

**TREATMENT OF SYNTHETIC KRAFT EVAPORATOR CONDENSATE AND  
THERMOMECHANICAL PULP PRESSATE USING NOVEL  
THERMOPHILIC AND MESOPHILIC BIOREACTORS**

**By**

**MEIRU ZHENG**

**A thesis submitted in conformity with the requirements  
for the Degree of Master of Science in Engineering,  
Faculty of Engineering of Lakehead University**

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## ABSTRACT

A comparative study on the treatment of synthetic kraft evaporator condensate and thermomechanical pulp (TMP) pressate between thermophilic (55°C) and mesophilic (30°C) temperature was conducted using sequencing batch reactors (SBRs) and membrane aerated biofilm reactors (MABRs), respectively. The performance of thermophilic and mesophilic SBRs was evaluated in terms of chemical oxygen demand (COD) removal, sludge flocculating ability and settleability for these two types of wastewater. Sludge characteristics, including floc size distribution, zeta potential, morphological mapping, were evaluated for sludge from both SBRs. The performance of the thermophilic and mesophilic MABRs was evaluated in terms of COD removal for these two types of wastewater. The main results and conclusions are summarized as below.

1.) For SBRs: Under tested conditions, a chemical oxygen demand (COD) removal efficiency of 90 ~ 98% was achieved at both thermophilic and mesophilic conditions for synthetic kraft evaporator condensate treatment. However, a higher level of effluent suspended solids was observed in thermophilic SBRs. The settleability of thermophilic sludge was poorer than that of the mesophilic sludge. The poorer settleability of thermophilic sludge was related to a higher level of filamentous microorganisms. The results suggest that treatment of synthetic kraft evaporator condensate at the thermophilic temperature (55°C) is feasible in terms of COD removal but faces challenge of biosolids separation.

2.) The results of particle size distribution indicate that thermophilic sludge contained a significant higher level of fine colloidal particles in treated effluent for synthetic kraft evaporator condensate treatment. The average floc diameter of thermophilic sludge was smaller or larger than that of mesophilic sludge, depending on the level of filaments in sludge. There was no significant difference in

zeta potential between thermophilic and mesophilic sludge. Fourier transform infrared spectroscopy study suggests that there was a characteristic peak at  $1080\text{ cm}^{-1}$  (corresponding to the sugar groups in polysaccharides) existing in the thermophilic sludge but not showing in the mesophilic sludge. The level of filamentous microorganisms in thermophilic sludge was significantly higher than that in mesophilic sludge. The poorer settleability of thermophilic sludge was associated with a significant higher level of filaments. These results suggest that significant differences in characteristics and structure of sludge flocs exist between thermophilic and mesophilic sludge treating synthetic kraft evaporator condensate.

3.) For MABRs: Under tested conditions, a chemical oxygen demand (COD) removal efficiency of 80 ~ 95% was achieved at both thermophilic and mesophilic conditions, and the COD removal efficiency of thermophilic MABR (80 ~ 90%) was slightly lower than that of the mesophilic MABR (85 ~ 95%) for synthetic kraft evaporator condensate treatment. Simultaneous COD removal and denitrification were observed in the mesophilic MABR, while the thermophilic MABR contributed mainly for COD removal. Nitrification was not significant in both the thermophilic and mesophilic MABRs. The results suggest that treatment of evaporator condensate is feasible at both thermophilic and mesophilic MABRs in terms of COD removal.

4.) With a total influent chemical oxygen demand (COD) of 3700 ~ 4100 mg/L for TMP pressate, a COD removal efficiency of about 60, 80, and 90% was achieved at an hydraulic retention time of 6, 12 and 24 hours, respectively, under both thermophilic and mesophilic conditions (SBRs). Excellent sludge settleability (a small sludge volume index) was obtained at both thermophilic and mesophilic conditions (SBRs). A higher level of effluent suspended solids was observed in the thermophilic SBR. The results suggest that treatment of TMP pressate in thermophilic temperature is feasible.

