

Treatment of Wastewater from Biodiesel Plant Using MBR Technology

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A Thesis Submitted in Fulfillment of the Requirements for the Degree of Master of Engineering in Chemical Engineering Prince of Songkla University

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ABSTRACT

Biodiesel wastewater contains high amount of organic pollutants; therefore, pretreatment of biodiesel wastewater with H₂SO₄ was used followed by MBR treatment. In pretreatment step, H₂SO₄ with different pH of 2, 2.5 and 3 added to biodiesel wastewater and significant reduction in organic pollutants were observed at pH of 2.5 such COD and oil and grease (O&G) were found to be 74-84% and 84.2-92.6%, respectively. In second step, MBR was operated at different HRTs of 15, 12, 9 and 6 hrs along with increased in OLRs (range from 1-3 g/L·day) on individual HRT. However, overall COD and O&G removal efficiency remained in the range of 91.7-97.20% and 95.5-97.9%, respectively. Membrane fouling mechanism correlated with HRT along with its impact on DO, MLSS, particle size and SMP. Decreased in HRT, caused to decrease in DO concentration due to increase in higher oxygen utilization rate at lower HRT while MLSS, particle size and SMP were found increasing in trend. At lower HRT of 6 hrs, increased in particle size reported as 27.9-62.7 µm while SMP_n and SMP_c reported as 20-60 mg/L and 19-59 mg/L, respectively. Higher the SMP level caused to increase the particle size with irregular shape, which led to severe membrane fouling.

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CHAPTER 1

INTRODUCTION

1.1 Rational/ Problem Statement

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 litres 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/m³ (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 economic way for 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 became 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 fulfil 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.

1.2 Research Objectives

1) To study the performance of aerobic MBR for wastewater treatment of biodiesel plant.

2) To evaluate optimum operational parameters for smooth operation of MBR such as HRTs, OLRs and dissolved oxygen (DO) concentration.

3) To find out the influencing factors which are involved in membrane fouling.

1.3 Scopes of Research Work

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.

1.4 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 2

THEORY AND LITERATURE REVIEW

2.1 Membrane Technology

2.1.1 Membranes and membrane separation processes

A membrane as applied to water and wastewater treatment is simply a material that allows some physical or chemical components to pass more readily through it than others. It is thus perm-selective, since it is more permeable to those constituents passing through it (which then become the permeate) than those which are rejected by it (which form the retentate). The degree of selectivity depends on the membrane pore size. The four key membrane separation processes in which water forms the permeate product are RO, nanofiltration (NF), ultrafiltration (UF) and MF (Fig. 2.1).

Membranes themselves can thus be defined according to the type of separation duty to which they can be put, which then provides an indication of the pore size. The range of membrane processes available is given in Table 2.1, along with an outline of the mechanism by which each process operates. Membrane technologies as applied to the municipal sector are predominantly pressure driven and, whilst the membrane permselectivity and separation mechanism may vary from process to another, such processes all have the common elements of a purified permeate product and a concentrated retentate waste (Fig. 2.2).

2.1.2 Membrane materials

There are mainly two different types of membrane material, these being polymeric and ceramic. Metallic membrane filters also exist, but these have very specific applications which do not relate to membrane bioreactor (MBR) technology. The membrane material, to be made useful, must then be formed (or configured) in such a way as to allow water to pass through it. A number of different polymeric and ceramic materials are used to form membranes, but generally nearly always comprise a thin surface layer which provides the required permselectivity on top of a more open, thicker porous support which provides mechanical stability. A classic membrane is thus anisotropic in structure, having symmetry only in the plane orthogonal to the membrane surface (Fig. 2.3).



Figure 2.1 Membrane separation processes overview (Judd and Jefferson, 2003).



Figure 2.2 Schematic of membrane.

Polymeric membranes are also usually fabricated both to have a high surface porosity, or % total surface pore cross-sectional area (Fig. 2.4), and narrow pore size distribution to provide as high a throughput and as selective a degree of rejection as possible.

Whilst, in principal, any polymer can be used to form a membrane, only a limited number of materials are suitable for the duty of membrane separation, the most common being:

- Polyvinylidene difluoride (PVDF)
- Polyethylsulphone (PES)
- Polyethylene (PE)
- Polypropylene (PP)

All the above polymers can be formed, through specific manufacturing techniques, into membrane materials having desirable physical properties, and they each have reasonable chemical resistance. However, they are also hydrophobic, which makes the susceptible to fouling by hydrophobic matter in the bioreactor liquors they are filtering. This normally necessitates surface modification of the base material to produce a hydrophilic surface using such techniques as chemical oxidation, organic chemical reaction, plasma treatment or grafting.

2.1.3 Membrane configurations

The configuration of the membrane, that is, its geometry and the way it is mounted and oriented in relation to the flow of water, is crucial in determining the overall process performance. There are six principal configurations currently employed in membrane processes, which all have various practical benefits and limitations (Table 2.2). The configurations are based on either a planar or cylindrical geometry and comprise:

- 1) Plate-and-frame/flat sheet (FS)
- 2) Hollow fibre (HF)
- 3) (Multi)tubular (MT)
- 4) Capillary tube (CT)
- 5) Pleated filter cartridge (FC) and 6) Spiral-wound.

Pressure-driven	Extractive/diffusive
Reverse osmosis (RO)	Electrodialysis (ED)
Separation achieved by virtue of differing	Separation achieved by virtue of
solubility and diffusion rates of water	differing ionic size, charge and charge
(solvent)	density of solute ions, using ion-
and solutes in water.	exchange membranes.
Nanofiltration (NF)	Pervaporation (PV)
Formerly called <i>leaky RO</i> . Separation	Same mechanism as RO but with the
achieved	(volatile) solute partially vapourised in
through combination of charge rejection,	the membrane by partially vacuumating
solubility-diffusion and sieving through	the permeate.
micropores (<2 nm).	
Ultrafiltration (UF)	Membrane extraction (ME)
Separation by sieving through mesopores	Constituent removed by virtue of a
(2–50 nm)*.	concentration gradient between retentate
	and permeate side of membrane.
Microfiltration (MF)	Gas transfer (GT)
Separation of suspended solids from water	Gas transferred under a partial pressure
by	gradient into or out of water in
sieving through macropores (>50 nm)*.	molecular form.

Table 2.1 Dense and porous membranes for water treatment (IUPAC, 1985).



Figure 2.3 Anisotropic UF membranes: (a) polymeric (thickness of "skin indicated) and (b) ceramic (by kind permission of Ionics (a) and Pall (b)).



Figure 2.4 Surface of membrane and pore-size distribution with respect to rejection of homodispersed latex (by kind permission of Asahi-Kasei).

Of the above configurations, only the first three (Fig. 2.5, Table 2.2) are suited to MBR technologies because selection criteria for membrane configurations depend on module of membranes. The modules must permit turbulence promotion, cleaning or, preferably, both.

Table 2.2 Membrane configurations.

Configuration	Cost	Turbulence promotion	Backflushable?	Application
FC	Very low	Very poor	No	DEMF, low
				TSS waters
FS	High	Fair	No	ED , UF, RO
SW	Low	Poor	No	<i>R0/NF</i> , UF
MT	Very high	Very good	No	CFMF/UF,
				high TSS
				waters, NF
CT	Low	Fair	Yes	UF
HF	Very low	Very poor	Yes	MF/UF, RO

Bold text: most important alternative application; Italic text: MBR configurations.

* Can be <50 for a cassette.

* DE: dead-end, CF: crossflow.

* Capillary tube used in UF: water flows from inside to outside the tubes.

* HF used in MF and RO: water flows from outside to inside the tubes.

The MT module operates with flow passing from inside to outside the tube ("lumen-side" to "shell-side"), whereas the HF operates outside-to-in, the interstitial distance is defined by (Fig. 2.6):

- The tube diameter for a MT
- The distance between the filaments for an HF
- The channel width for an FS



Figure 2.5 (Clockwise from top) FS, MT and HF modules (by kind permission of Kubota, Wehrle & Memcor).



