22nd Thai Institute of Chemical Engineering and Applied Chemistry Conference; 25-26 October 2012. Nakornratchasima, Thailand.

Journal Submission:

1. Khan, Y.A., Yamsaengsung, R., and Chetpattananondh, P., and Khongnakorn, W. **Treatment of Wastewater from Biodiesel Plant Using MBR Technology**. Submitted to **International Journal of Environmental Science and Technology**, **Impact Factor, 3.157**. Under Revision.