The COD removal efficiency (40 ~ 80%) of MABRs was lower than that of SBRs (60 ~ 90%) for TMP pressate treatment. The COD removal efficiency of thermophilic MABR (40 ~ 65%) was slightly lower than that of mesophilic MABR (50 ~ 80%). Effluent suspended solids in treated effluents of MABRs was higher than that of mesophilic SBR, suggesting a significant detachment of biofilms from membrane surfaces and the need of biosolids separation after MABRs to improve the quality of treated effluents.

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## NOMENCLATURE

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ASP	Activated sludge process
BOD	Biochemical oxygen demand [mg/L]
COD	Chemical oxygen demand [mg/L]
COM	Conventional optical microscopy
CTMP	Chemi-thermomechanical pulp
DLVO	Derjaguin and Landau (1941) and Verwey and Overbeek (1948)
DMDS	Dimethyl disulphide
DMS	Dimethyl sulphide
DO	Dissolved oxygen [ppm]
EPS	Extracellular polymeric substances
ESS	Effluent suspended solids [mg/L]
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometry
HAP	Hazardous air pollutant
HRT	Hydraulic retention time [hour]
KHP	Potassium hydrogen phthalate
LWE	Lipophilic wood extractives
MAB	Membrane attached biofilms
MABR	Membrane aerated biofilm reactor
MBR	Membrane bioreactor
MDL	Method detection limit [mg/L]
MLSS	Mixed liquor suspended solids [mg/L]
RMP	Refiner mechanical pulping
RSC	Reduced sulfur compounds
SBR	Sequencing batch reactor
SGW	Stone groundwood pulping
SRT	Sludge retention time [day]
SND	Simultaneous nitrification and denitrification
SVI	Sludge volume index [mL/gMLSS]

TABT	Thermophilic aerobic biological treatment
TEM	Transmission electron microscopy
TMP	Thermomechanical pulp
TRS	Total reduced sulphur
$V_o$	Volume of each SBR [L]
VOC	Volatile organic compounds
$Q_E$	Amount of discharged effluent per day from each reactor [L]
$Q_w$	Amount of the sludge wasted per day from each SBR [L]
X	MLSS concentration measured at the end of one cycle [mg/L]
$X_E$	ESS concentration in treated effluent [mg/L]

## 1. Introduction

### 1.1 Current problems associated with pulp and paper wastewater treatment

The pulp and paper industry, a very water intensive industry, has been considered to be a major consumer of natural resources and energy, and a significant contributor of pollutant discharges to the environment [1]. Regulations have become more stringent to protect the environment from pulp effluent pollution. Almost all pulp and paper mills have installed biological secondary treatment systems to treat their mill effluent in order to comply with government regulations. To reduce the overall demand for freshwater, many pulp and paper mills have, or will be adopting, water reduction strategies by improving pulping and paper making technologies as well as wastewater treatment technologies. An alternative approach is to treat the wastewater to such an extent that it can be re-used within the mill. Indeed, the concept of “zero liquid effluent” has been suggested for mills making certain grades of paper [2, 3]. The same concept would be applicable in areas where water sources were extremely limited [4]. Water usage in the Canadian pulp and paper industry has steadily been declining over the last 40 years [5] by increasing the degree of water system closure. However, as the degree of water minimizations increases, the concentrations of contaminants and toxicity of the untreated effluent are also likely to increase, which creates challenges for biological treatment processes of pulp and paper effluents. Advanced wastewater treatment technologies and strategies for high strength wastewater are needed to be explored for in-mill treatment and closed cycle operation to minimize the environmental impacts from pulp and paper mills effluents.