Figure 2.6 Schematics showing flow through membrane configured as: (a) FS, (b) CT or MT and (c) HF.

2.1.4 Membrane process operation

2.1.4.1 Flux, pressure, resistance and permeability

The key elements of any membrane process relate to the influence of the following parameters on the overall permeate flux:

- The membrane resistance
- The operational driving force per unit membrane area
- The hydrodynamic conditions at the membrane: liquid interface
- The fouling and subsequent cleaning of the membrane surface

The flux (normally denoted J) is the quantity of material passing through a unit area of membrane per unit time. This means that it takes SI units of $m^3/m^2/s$, or simply ms⁻¹, and is occasionally referred to as thepermeate or filtration velocity. Other non- SI units used are litres per m² per hour (or LMH) and m/day, which tend to give more accessible numbers: MBRs generally operate at fluxes between 10 and 100 LMH. The flux relates directly to the driving force (i.e. the TMP for conventional MBRs) and the total hydraulic resistance offered by the membrane and the interfacial region adjacent to it. Trans-membrane pressure (TMP) can be calculated by using the resistance-in-series model (Lee et al., 2001).

$$R_{t} = \frac{TMP}{\eta J}$$
(2.1)

$$\mathbf{R}_{\mathrm{t}} = \mathbf{R}_{\mathrm{m}} + \mathbf{R}_{\mathrm{c}} + \mathbf{R}_{\mathrm{f}} \tag{2.2}$$

Where J = permeate flux; TMP = transmembrane pressure; η = dynamic viscosity of the permeate; R_t = total resistance; R_m = intrinsic membrane resistance; R_c = (reversible) cake resistance caused by the cake layer deposited over the membrane surface; and R_f = (irreversible) fouling resistance produced by adsorption of dissolved matter (pore narrowing) and/or pore blockage within the membrane (plugging). According to this model the flux is inversely proportional to the total resistance, the latter being the sum of individual, supposedly discrete resistances.

The resistances are conventionally measured through a series of filtration experiments comprising pure-water filtration, sludge filtration, and pure-water filtration following filter cake removal. However, such experiments are not always practical and, in any case, assume complete decoupling of all resistances. In spite of this, many authors identify components of resistance in their work. For example, the reversible fouling component has been considered as comprising a gel layer resistance coupled with a concentration polarization resistance, these being additive (Choo et al., 1996). However, the validity of differentiating between the various resistance components on the basis of arbitrary physical tests is questionable, and some authors prefer to quote a single resistance value, R_f, including all resistances offered other than that of the clean membrane(Chang et al., 2001).

2.1.4.2 Dead-end and crossflow operation

Conventional pressure-driven membrane processes with liquid permeation can operate in one of two modes. If there is no retentate stream then operation is termed "dead-end" or "full-flow"; if retentate continuously flows from the module outlet then the operation is termed crossflow (Fig. 2.7). Crossflow implies that, for a single passage of feedwater across the membrane, only a fraction is converted to permeate product. This parameter is termed the "conversion" or "recovery". The recovery is reduced further if product permeate is used for maintaining process operation, usually for membrane cleaning.



Figure 2.7 (a) Dead-end and (b) Crossflow filtration.

Filtration always leads to an increase in the resistance to flow. In the case of a dead-end filtration process, the resistance increases according to the thickness of the cake formed on the membrane, which would be expected to be roughly proportional to the total volume of filtrate passed. Rapid permeability decay then results, at a rate proportional to the solids concentration and flux, demanding periodic cleaning (Fig. 2.8). For crossflow processes, this deposition continues until the adhesive forces binding the cake to the membrane are balanced by the scouring forces of the fluid (either liquid or a combination of air and liquid) passing over the membrane.



Figure 2.8 Flux transients for: (a) dead-end and (b) crossflow filtration for constant pressure operation.

Filtration proceeds according to a number of widely recognized mechanisms, which have their origins in early filtration studies (Grace, 1956), comprising (Fig. 2.9):

- Complete blocking
- standard blocking
- intermediate blocking
- Cake filtration

All models imply a dependence of flux decline on the ratio of the particle size to the pore diameter. The standard blocking and cake filtration models appear most suited to predicting initial flux decline during colloid filtration or protein filtration (Bowen et al., 1995). All of the models rely on empirically derived information and some have been refined to incorporate other key determinants.



Figure 2.9 Fouling mechanisms: (a) Complete blocking, (b) Standard blocking, (c) Intermediate blocking and (d) Cake filtration.

2.1.4.3 Physical and chemical cleaning

Since the flux and driving force are interrelated, either one can be fixed for design purposes. For conventional pressure-driven water filtration, it is usual to fix the value of the flux and then determine the appropriate value for the TMP. The main impact of the operating flux is on the period between cleaning, which may be by either physical or chemical means (Fig. 2.10). In MBRs, physical cleaning is normally achieved either by backflushing, that is, reversing the flow, or relaxation, which is simply ceasing permeation whilst continuing to scour the membrane with air bubbles. These two techniques may be used in combination, and backflushing may be enhanced by combination with air. Chemical cleaning is carried out with mineral or organic acids, caustic soda or, more usually in MBRs, sodium hypochlorite, and can be performed either *in situ* ("cleaning in place" or CIP).

Physical cleaning is less onerous than chemical cleaning on a number of bases. It is generally a more rapid process than chemical cleaning, lasting no more than 2 min. It demands no chemicals and produces no chemical waste, and also is less likely to incur membrane degradation. On the other hand, it is also less effective than chemical cleaning. Physical cleaning is less onerous than chemical cleaning on a number of bases. It is generally a more rapid process than chemical cleaning, lasting no more than 2 min. It demands no chemicals and produces no chemical waste, and also is less likely to incur membrane degradation.



Figure 2.10 Membrane cleaning methods.

On the other hand, it is also less effective than chemical cleaning. Physical cleaning removes gross solids attached to the membrane surface, generally termed "reversible" or "temporary" fouling, whereas chemical cleaning removes more tenacious material often termed "irreversible" or "permanent" fouling, which is obviously something of a misnomer. Since the original virgin membrane permeability is never recovered once a membrane is fouled through normal operation, there remains a residual resistance which can be defined as "irrecoverable fouling". It is this fouling which builds up over a number of years and ultimately determines membrane life.

Since flux, amongst other things, determines the permeability decline rate (or pressure increase dP/dt), it also determines the period between physical cleaning (backflushing or relaxation), that is, the physical cleaning cycle time. If backflushing is used, this period can be denoted tp and, assuming no changes to other operating conditions, increasing the flux decreases tp. Since backflushing does not, in practice, return the permeability to the original condition only a finite number of backflush cycles can be performed before a threshold pressure is reached (P_{max}) beyond which operation cannot be sustained. At this point chemical cleaning must be conducted to return the pressure to close to the original baseline value (Fig. 2.11).



Figure 2.11 Pressure transient for constant flux operation of a dead-end filter.

As with physical cleaning, chemical cleaning never recovers the original membrane permeability but is normally considerably more effective than physical cleaning.

2.1.4.4 Concentration polarisation

For membrane filtration processes, the overall resistance at the membrane: solution interface is increased by a number of factors which each place a constraint on the design and operation of membrane process plant:

- a) The concentration of rejected solute near the membrane surface
- b) The precipitation of sparingly soluble macromolecular species (gel layer formation) at the membrane surface
- c) The accumulation of retained solids on the membrane (cake layer formation)

All of the above contribute to membrane fouling, and (a) and (b) are promoted by CP. CP describes the tendency of the solute to accumulate at membrane:solution interface within a concentration boundary layer, or liquid film, during crossflow operation (Fig. 2.12).



Figure 2.12 Concentration polarization.

This layer contains near-stagnant liquid, since at the membrane surface itself the liquid velocity must be zero. This implies that the only mode of transport within this layer is diffusion, which is around two orders of magnitude slower than convective transport in the bulk liquid region. However, it has been demonstrated (Romero and Davis, 1991) that transport away from the membrane surface is much greater than that governed by Brownian diffusion and is actually determined by the amount of shear imparted at the boundary layer; such transport is referred to as "shear-induced diffusion".

2.1.4.5 Fouling control

In MBRs, as with many other membrane filtration processes, it is the balance between the flux, physical and chemical cleaning protocol and, when relevant, the control of CP which ultimately determines the extent to which fouling is successfully suppressed. Ultimately, CP-related fouling can be reduced by two methods: (i) promoting turbulence and (ii) reducing flux.

2.2 Biotreatment

2.2.1 Biotreatment rationale

Biological treatment (or biotreatment) processes are those which remove dissolved and suspended organic chemical constituents through biodegradation, as well as suspended matter through physical separation. Biotreatment demands that the appropriate reactor conditions prevail in order to maintain sufficient levels of viable (i.e. living) micro-organisms (or, collectively, biomass) to achieve removal of organics. The latter are normally measured as biochemical or chemical oxygen demand (BOD and COD, respectively); these are indirect measurements of organic matter levels since both refer to the amount of oxygen utilised for oxidation of the organics. The microorganisms that grow on the organic substrate on which they feed derive energy and generate cellular material from oxidation of the organic matter, and can be aerobic (oxygen-dependent) or anaerobic (oxygen-independent). They are subsequently separated from the water to leave a relatively clean, clarified effluent.

The most attractive feature of biological processes is the very high chemical conversion efficiency achievable. Unlike chemical oxidation processes, aerobic processes are capable of quantitatively mineralising large organic molecules, that is, converting them to the end mineral constituents of CO₂, H₂O and inorganic nitrogen products, at ambient temperatures without significant onerous byproduct formation. In doing so a variety of materials are released from the biomass in the reactor which are collectively referred to as extracellular polymeric substances (EPS) and which contain a number of components which contribute to membrane fouling in an MBR. The relative and overall concentrations of the various components are determined both by the feed characteristics and operational facets of the system, such as microbial speciation. Anaerobic processes generate methane as an end product, a possible thermal energy source, and similarly generate EPS. Biotreatment processes are generally robust to variable organic loads, create little odour (if aerobic) and generate a waste product (sludge) which is readily processed. On the other hand, they are slower than chemical processes, susceptible to toxic shock and consume energy associated with aeration in aerobic systems and mixing in all biotreatment systems.

2.2.2 Processes

Processes based on biodegradation can be classified according to the process configuration, feeding regime and oxidation state (Table 2.3). Process configuration defines the way in which the water is contacted with the biomass, which can form a layer on some supporting media to form a fixed biofilm or be suspended in the reactor, or sometimes a combination of these. Suspended growth systems provide higher mass transfer but the biomass subsequently needs to be separated from the water. Both configurations generate excess biomass which needs to be disposed of. Feeding regime defines the way in which the feedwater is introduced, which can be either continuous or batch-wise. Feeding in batches allows the same vessel to be used both for biodegradation and separation, thus saving on space. This is the case for the sequencing batch reactor (SBR). Finally, the reduction-oxidation (redox) conditions are defined by the presence of either dissolved oxygen (DO) (aerobic conditions) or some other compound capable of providing oxygen for bioactivity (anoxic conditions) or the complete absence of any oxygen (anaerobic conditions). The different redox conditions favour different microbial communities and are used to affect different types of treatment.

	Process configuration		Feeding regime		Redox conditions		
	Fixed film	Suspended growth	Continuous	Fed-batch	Aerobic	Anoxic	Anaerobi c
AD		X	Х	Х			Х
AF	Х		Х				Х
ASP		Х	Х		Х	Х	Х
BAF	Х		Х		Х		
RBC	Х		Х		Х		
SBR		Х		Х	Х	Х	
TF	Х				Х		
UASB		Х	Х				Х
MBR		X	Χ		Χ	Χ	

Table 2.3 Examples of biological processes and their characteristics.

Keywords: AD: Anaerobic digestion; AF: Anaerobic filter; ASP: Activated sludge process; BAF: Biological Aerated Filters; RBC: Rotating biological contactor; SBR:

Sequencing batch reactor; TF: Tricking filter; UASB: Upflow anaerobic sludge blanket.

Aerobic treatment is used to remove organic compounds (BOD or COD) and to oxidise ammonia to nitrate. Aerobic tanks may be combined with anoxic and anaerobic tanks to provide biological nutrient removal (BNR). The removal of nutrients (nitrogen and phosphorus). However, almost all biological processes are configured according to the sub-categories listed in Table 2.3, and their function and performance depends on which specific sub-categories apply. Moreover, unit biotreatment processes can be combined so as to achieve multiple functions. So, for example, within an individual bioreactor, both aerobic and anoxic processes can be designed to occur within different zones.

The classic sewage treatment process (Fig. 2.13) is the combination of screening of gross solids, and then sedimentation of settlable solids followed by a biological process. The latter can include an anoxic zone preceding an aerobic zone within a single reactor or a separate post-denitrification reactor for the complete removal of nitrogen. Various configurations that include a preliminary anaerobic zone to remove phosphorus biologically are also available. Aerobic processes may be configured either as suspended growth (the activated sludge process, ASP) or fixed film (a trickling filter, TF). Total removal of organic nitrogen (ON) from the feedwater can be achieved by recycling the nitrate-rich sludge from the ASP to some point upstream of the aerobic process where anoxic conditions then prevail. Nitrification and denitrification are thus carried out sequentially. Aerobic MBRs can be configured similarly since, in essence, the biological function remains unaltered by the membrane.


Figure 2.13 Classic sewage treatment process, with mass flows for ASP indicated (Drews et al., 2005).

2.2.3 Operation conditions

2.2.3.1 Organic loading rate (OLR)

As organic loading rate increases, the concentration of soluble organics near the membrane increases and the polarization affect increases. This results in gradual formation of a layer of cake, acceleration of the resistance, and increase of pressure over the membrane. The membrane pressure could increase rapidly in a short time as organic loading rate increases, which indicate the beginning of membrane fouling. Therefore, organic loading rate should be controlled within a proper range to avoid the system burden (Trussell et al., 2006).

2.2.3.2 Hydraulic retention time (HRT)

After a membrane module and reactor size are selected, the HRT becomes a decisive parameter influencing permeate flux. A long HRT requires low permeate flux, while a short HRT increases the flux and the concentration of dissolved organic matter (such as SMP) in reactor, resulting in acceleration of membrane fouling and eventually, declining permeate flux (Jeong et al., 2007).

2.2.3.3 SRT and F:M ratio

SRT values for activated sludge plants treating municipal wastewaters are typically in the range of 5–15 day with corresponding F:M values of 0.2–0.4 /day. Increasing SRT increases the reactor concentration of biomass, which is often referred to as the MLSS. Conventional ASPs operating at SRTs of 8 days have an MLSS of around 2.5 g/L, whereas one with a SRT of 40 days might have a MLSS of 8–12 g/L. A low F:M ratio implies a high MLSS and a low sludge yield, such that increasing SRT is advantageous with respect to waste generation. This represents one of the key advantages of MBRs, and an analysis of data from the review by Stephenson et al., 2000, reveals that most MBRs, where SRT can be readily extended, operate at F/M ratios of <0.12 (Fig. 2.14).



Figure 2.14 Statistical analysis of data from municipal and industrial effluent Stephenson et al., 2000).

On the other hand, high MLSS values are to some extent detrimental to process performance. Firstly they would be expected to lead to an accumulation of inert compounds, reflected in a decrease in the MLVSS/MLSS ratio where MLVSS represents the volatile (organic) fraction of the MLSS, though this does not appear to be the case in practice (Huang et al., 2001; Rosenburger et al., 1999). Secondly, high solids levels increase the propensity for clogging or "sludging" – the accumulation of solids in the membrane channels. Lastly, and possibly most significantly, high MLSS levels reduce aeration efficiency.

2.2.3.4 MLSS and MLVSS

In general, the high concentration of sludge (MLSS) causes the low capacity of permeation. The sludge will deposit on the surface of membrane easier if the MLSS increases (Sven et al., 2007). Under a constant HRT, the biomass synthesis rate and endogenous respiration rate reaches a dynamic equivalence, and MLVSS eventually becomes stable. The accumulation of inorganic substances, digestion of dead biomass and other residual material lead to the increase of MLSS (or the decline of the fraction of active biomass in the sludge), which ultimately affects the MBR efficiency.