Kraft pulping is the dominant method for pulp production in the world because of its pre-eminent quality and commercial position. In the kraft pulping process, condensate, formed by the condensation in the digester and black liquor evaporators, may account for as much as 40% of the total BOD



discharged from a bleached kraft mill regardless of the fact that it may represent only 5% of the total mill effluent volume [6]. Although the cleaner fraction of the evaporator condensate in a kraft pulp mill can be reused as process water, the fouler fraction of the evaporator condensate cannot be reused without treatment because of the high strength of organic and odorous compounds it contains [7]. For an unbleached-kraft mill, more than 90% of the normal mill COD load could be from foul condensate. The low-volume, high temperature, and high strength foul condensates, therefore, need to be seriously considered for an effectively in-mill biological treatment.

Mechanical pulp, high yield pulp, is one of the two branches of pulp and paper making industry. Forty percent of all Canadian mills are thermomechanical pulp (TMP) mills [8]. It is not a major cause for environmental concern since most of the organic material is retained in the pulp, and the chemicals used (hydrogen peroxide and sodium dithionite) produce benign byproducts (water and sodium sulfate respectively) [9]. However, the significant toxic influence of the effluent generated from TMP mills on fish were observed by previous investigations [10-12]. TMP pressate is the most concentrated flow and contains most of the COD generated in the TMP plant. In-mill treatment of TMP pressate would maintain a stable operation in general, a good heat balance, promote “zero effluent” technology, thus reduce the final environmental impact.

## 1.2 A rational approach to improving the treatment of pulp and paper wastewater treatment

In this study, a research was conducted to explore novel biological wastewater treatment technologies, thermophilic membrane aerated biofilm reactors (MABRs) technology and thermophilic sequencing batch reactors (SBRs) technology, for the treatment and reutilization of the foul fraction of the evaporator condensates and TMP pressate, which all have a temperature of 50 ~ 70°C. The novel

biological treatment technologies may prove to be more efficient than stripping and conventional mesophilic biological treatment for the in-mill removal of contaminants of concern from the foul fraction of the evaporator condensate and TMP pressate which are plenty of hazardous air pollutants (HAPs). The high strength and high temperature of contaminants in foul fraction of the evaporator condensate and TMP pressate require pure oxygen aeration, thus, high oxygen uptake rate, a unique quality of MABR, may meet the demand well. Since, this biological wastewater treatment system is operated at a high temperature ( $55^{\circ}\text{C}$ ), therefore, no cooling of the hot condensates to about  $35^{\circ}\text{C}$  for the conventional biological treatment and no reheating to about  $55^{\circ}\text{C}$  for reusing in the process [3] are required in the effluent treatment and reuse system, unlike the conventional mesophilic biological technologies. Therefore, the treated water could remain at an elevated temperature closer to the mill process temperature, thereby resulting in the energy saving along with high recovery of the preheated quantity of condensates.

MABRs characterized by the efficient way of bubbleless aeration represent a new technology for aerobic wastewater treatment. A gas permeable membrane possesses two key functions: first, to provide bubbleless aeration for the oxygen mass transfer as an oxygen supplemental material; and second, to support the formation of biofilm during the biological treatment for bacterial immobilization, where oxidation of pollutants takes place, as illustrated in Figure 1.1 [13]. The unique aeration style makes MABR an ideal and high efficient (100% utilization of the oxygen) bioreactor [14-18] for removing the contaminants from a high strength industrial wastewater containing volatile organic compounds (VOCs) and a promising commercial potential for wastewater treatment. However, MABRs' inherent inability to control the thickness of a biofilm formed during treatment, affects the efficiency of the process thereby discourages its commercial application.