2.2.3.5 Aeration

In conventional aerobic biological wastewater treatment processes, oxygen is usually supplied as atmospheric air, either via immersed air-bubble diffusers or surface aeration. Diffused air bubbles (via fine-bubble aeration) are added to the bulk liquid (as in an ASP, biological aerated filters (BAFs), fluidised bioreactors, etc.), or oxygen transfer occurs from the surrounding air to the bulk liquid via a liquid/air interface (as for a TF or rotating biological contactor (RBC)).

The oxygen requirement to maintain a community of micro-organisms and degrade BOD and ammonia and nitrite to nitrate can be found by a mass balance on the system (Metcalf and Eddy, 2003):

$$m_0 = Q(S - S_e) - 1.42P_x + 4.33Q(NO_x) - 2.83Q(NO_x)$$
 (2.3)

Where m_0 is the total oxygen required (g/day). The first term in Eq. 2.3, refers to substrate oxidation, the second refers to biomass respiration, the third refers to nitrification and the final term refers to denitrification. Certain terms thus disappear from the expression depending on whether or not the system is nitrifying and/or denitrifying.

2.3 Membrane bioreactor technology

A classical MBR comprises a conventional activated sludge process (ASP) coupled with membrane separation to retain the biomass. Since the effective pore size can be below 0.1 μ m, the MBR effectively produces a clarified and substantially disinfected effluent. In addition, it concentrates up the biomass and, in doing so, reduces the necessary tank size and also increases the efficiency of the biotreatment process. MBRs thus tend to generate treated waters of higher purity with respect to dissolved constituents such as organic matter and ammonia, both of which are removed by biotreatment. Moreover, by removing the requirement for biomass sedimentation, the flow rate through an MBR cannot affect product water quality through impeding solids settling, as is the case for an ASP. On the other hand, hydraulic and organic shocks can have other onerous impacts on the operation of an MBR.

2.3.1 MBR configurations

The word "configuration" can be used with reference to both the MBR process (and specifically how the membrane is integrated with the bioreactor) and the membrane module. There are two main MBR process configurations (Fig. 2.15): submerged or immersed (iMBR), and sidestream (sMBR). There are also two modes of hydraulic operation: pumped and airlift. These configurations and bulk liquid transfer modes are employed commercially for what can be referred to as conventional biomass rejection MBRs, as outlined above. However, there are also two other membrane process modes, these being extractive (eMBR) and diffusive (dMBR) (Fig. 2.16), which employ a membrane for a purpose other than to separate the

biomass from the treated water. Finally, whilst a number of membrane geometries and configurations exist in the membrane market place in general (Table 2.3), three predominate in existing commercial MBR technologies, these being FS, HF and MT.



Figure 2.15 Configurations of a membrane bioreactor: (a) sidestream and (b) immersed.

iMBRs are generally less energy-intensive than sMBRs, since employing membrane modules in a pumped sidestream crossflow incurs an energy penalty due to the high pressures and volumetric flows imposed. To make the most use of this latent energy, the flow path must be as long as possible, such that as much as possible of the energy intrinsic in the liquid flowing at high pressure is used for permeation. To achieve a reasonable conversion of 40–50% conversion along the length of the module, a long flow path, often in excess of 20 m, is required. This then demands a large number of membrane modules in series incurring a significant pressure drop along the retentate flow channels.



Figure 2.16 Principal configurations of MBR technologies.

With sMBRs, there is always a trade-off between pumping energy demand and flux. In order to maximise the flux, a high TMP is required combined with a high CFV or retentate velocity U_R . Since the energy demand is directly proportional to $Q_R \Delta P$ (retentate flow rate X pressure), it is of interest to reduce both these parameter values as much as possible. However, since Q_R determines $U_R \ (U_R$ $=Q_R/A_t$, A_t being the tube cross-sectional area) and ΔP relates to TMP, reducing $Q_R\Delta P$ inevitably reduces flux. Moreover, if Q_R is reduced by decreasing the cross-sectional area A_{t} , this has the effect of increasing the pressure drop along the length of the module on the retentate side, since the resistance to flow is inversely proportional to At. sMBRs have an inherently higher fouling propensity than iMBRs since higher flux operation always results in lower permeabilities because fouling itself increases with increasing flux, particularly above the so-called "critical flux". Moreover, it is thought that the higher shear imparted by liquid pumping of the sidestream imparts sufficient shear stress on the flocs to cause them to break-up (Tardieu et al., 1999; Wisniewski and Grasmick, 1998). This both reduces particle size and promotes the release of foulant materials bound within the flocs. Wisniewski and Grasmick, (1998) studied the effects of the recirculation on the particle size in an sMBR. Without recirculation, floc size ranged from 20 µm to more than 500 µm. Only 15% of the particles were lower than 100 μ m. With recirculation, reduction in particle size was directly proportional to the magnitude of the shear stress and the experiment time; at 5 m/s

CFV 98% of the particles were smaller than 100 μ m. iMBRs are therefore higher in energy efficiency, manifested as the specificenergy demand in kWh/m³ permeate product, than sMBR technologies. The immersed configuration employs no liquid pumping for permeation, instead relying on aeration to promote mass transfer of liquid across the membrane (i.e. enhancing flux) by generating significant transient shear at the membrane:solution interface. Whilst sMBRs cannot provide the same low energy demand as the immersed configuration, they do offer a number of advantages:

- 1. Fouling has been shown to decrease linearly with increasing CFV. For example a bench-scale study revealed that CFV values of 2 and 3 m/s were sufficient to prevent the formation of reversible fouling in UF (30 kDa) and MF (0.3 μ m) systems, and that fouling was suppressed for CFV values up to 4.5 m/s test (Choi et al., 2005b).
- 2. The membranes can also be chemically cleaned "*in situ*" (CIP) easily without any chemical risk to the biomass.
- 3. Maintenance and plant downtime costs, particularly with reference to membrane module replacement, are generally slightly lower because of the accessibility of the modules which can be replaced in 5 min.
- 4. Precipitation of sparingly soluble inorganic solids (i.e. scalants) and organic matter (gel-forming constituents) is more readily managed in sidestream MT systems by control of the hydrodynamics both during the operation and the CIP cycle.
- 5. It is generally possible to operate sMBRs at higher MLSS levels than HF iMBRs.
- 6. Aeration can be optimised for oxygen transfer and mixing, rather than demanding a compromise between membrane aeration and oxygen dissolution, as would be the case for single-tank iMBRs.

2.3.2 Elements of an immersed biomass-rejection MBR

MBRs employing immersed membranes to reject biomass represent the most widely employed of all MBR configurations, since they incur the lowest specific energy demand and therefore become the most economically viable for large-scale applications. There are essentially five key elements of the iMBR process, which are key to its design and operation (Fig. 2.17). These are:

- 1. The membrane, its design and the sustaining of permeability
- 2. Feedwater, its characteristics and its pretreatment
- 3. Aeration of both membrane and the bulk biomass
- 4. Sludge withdrawal and residence time
- 5. Bioactivity and nature of the biomass

These elements are obviously largely inter-related (Fig. 2.18), in particular the latter three which obviously relate to operation. The rate at which sludge is withdrawn controls the residence time (i.e. the SRT) which then determines the concentration of the biomass (or, strictly speaking, the mixed liquor). The MLSS concentration then impacts both on the biological properties, that is, the bioactivity and microbial speciation, and also on the physical properties such as the viscosity and oxygen transfer. The feedwater chemistry provides the biggest impact on MBR operation, in that the membrane fouling propensity of the mixed liquor is generally mainly dictated by the nature of the feedwater from which it is generated. Similarly, the rigour of the pretreatment of the feedwater by screening has a significant impact on the clogging propensity.

Whilst governing principles and the nature of inter-relationships can be appreciated (Fig. 2.18), actual operating conditions and the associated absolute operating parameter values can generally only be arrived at heuristically. Having said this, an understanding of the fundamentals of MBR design, operation and maintenance can proceed through a comprehensive examination of the biological, chemical and physical phenomena occurring in MBRs, since these interact to generate fouling through a number of mechanisms. In the following sections, the elements of the iMBR are considered in turn, namely the membrane itself, the feedwater and biomass characteristics and the operation and maintenance aspects, with a view to appraising mechanisms of fouling and, ultimately, developing methods for its control.



Figure 2.17 Elements of an MBR (Hai et al., 2005).



Figure 2.18 Inter-relationships between MBR parameters and fouling.

2.3.3 Membrane characteristics

Key membrane design parameters are configuration, that is, the geometry and flow direction, the surface characteristics (normally denoted by the pore size and material but also including such things as the surface charge, hydrophobicity and porosity, pore tortuosity and shape, and crystallinity), and the inter-membrane separation. The pore size of commercial MBR materials tends to be in the coarse UF to fine MF region, since experience indicates that this pore size range offers sufficient rejection and reasonable fouling control under the conditions employed. The range of organic membrane materials employed is also, in practice, limited to those polymers which are:

- a) Sufficiently mechanically and chemically robust to withstand the stresses imposed during the filtration and cleaning cycles
- b) Readily modified to provide a hydrophilic surface, which then makes them more resistant to fouling, particularly by EPS
- c) Readily attached to a substrate to provide the mechanical integrity required
- d) Manufactured at a relatively low cost

Point (d) is especially important in the case of iMBRs, since these operate at relatively low fluxes and so demand much larger membrane areas than sMBRs.

2.3.3.1 Physical parameters

Pore size: The effects of pore size on membrane fouling are strongly related to the feed solution characteristics and, in particular, the particle size distribution. This can, in part, be attributed to the complex and changing nature of the biological suspension in MBR systems and the comparatively large pore size distribution the membranes used (Chang and Le-Clech, 2002; Le-Clech et al., 2003), along with operational facets such as the system hydrodynamics and the duration of the test. A direct comparison of MF and UF membranes at a CFV of 0.1 m/s has shown an MF membrane to provide a hydraulic resistance of around twice that of a UF membrane (Choi et al., 2005b). Interestingly, the DOC rejection of both

membranes was similar following 2 hr of operation, indicating the dynamic membrane layer formed on the membranes to have provided the perm-selectivity rather than the membrane substrate itself.

Conventional wisdom considers smaller pores to afford greater protection of the membrane by rejecting a wider range of materials, with reference to their size, thus increasing cake (or fouling layer) resistance. Compared to that formed on membranes having larger pores, the layer is more readily removed and less likely to leave residual pore plugging or surface adsorption. It is the latter and related phenomena which cause irreversible and irrecoverable fouling. However, when testing membranes with pores ranging from 0.4 to 5 μ m, Gander et al., 2000, conversely observed greater initial fouling for the larger pore-size membranes and significant flux decline when smaller pore-size membrane were used over an extended period of time, though these authors used isotropic membranes without surface hydrophilicisation.

Characterisation of the distribution of MW compounds present in the supernatant of MBRs operated with membranes of four pore sizes (ranging from 0.1 to 0.8 μ m) has also been presented (Lee et al., 2005). Although providing a lower fouling rate, the 0.8 μ m pore-size MBR nonetheless had a slightly higher supernatant concentration of most of the macromolecules. According to these results, it seems unlikely for the small differences in MW distribution to cause significant variation in fouling rates observed between the four MBR systems. In another study based on short-term experiments, sub-critical fouling resistance and fouling rate increased linearly with membrane resistance ranging from 0.4 to 3.5 X 10⁹ m⁻¹, corresponding to membrane pore size from 1 down to 0.01 μ m (Le-Clech et al., 2003). These results suggest that a dynamic layer is created of greater overall resistance for the more selective membranes operating under sub-critical conditions, and supports the notion that larger pores decrease deposition onto the membrane at the expense of internal adsorption. Long-term trials have revealed that progressive internal deposition eventually leads to catastrophic increase in resistance (Cho and Fane, 2002)

Porosity/pore size distribution/roughness: Membrane roughness and porosity were identified as possible causes of differing fouling behaviour observed when four MF membranes with nominal pore sizes between 0.20 and 0.22 μ m were

tested in parallel (Fang and Shi, 2005). The track-etched membrane, with its dense structure and small but uniform cylindrical pores, provided the lowest resistance due to its high surface isoporosity whereas the other three membranes were more prone to pore fouling due to their highly porous network. Although all membranes were of similar nominal pore size, the PVDF, mixed cellulose esters (MCE) and PES membranes resulted in relative pore resistance of 2, 11 and 86% of the total hydraulic resistance, respectively. It was suggested that membrane microstructure, material and pore openings all affected MBR fouling significantly (Fang and Shi, 2005).

Membrane configuration: The immersed process configuration is generally favoured over the pumped sidestream configuration for medium to largescale domestic wastewater treatment (Fane et al., 2002; Judd, 2005; Le-Clech et al., 2005). This relates mainly to the impact of aeration, which suppresses fouling through generating shear.

iMBR membranes are largely configured either as HF or FS whereas sMBRs are either FS or MT (Fig. 2.5). Whilst HF modules are generally less expensive to manufacture, allow high membrane density and tolerate vigorous backflushing, they are also less readily controlled hydrodynamically than FS or MT membranes where the membrane channel width is well defined. A discussion of the relative merits of FS and HF membranes was initiated by Gunder and Krauth (1998), who demonstrated the superior hydraulic performance (i.e. higher permeability) attainable from the FS membrane. On the other hand, in a comparative study of FS and HF membranes of the same pore size (0.4 μ m) used for anaerobic treatment (Hai et al., 2005), the authors found the FS membrane to foul slightly more than the HF membrane and the permeability was not recovered following cleaning with water.

An important parameter for HF systems is the packing density. The separation distance between adjacent membranes has a direct impact on clogging, shear and aeration energy demand. For a given liquid upflow rate, as provided by airlift, increasing the separation reduces the risk of clogging by gross solids. Reducing the separation will also, for a given bubble volume, retard the rising bubble as a consequence of the gas:membrane contact area increasing, thereby increasing the downward drag force. This might then be expected to decrease the flux because shear forces are reduced as a result. On the other hand, for a given liquid upflow velocity and thus the same shear, increasing channel width also increases the aeration energy demand since a larger volume of liquid (dictated by the channel width) is being passed over the same membrane area; it is the volumetric flow rate that determines energy demand.

2.3.3.2 Chemical parameters

Since hydrophobic interactions take place between solutes, microbial cells of the EPS and the membrane material, membrane fouling is expected to be more severe with hydrophobic rather than hydrophilic membranes (Yu et al., 2005a; Yu et al., 2005b). In the literature, changes in membrane hydrophobicity are often linked with other membrane modifications such as pore size and morphology, which make the correlation between membrane hydrophobicity and fouling more difficult to assess. In a recent anMBR study, for example, the contact angle measurement demonstrated that the apparent hydrophobicity of PES membranes decreased (from 55 to 47°) with increasing MWCO (from 20 to 70 kDa membranes, , respectively) (He et al., 2005). The effect of membrane hydrophobicity in an aerobic MBR, from a comparison of two UF membranes of otherwise similar characteristics, revealed greater solute rejection and fouling and higher cake resistance for the hydrophobic membrane (Chang and Bag, 2001). It was concluded that the solute rejection was mainly due to the adsorption onto or sieving by the cake deposited on the membrane, and, to a lesser extent, direct adsorption into membrane pores and at the membrane surface. Since fouling is expected to be more severe at higher hydrophobicities, efforts have naturally been focused on increasing membrane hydrophilicity by chemical surface modification. Recent examples of MBR membrane modification include NH₃ and CO₂ plasma treatment of PP HFs (Yu et al., 2005a; Yu et al., 2005b) to functionalise the surface with polar groups. In both cases, membrane hydrophilicity significantly increased and the new membranes yielded better filtration performance and flux recovery than those of unmodified membranes.