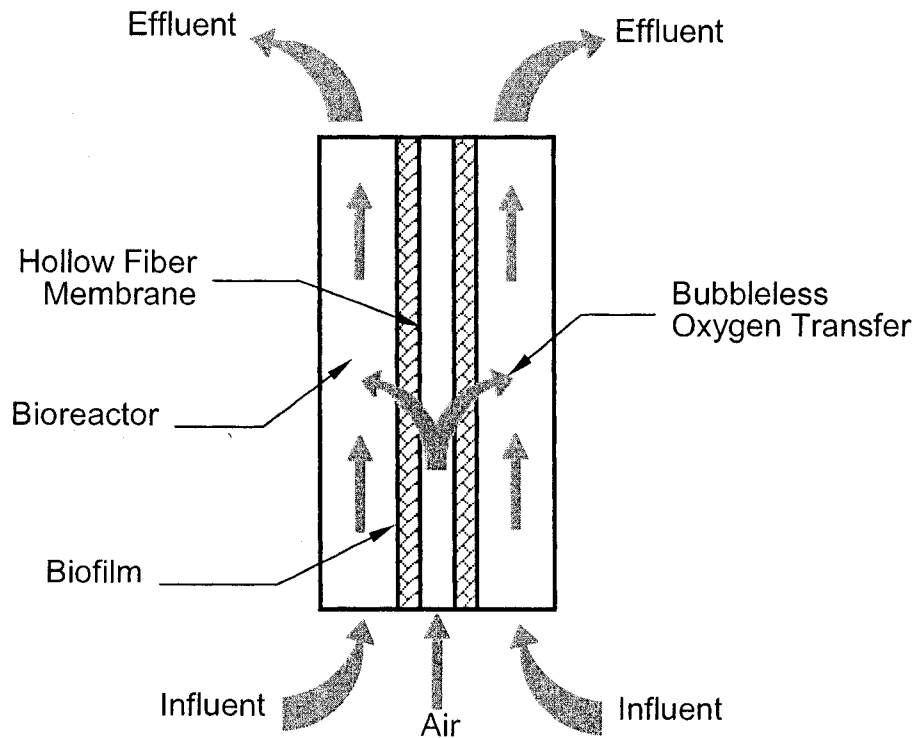


Figure 1.1 Schematic diagram of membrane aerated biofilm reactors, in this case through a single hollow fiber with attached biofilm growth [13]

Thermophilic aerobic biological treatment (TABT) has gained an increasing interest due to its unique characteristics over mesophilic treatment such as elevated operational temperature (functional at a high temperature of wastewater, such as the evaporator condensate and TMP pressate – beneficial to the process due to no need for cooling), rapid biodegradation rates, low sludge yields, along with an excellent process stability [19-24]. However, the main challenge still remaining with TABT technology is the high turbidity, high oxygen transportation demand, and biomass retention problems in the conventional aerated biological treatment processes [19, 21, 25].

Keeping in view of the potentials of MABR and TABT and to overcome their built-in limitations but harnessing the benefits from both of these technologies, combining of these two (TABT & MABR) seems to be a plausible step. The combination will certainly be advancement in the improvement of biofilm thickness control, high oxygen up-take rate and remaining an optimal operational temperature to gain the maximum heating recovery of evaporator condensates and TMP pressate in wastewater treatment, which in turn helps in saving the energy to a large extent.

### 1.3 Motivation of the present study

There is increasing interest in treating and reusing the foul fraction of the evaporator condensate and TMP pressate from pulp and paper mills to make the closed cycle operation. Treatment technologies, which are currently in use, such as steam stripping and conventional mesophilic biological treatment, have their limitations and therefore encourage the development of better treatment technologies with higher efficiency and lower costs.

Reusing treated evaporator condensate and TMP pressate would promote recirculation of the process waters, thus reduce the amount of freshwater requirements. Also, Recycling of used water at the required range of temperature would help in reducing the energy requirements, along with the contaminant load to the existing mill effluent treatment system. This in turn will help in reducing the impact of discharging treated wastewater into the environment, so much as, fulfilling the goal of zero effluent, reducing the HAP emission and trimming down the penalties. The reused foul evaporator condensate could be utilized in recausticizing, brownstock washing, bleaching, as well as paper making, as schematized in Figure 1.2 [26]. And the in-mill treated TMP pressate can be used in the TMP plants as process water as well.