2.3.4 Feed and biomass characteristics

2.3.4.1 Feed nature and concentration

Whilst membrane fouling in physical wastewater filtration depends directly on the water quality (Fuchs et al., 2005; Schrader et al., 2005), MBR membrane fouling is mostly affected by the interactions between the membrane and biological suspension rather than feed water (Choi et al., 2005a). More recalcitrant feedwaters, such as landfill leachate, may undergo more limited biochemical transformation such that the membrane is challenged in part by the raw, unmodified feed. Biological transformations which take place which are influenced both by the operating conditions and the feedwater quality (Jefferson et al., 2004).

2.3.4.2 Biomass foulants

Two types of foulant study dominate the MBR scientific literature: characterisation and identification. Characterisation refers to properties (usually relating to membrane permeability) the foulant demonstrates either in situ, that is, within the MBR, or ex situ in some bespoke or standard measurement, such as capillary suction time (CST) or specific resistance to filtration (SRF). Identification refers to physical and/or chemical classification of the foulant, invariably through extraction and isolation prior to chemical analysis. Of course, foulant isolates may also be characterised in the same way as the MBR biomass. In general, foulants can be defined in three different ways (Table 2.4):

- 1. Practically, based on permeability recovery
- 2. Mechanistically, based on fouling mechanism
- 3. By material type, based on chemical or physical nature or on origin

2.3.5 Fouling control and amelioration in MBRs

Whilst an understanding of fouling phenomena and mechanisms may be enlightening, control of fouling and clogging in practice is generally limited to five main strategies:

- 1. Applying appropriate pretreatment to the feedwater
- 2. Employing appropriate physical or chemical cleaning protocols
- 3. Reducing the flux
- 4. Increasing the aeration
- 5. Chemically or biochemically modifying the mixed liquor
- All of the above strategies are viable for full-scale operating MBRs,

and each are considered in turn below.

Table 2.4 Foular	nt definitions.
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Practical	Mechanism	Foulant material type
Reversible/temporary:Removed by physical cleaning	Pore blocking/filtration modelsComplete blocking	 Size: Molecular, macro- molecular colloidal or particulate
Irreversible/permanent:Removed by chemical cleaning	Standard blockingIntermediate blockingCake filtration	 Surface charge/chemistry: Positive or negative (cationic or anionic)
 Irrecoverable/absolute^a: Not removed by any cleaning regime 		 Chemical type: Inorganic (e.g. scalants) or organic (e.g. humic materials, EPS) Carbohydrate or protein (fractions of EPS)
		 Origin: Microbial (autochthonous), terrestrial (allochthonous) or man-made (anthropogenic) (Extracted) EPS ((e)EPS) or soluble microbial product (SMP)^b

^aIrrecoverable fouling is long-term and insidious. ^beEPS refers to microbial products directly associated with the cell wall; SMP refers to microbial products unassociated with the cell.

2.3.5.1 Feed pretreatment

It is generally recognised that the successful retrofitting of an ASP or SBR with an MBR is contingent on upgrading the pretreatment and, specifically, the screening. Whilst an MBR can effectively displace primary sedimentation, biotreatment and secondary solid-liquid separation, as well as tertiary effluent polishing, classical screens of around 6 mm rating are normally insufficient for an MBR. Such relatively coarse screens increase the risk of clogging of the membrane module retentate flow channels, especially by hairs in municipal wastewaters, which aggregate and clog both the membrane interstices and aeration ports. HF membranes have a tendency for aggregates of hair and other debris to collect at the top of the membrane element. Hairs may then become entwined with the filaments and are not significantly removed by backflushing. FS membrane clogging occurs when debris agglomerate at the channel edges and entrance. If the aeration fails to remove these aggregates, sludge accumulates above the blockage, increasing the affected excluded area. Fibres collecting in the aeration system can change the flow pattern and volume of air to the membranes, reducing the degree of scouring. As a result of the decreased scouring, membrane fouling is increased. Aerators are thus normally designed to resist clogging and/or allow periodic flushing with water.

2.3.5.2 Employing appropriate physical or chemical cleaning protocols

Physical cleaning: Key general cleaning parameters are duration and frequency, since these determine process downtime. For backflushing, a further key parameter is the backflush flux, generally of 1–3 times the operational flux and determined by the backflush TMP. Less frequent, longer backflushing (600 s filtration / 45 s backflushing) has been found to be more efficient than more frequent but shorter backflushing (200 s filtration / 15 s backflush). In another study based on factorial design, backflush frequency (between 8 and 16 min) was found to have more effect on fouling removal than either aeration intensity (0.3 to 0.9 m³/h per m² membrane area) or backflush duration (25–45 s) for an HF iMBR (Schoeberl et al., 2005). Hence, although more effective cleaning would generally be expected for more frequent and longer backflushing, the possible permutations need exploring to minimize energy demand. This has been achieved through the design of a generic

control system which automatically optimized backflush duration according to the monitored TMP value (Smith et al., 2005). However, increasing backflush flux leads to more loss product and reduces the net flux.

Chemical cleaning: Physical cleaning is supplemented with chemical cleaning to remove "irreversible" fouling (Fig. 2.10), this type of cleaning tending to comprise some combination of:

- CEB (on a daily basis)
- Maintenance cleaning with higher chemical concentration (weekly)
- Intensive (or recovery) chemical cleaning (once or twice a year)

Maintenance cleaning is conducted in situ and is used to maintain membrane permeability and helps reduce the frequency of intensive cleaning. It is performed either with the membrane in situ, a normal CIP, or with the membrane tank drained, sometimes referred to as "cleaning in air" (CIA). Intensive, or recovery, cleaning is either conducted ex situ or in the drained membrane tank to allow the membranes to be soaked in cleaning reagent. Intensive cleaning is generally carried out when further filtration is no longer sustainable because of an elevated TMP. Recovery chemical cleaning methods recommended by suppliers (Table 2.5) are all based on a combination of hypochlorite for removing organic matter, and organic acid (either citric or oxalic) for removing inorganic scalants. Whilst some scientific studies of the impacts of chemical cleaning on the MBR system, such as the microbial community (Lim et al., 2004), have been conducted, there has been no systematic study comparing the efficacy of a range of cleaning reagents or cleaning conditions on permeability recovery.

2.3.5.3 Reducing the flux

Reducing the flux always reduces fouling but obviously then impacts directly on capital cost through membrane area demand. A distinction must be made, however, between operating (i.e. gross) flux and net flux (the flux based on throughput over a complete cleaning cycle), as well as peak and average flux. Modern practice appears to favour operation at net fluxes of around 25 LMH for municipal wastewater, incorporating physical cleaning every 10–12 minutes, regardless of

membrane configuration. Maintenance cleaning, if employed, adds insignificantly to downtime.

2.3.5.4 Increasing aeration

Whilst increasing aeration rate invariably increases the critical flux up to some threshold value, increasing membrane aeration intensity is normally prohibitively expensive. Therefore, much attention has been focused on commercial development of efficient and effective aeration systems to reduce the specific aeration demand, with possibly the most important publications arising in the patent literature (Cote, 2002) and including cyclic aeration (Rabie et al., 2003).

Technology	Туре	Chemical	Concentration	Protocols
			(%)	
Mitsubishi	CIP	NaOCl	0.3	Backflow through
		Citric acid	0.2	membrane $(2 h) +$
				soaking (2 h)
Zenon	CIA	NaOCl	0.2	Backpulse and
		Citric acid	0.2-0.3	recirculate
Memcor	CIA	NaOCl	0.01	Recirculate through
				lumens,
				mixed liquors and in-
				tank
				air manifolds
Kubota	CIP	Citric Acid	0.2	Backflow and soaking
		NaOCl	0.5	(2 h)
		Oxalic acid	1	

Table 2.5 Examples of intensive chemical cleaning protocols, four MBR suppliers.

* Exact protocol for chemical cleaning can vary from one plant to another.

* CIP: Cleaning in place, without membrane tank draining; chemical solutions generally backflushed under gravity in-to-out.

* CIA: Cleaning in air, where membrane tank is isolated and drained; module rinsed before soaking in cleaning solution and rinsed after soaking to remove excess reagent.

2.3.5.5 Chemically or biochemically modifying the mixed liquor

Coagulant/flocculant: Ferric chloride and aluminium sulphate (alum) have both been studied in relation to membrane fouling amelioration, most extensively for potable systems but also for MBRs. In MBR-based trials, addition of alum to the reactor led to a significant decrease in SMP_c concentration, along with an improvement in membrane hydraulic performances (Holbrook et al., 2004).

Adsorbent agents: Addition of adsorbents into biological treatment systems decreases the level of organic compounds. Dosing with PAC produces biologically activated carbon (BAC) which adsorbs and degrades soluble organics and has been shown to be effective in reducing SMP and EPS levels in a comparative study of a sidestream and immersed hybrid PAC–MBR (Kim and Lee, 2003).

2.4 Literature review

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/RuO₂ 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, BOD₅ 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/m³) compared with the electro-coagulation process (1.78 USD/m³). 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 H₃PO₄ 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 CH₄/g COD removed (1 atm, 25 °C). Although, these processes are the most efficient and economic 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–flocculation pre-treatments, respectively. In the second step, anaerobic digestion is carried out with acidification–electrocoagulation and acidification–flocculation wastewaters. The biodegradability of

electrocoagulation and coagulation- flocculation wastewaters are 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, KH₂PO₄ and MgSO₄.7H₂O 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). Backflushing is completed by reversing the flow of air or water through the membrane to unclog the pores (Scott et al., 2007).

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. 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 equipments 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.

CHAPTER 3

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 μ m and effective surface of 0.23 m² (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.

|--|

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 O₂ 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. A pH was monitored by pH meter and maintained in the range of 6.00-8.00 by dosing the 1 N H₂SO₄ 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.

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 3.2 Operating conditions of MBR.

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

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

* 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 to 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 NaOC1 (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 prefiltration 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 polysacharride (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 polysacharride.

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	Polysacharride analysis	Anthrone Method

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

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) conc. 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 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 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:

Bonferroni correction =
$$\frac{\alpha}{n}$$
 (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 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.

Source	Sum of Squares (SS)	Degree of Freedom (df)	Mean Square MS=SS/df	F-Statistics	<u>P-value</u> /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			

Table 3.5 Description of Anova table.

*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 4

RESULTS AND DISCUSSIONS

4.1 Pretreatment of biodiesel wastewater with H₂SO₄

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 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 (H₂SO₄).

Parameters	PCD standards (Thai)	EPA standards	Avg values of raw biodiesel wastewater
pН	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

Table 4.1 Characteristics of raw biodiesel wastewater.

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

рН	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

Table 4.2 Mean value of organic pollutants after pretreatment with H₂SO₄.

To find out the significant difference for the mean values of COD, BOD and O&G obtained after the pretreatment with H₂SO₄ 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 Fstatistics 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 H₂SO₄ 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 conc. 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 conc. 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 conc. 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 conc. 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 conc. at HRTs of 15, 12, 9 and 6 hrs are shown in Table 4.5.

	MLSS (mg/L)									
HRT	OL	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
(hrs)	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	
	Value	Value	Value	Value	Value	Value	Value	Value	Value	
15	2 239	2 862	2 5 5 0	3 656	4 725	/ 190	5 333	6 290	5 812	
15	2,239	2,802	2,330	5,050	4,723	4,190	5,555	0,290	5,012	
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	

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

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 conc. with membrane. Different authors correlated the MLSS conc. with membrane fouling on the basis of derived results, some authors correlated impact of MLSS conc. on viscosity of sludge, while other authors discussed the positive and negative impact of MLSS conc. on TMP. Tanaka et al., 1994 defined the critical value of MLSS conc. 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.

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		

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

* 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.

				HRT	(hrs)			
Parameters		15	1	12	(9		6
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Removal (%) of	97	97 9	94 7	964	92.9	93 3	90.8	91.2
COD (after 10 days)	71)1.)	74.7	70.4)2.)	15.5	70.0	/1.2
Removal (%) of	977	98.6	95.8	97	94	95 2	917	92.8
COD (after 15 days)	<i>)</i>	20.0	25.0	71	71	75.2	71.7	12.0
Removal (%) of	97 5	98.4	97 1	974	96 1	964	95.2	95 3
O&G (after 10 days)	71.5	<i>J</i> 0.1	27.1	27.1	20.1	20.1	13.2	10.0
Removal (%) of	97 9	98 7	97.2	97 9	96.6	97	95 5	96
O&G (after 15 days)	5115	20.7	21.2	<i></i>	20.0	21	10.0	70
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
Polysacharride(mg/L)	7	25	12	37	20	49	19	59
Membrane clogging (days)	12	17	6	12	5	8	3	6

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

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 conc. 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 conc. 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.

		MLVSS/MLSS											
HRT	OLR of 1 g/L·day			0	LR of 2 g/L	·day	OLF	OLR of 3 g/L·day					
(hrs)	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean				
	Value	Value	Value	Value	Value	Value	Value	Value	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				

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



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.

	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
HRT (hrs)	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 4.7 Removal (%) of COD after 10 days operation.

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

	OLR of 1 g/L·day			OLR of 2 g/L.day			OLR of 3 g/L.day		
HRT (hrs)	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 conc. 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 conc. 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 > α/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.



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.

	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
HRT (hrs)	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 4.9 Removal (%) of O&G after 10 days operation.

	OLR of 1 g/L·day			OLR of 2 g/L·day			OLR of 3 g/L·day		
HRT	Input	Output		Input	Output		Input	Output	
(hrs)	O&G	O&G	(%)	O&G	O&G	(%)	O&G	O&G	(%)
	(mg/L)	(mg/L)	. ,	(mg/L)	(mg/L)	. ,	(mg/L)	(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

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



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 conc. on TMP

The impact of HRT on DO conc. was analyzed and it was found that decreased in HRT had a greater impact on DO conc. When the reactor was run at HRT of 15 hrs then the mean DO conc. 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.

HRT		DO (mg/L)	
(hrs)	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)

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

Decreased in DO conc. was observed due to an increase in OLR at HRT of 15 hrs because at higher OLR, MLSS conc. 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 conc. 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 conc. in bioreactor, which caused the higher utilization of DO conc. 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 conc. 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 conc. 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, filamentous as 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.

HRT	_	Particle size (µm)	
(hrs)	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)

Table 4.12 Mean particle size distribution at different OLRs.

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 conc. 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 (polysacharride) 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 conc. 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 conc. at shorter HRT and higher OLRs. Similar trends were also observed for HRT of 12, 9 and 6 hrs.

HRT	Protein (mg/L)						
(hrs)	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 4.13 Mean protein conc. at different OLRs.

Table 4.14 Mean	polysacharride conc	. at different	OLRs
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HRT	Polysacharride (mg/L)				
(hrs)	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 polysacharride on TMP at OLR of 1 g/L·day.



Figure 4.23 Effect of polysacharride 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; Drews and Vocks, 2005) observed that, the effect of the protein fraction contained in the SMP solution on MBR fouling has been more 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 5

ECONOMIC ANALYSIS OF MBR

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.

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

Where Q_{air} is aeration requirement (m³/min) P is power demand (kWh)

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

 $P = 0.7 \ge 0.01415 = 0.009905 \text{ kWh}$

5.2 Power consumption of permeate pump

Power consumption of permeate pump can be calculated by:

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

* 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.