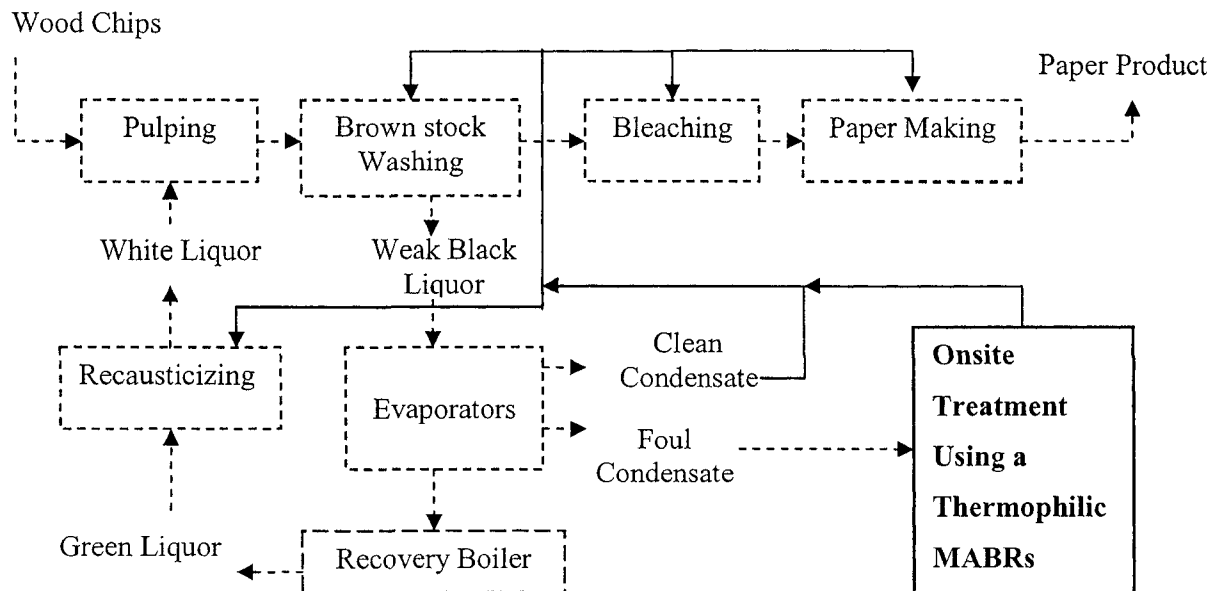


Figure 1.2 Schematic diagram of a bleached kraft pulping process with treated evaporator condensate reuse (solid lines) [26]

#### 1.4 Objectives

The overall objective of this study was to develop better treatment technologies for in-mill kraft evaporator condensate and TMP pressate treatment and closed cycle operation and to explore novel biological treatment technologies – thermophilic SBR and thermophilic MABR for evaporator condensates and TMP pressate treatment. Specific objectives include:

- 1.) Compare the performance between thermophilic and mesophilic SBRs;
- 2.) Compare the performance between thermophilic and mesophilic MABRs;
- 3.) Compare the performance between MABRs and SBRs; and
- 4.) Characterize structure and properties of biofilms and microbial flocs under thermophilic and mesophilic conditions.

## 2. Literature Review

Since the purpose of this study is to develop thermophilic sequencing batch reactors (SBRs) and membrane aerated biofilm reactors (MABRs) for warm high strength pulp and paper effluent treatment, literature review on MABRs, thermophilic processes, pulp and paper effluent treatment was conducted to elucidate the state-of-the-art progresses in these areas.

### 2.1 Membrane aerated biofilm reactors

#### 2.1.1 Introduction of MABRs

Combining hydrophobic membrane technology with biological reactors for the treatment of municipal and industrial wastewaters has led to the development of MABRs. The immobilization of biofilms on permeable hydrophobic membranes for the biodegradation of pollutants is becoming of increasing interest for applications where conventional treatment technologies are unsuitable although the bubbleless MABRs technology is still in the development stages.