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

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

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,	$J = 3 \ge 0.23 = 14 L/m^2.hr$
At HRT of 12 hrs,	$Q_2 = \frac{50}{12} = 4$ L/hr,	$J = 4 \ge 0.23 = 18 \text{ L/m}^2.\text{hr}$
At HRT of 9 hrs,	$Q_3 = \frac{50}{9} = 6 L/hr,$	$J = 6 \ge 0.23 = 24 \text{ L/m}^2.\text{hr}$
At HRT of 15 hrs,	$Q_4 = \frac{50}{6} = 8 L/hr,$	$J = 8 \ge 0.23 = 36 L/m^2.hr$

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, HP =
$$\frac{3 \times 0.0044 \times 20}{1713 \times 0.90} = 0.000171$$
 HP or0.000128 kWh
HP at HRT of 12 hrs, HP = $\frac{4 \times 0.0044 \times 20}{1713 \times 0.90} = 0.000228$ HP or 0.00017 kWh

HP at HRT of 9 hrs,
$$HP = \frac{6 \times 0.0044 \times 20}{1713 \times 0.90} = 0.000343 \text{ HP}$$
 or 0.000256 kWh
HP at HRT of 6 hrs, $HP = \frac{8 \times 0.0044 \times 20}{1713 \times 0.90} = 0.000457 \text{ HP}$ 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 as functions of HRT and target MLSS concentration because small change of target MLSS may cause more significant change of oxygen requirement 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/m³ and 1.78 USD/m³, respectively (Ngamlerdpokin et al., 2011), which was found to be much higher than operating cost of MBR as illustrated in Table 5.1.

HRT (hrs)	Permeate flowrate (L/hr)	Total power consumption (kWh)	(kWh/L)	(kWh/m ³)	Cost (Baht/m ³)	Cost (USD/m ³)
15	3	0.010	0.003	3.34	10.0	0.34
12	4	0.010	0.003	2.52	7.6	0.26
9	6	0.010	0.002	1.69	5.1	0.17
6	8	0.010	0.001	1.28	3.8	0.13

Table 5.1 Economic analysis of MBR.

* 1 kWh = 3 baht, 1USD = 29.63 baht.

CHAPTER 6

CONCLUSION

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, H₂SO₄ 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 H₂SO₄. 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 conc. 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 conc. in MBR effluent was resulted due to increased of O&G conc. in feed water. It was observed that when O&G conc. increased more than 690 mg/L in feed then it decreased the efficiency of MBR.

4) HRT was correlated with dissolved oxygen (DO), particle size distribution (PDS) and protein and polysacharride contents of soluble microbial product (SMP) in order to investigate their impact on membrane fouling mechanism. Transmembrane 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 conc. 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.

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Appendix

Appendix A COD input calculations for MBR

1. Calculation of COD input

$$HRT = \frac{V}{J X A}$$
(1)
Or
$$J = \frac{V}{HRT X A}$$

WhereHRT is hydraulic retention time (hrs)V is volume of reactor (L)A is filtration area (m²)J is permeate flux (L/m².hr)

$$VOLR = \frac{SO X Q}{V}$$
Or
$$S_0 = \frac{VOLR X V}{Q}$$
(2)

Where VOLR is volumetric organic loading rate $(g/L \cdot day)$ V is volume of reactor (L) Q is permeate flow rate (L/day) S_0 is COD input (mg/L)

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 A1 Values of operation parameters used in calculations.

Table A2 COD inj	put calculations	for MBR.
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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.

pН	Count	Sum	Average	Variance	Std. Dev.
pH 2	5	51,364	10,273	5,524	74
pH 2.5	5	53,089	10,618	4,470	67
рН 3	5	83,711	16,742	4,019	63

* COD value = mg/L

Anova

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

Table B2. t-test for COD analysis.

рН	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.

pН	Count	Sum	Average	Variance	Std. dev.
pH 2	5	112,983	22,597	3,814	62
pH 2.5	5	118,025	23,605	4,556	67
рН 3	5	123,509	24,702	3,911	63

Anova

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

Table B4. t-test for BOD analysis.

рН	P (T<=t) two-tail	Bonferroni correction (α/n)	True/Fals e
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

* $\alpha = 0.05$ (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.
рН 2	5	7,604	1,521	72.7	9
рН 2.5	5	12,055	2,411	131	11
рН 3	5	16,234	3,247	188.7	14

* O&G value = mg/L.

Anova

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

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

рН	P (T<=t) two-tail	Bonferroni correction (α/n)	True/Fals e
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

* $\alpha = 0.05$ (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.
15	3	37.65	13	0.084	0.29
12	3	54.1	18	0.006	0.08
9	3	75.26	25	0.042	0.20
6	3	66.41	22	0.017	0.13

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	265.8214	3	88.60712	2391.555	0.0000
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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	79.48	26	0.024	0.16
12	3	153.53	51	0.021	0.15
9	3	144.17	48	0.004	0.06
6	3	138.37	46	0.016	0.13

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	1123.942	3	374.6474	23257.99	0.0000
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.

		Bonferroni	
HRTs	P (T<=t) two-tail	correction	True/False
		(a/n)	
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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	171.11	57	0.007	0.08
12	3	240.09	80	0.006	0.08
9	3	240.07	80	0.008	0.09
6	3	205.55	69	0.025	0.16

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	1090.373	3	363.4577	31605.02	0.0000
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.

		Bonferroni	
HRTs	P (T<=t) two-tail	correction	True/False
		(α/n)	
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

2. COD analysis for 15days operation

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	26.19	9	0.007	0.09
12	3	44.61	15	0.012	0.11
9	3	55.27	18	0.172	0.41
6	3	54.36	18	0.012	0.11

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

* COD values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	182.3348	3	60.77828	1199.177	0.0000
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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	63.59	21	0.019	0.14
12	3	122.57	41	0.017	0.13
9	3	114.04	38	0.010	0.10
6	3	113.48	38	0.002	0.04

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	722.3798	3	240.7933	20305.83	0.0000
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.

		Bonferroni	
HRTs	P (T<=t) two-tail	correction	True/False
		(α/n)	
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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	129.7	43	0.011	0.10
12	3	189.1	63	0.006	0.08
9	3	203.54	68	0.008	0.09
6	3	184.93	62	0.005	0.07

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	1050.274	3	350.0915	46939.64	0.0000
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.

		Bonferroni	
HRTs	P (T<=t) two-tail	correction	True/False
		(α/n)	
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

3. O&G analysis for 10days operation

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	33.38	11	0.014	0.12
12	3	71.3	24	0.012	0.11
9	3	115.88	39	0.028	0.17
6	3	179.28	60	0.006	0.08

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

* O&G values = mg/L.

Anova

Source of Variation	SS	df	MS	F	P-value
Between					
Groups	3933.134	3	1311.045	87548.88	0.0000
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	True/False
		(α/n)	
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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	46.99	16	0.014	0.12
12	3	88.37	29	0.013	0.11
9	3	127.65	43	0.013	0.12
6	3	185.69	62	0.001	0.03

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	3486.564	3	1162.188	113384.2	0.0000
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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	65.3	22	0.012	0.11
12	3	91.84	31	0.028	0.17
9	3	148	49	0.010	0.10
6	3	205.59	69	0.021	0.15

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between	3886.213	3	1295.404	72368.97	0.0000
Groups					
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 (\alpha/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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	26.35	9	0.038	0.20
12	3	57.1	19	0.006	0.08
9	3	98.52	33	0.005	0.07
6	3	155.43	52	0.025	0.16

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	3119.906	3	1039.969	56468.89	0.0000
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

HRT (hrs)	Count	Sum	Average	Variance	Std. dev.
15	3	41.43	14	0.0247	0.16
12	3	75.7	25	0.006533	0.08
9	3	119.61	40	0.0121	0.11
6	3	164.58	55	0.0112	0.11

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

Anova

Source of Variation	SS	Df	MS	F	P-value
Between	2858.543	3	952.8475	69891.02	0.0000
Groups					
Within	0.109067	8	0.013633		
Groups					
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 (\alpha/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

HRT (hrs)	Count	Sum	Average	Variance	Std. Dev.
15	3	53.32	18	0.011	0.11
12	3	89.55	30	0.010	0.10
9	3	128.31	43	0.011	0.11
6	3	191.24	64	0.007	0.08

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

Anova

Source of Variation	SS	df	MS	F	P-value
Between Groups	3480.118	3	1160.039	117870.2	0.0000
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

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Presentations

- Ram Yamsaengsung, Pakamas Chetpattananondh and Watsa Khongnakorn. 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.
- Ram Yamsaengsung, Pakamas Chetpattananondh and Watsa Khongnakorn. 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.