An MABR is schematically shown in Figure 2.1.1 [14]. The limiting substrates for biofilm growth are generally the carbon substrate and/or oxygen which, in MABRs, are supplied from opposite sides of the biofilm. MABRs use gas-permeable hydrophobic membranes to improve the mass transfer of oxygen to the bioreactor by providing bubbleless oxygen. Membranes, either tubular or flat, can be of the hydrophobic porous type such as polypropylene, of the dense film type such as silicone, or of the composite type where a porous membrane is coated with a thin film of dense material. The membrane lumen can be either open or closed.

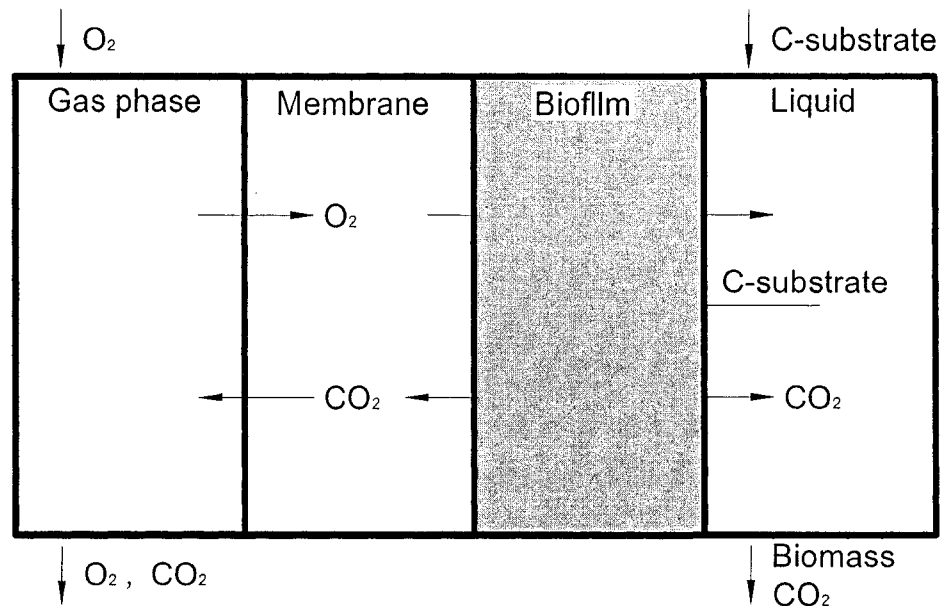


Figure 2.1.1 Schematic diagram of the MABR [14]

A number of studies have examined the concept of using gas permeable membranes for aerating water [27–31]. When these membranes are employed in wastewater treatment they rapidly become coated with biofilm which has a profound impact on the oxygen transfer behavior of the membranes [15, 32–34]. Table 2.1.1 lists some studies on MABRs. A wide variety of pollutants have been successfully treated using various system configurations and various types of membranes. Results from studies with MABRs have been reported for the degradation of chlorophenols [35], phenol [36], xylene [37], ammonia [38], and for simultaneous nitrification and organic carbon removal [39].

Table 2.1.1 Some studies on membrane aerated biofilm reactors [14]

Pollutant	Membrane	Configuration	Specific surface area (m <sup>2</sup> m <sup>-3</sup> )	Reactor volume (l)
Synthetic sewage	Teflon	Tubular, sealed end	550	2.85
Food processing wastewater	Silicone	Tubular <sup>a,b</sup>	--	--
Organic carbon and inorganic nitrogen	Gore-tex	Single tube <sup>b</sup>	19	3.15
2,4 Dichlorophenoxyacetate	Polyetherimide	Plate and frame, flow through	34	0.50
Glucose/peptone	Silicone with fibrous support	Tubular coil, flow through	62	6.00
Xylene	Silicone	Tubular coil, flow through	34	1.70
Organic carbon and inorganic nitrogen	Polytetrafluoroethane	Tubular coil <sup>b</sup>	60	5.76
BTEX	Silicone	Tubular coil, flow through	-	-
Xylene	Silicone	Hollow fibre, flow through	111	0.18
Organic carbon and inorganic nitrogen	Polypropylene	Hollow fibre, sealed end	5108	1.35
Organic carbon and inorganic nitrogen	Silicone with fibrous support	Hollow fibre <sup>b</sup>	5	0.23
Phenol	Silicone	Tubular coil, flow through	101	1.00
Chlorophenols	Silicone	Tubular coil, sealed end	200	19.00
Benzene, 2-chlorophenol, 2,4-dichloro-toluene	Silicone	Hollow fibre, flow through	54	-
Xylene and ethylbenzene	Silicone	Tubular coil, flow through	69	0.80
Organic carbon and inorganic nitrogen	Polypropylene	Hollow fibre, sealed end	185	0.43
Organic carbon and inorganic nitrogen	Silicone with fibrous support	Tubular, flow through	18	1.63
Organic carbon and inorganic nitrogen	Polypropylene	Hollow fibre, sealed end	185	0.43
Acetate	Silicone	Hollow fibre, flow through	15	1.5

<sup>a</sup>. Membrane was intended for aeration, but biofilm inadvertently formed.

<sup>b</sup>. No information given on whether flow through or closed.

### 2.1.2 Advantages of MABRs comparing with conventional biological processes

Membrane attached biofilms (MABs) grow in a very different manner than conventional biofilms, since nutrients from the wastewater and oxygen from the membrane diffuse into the biofilm from opposing directions. In recent years, the growth of a MAB is viewed by many as positive, since the biofilm is active in removing pollutants and the membrane is effective in delivering the oxygen directly to the



bacteria that need it. Different investigators have identified potential advantages of MABRs that include better performance in handling high organic loading rates [40], improved oxygen transfer efficiency [15], potential for simultaneous carbon oxidation, nitrification, and denitrification [41], and elimination of VOCs stripping to the atmosphere [15]. Some of the advantages of MABRs are further discussed in the following paragraphs.

Lower operating cost : High oxygen uptake rates (as high as  $20 \text{ g/m}^2\text{d}$  can be achieved according to the experiments [42]) would allow MABRs to operate with much greater thicknesses of active biomass than that of conventional biofilm reactors (generally not higher than  $10 \text{ g/m}^2\text{d}$  [43]). Virtually, all of the gas passing through the membrane can be utilized within the biofilm. Good fluidization of the fibres ensures they are distributed uniformly in the wastewater, providing excellent contact between the attached biofilm and the wastewater. Close to 100% oxygen conversion efficiencies for the treatment of high-strength wastewaters are achievable [14-18]. As a result, the power consumption, thus the operating cost, for MABRs aeration would be reduced.

Fewer odor: Biodegradation of volatile organic compounds (VOCs) frequently results in VOCs losses to the atmosphere due to stripping when bubble aerated biological processes are used [44,45]. The problem can be prevented by using MABRs because bubbleless aeration is used, less stripping of VOCs is achieved. Thus, odor problems caused by bubble aeration can be eliminated by the use of MABRs (shown as in Table 2.1.1).

Higher rate organic removal : Biofilms in wastewater treatment systems are generally relatively thick, resulting in only partial penetration of oxygen to a depth of between 50 and 150  $\mu\text{m}$ , varying with the

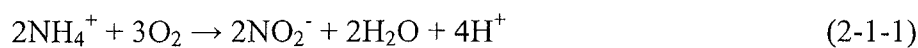
structure of the biofilm and the utilization rate of the cells [14, 46]. When the wastewater loading rate is high, this limits the removal of pollutants. Aeration with pure oxygen can overcome this problem. But in conventional biofilm systems, a high fraction of the oxygen supplied is lost to the atmosphere, thereby providing a non-economical solution. An alternative is to use the MABRs with high intra-membrane oxygen pressure to achieve complete oxygen penetration ensuring the high rate organic removal.

Simultaneous nitrification and denitrification: In conventional biofilm reactors, autotrophic nitrifying organisms may be excluded from the oxic layer of the biofilm due to the faster growth of heterotrophs. As a result, substantial nitrification only occurs when the carbon substrate loading rate of the wastewater is low. Whereas, the MABR appears to be a promising system for one-stage organic carbonaceous pollutants removal, nitrification and denitrification [41, 47, 48].

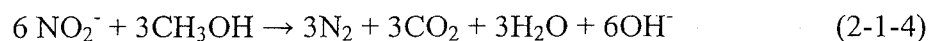
### 2.1.3 Simultaneous organic carbonaceous pollutant removal, nitrification and denitrification

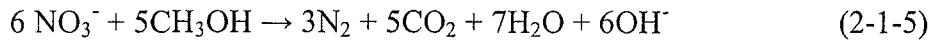
Biological nitrogen removal is a promising way to remove nitrogen compounds in wastewater by two successive reactions: nitrification to convert ammonia into nitrite or nitrate under aerobic conditions and denitrification to convert nitrite or nitrate into nitrogen gas under anoxic conditions [49]. The reactions are as follows:

Nitrification:



Denitrification (using methanol as the electron donor):





The two processes have complementary relations as follows:

- Nitrification produces nitrite or nitrate that is an electron acceptor in denitrification;
- Nitrification reduces the pH that is raised in denitrification;
- Denitrification generates the alkalinity that is required in nitrification [50, 51].

Exemplifying that the two reactions are conducted separately, two reactors with circulation are necessary and pH adjustment in each reactor have to be considered separately. Therefore, there are obvious advantages to performing simultaneous nitrification and denitrification (SND) in a single reactor.

An MABR for nitrogen removal is of significant interest because the biofilm structure of an MABR is suitable for SND, thus, can make use of the above-mentioned relations; i.e. the alkalinity which is essential for nitrification is supplied by denitrification; therefore, theoretically pH adjustment is not required. In an MABR, a hollow-fiber membrane plays two roles: the oxygen supplemental material and the carrier for bacterial immobilization [13]. As schematically shown in Figure 2.1.2, the counter-diffusion of oxygen and nutrients creates microbial stratification within the biofilm [52].

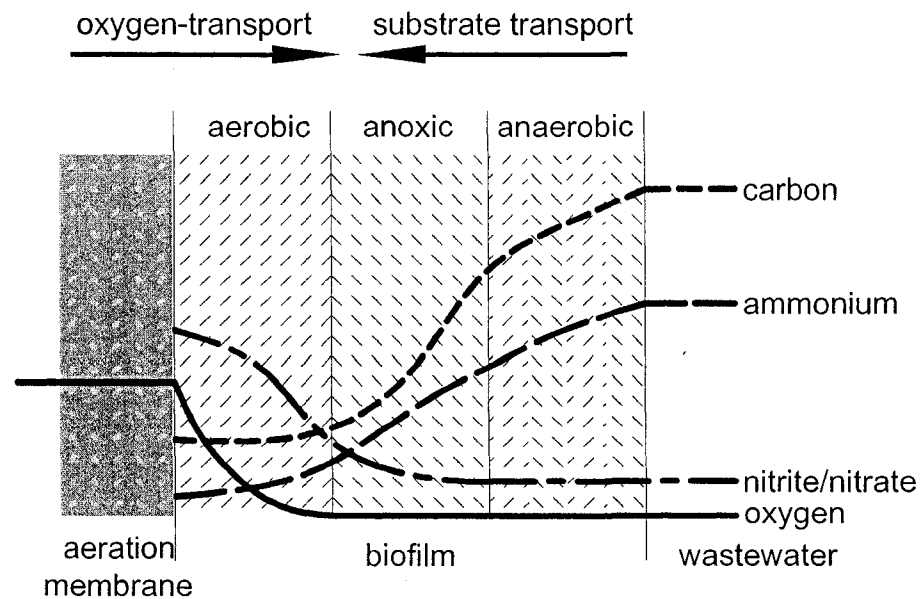


Figure 2.1.2 Simultaneous organic carbonaceous removal, nitrification and denitrification in an MABR [52]

The high oxygen concentrations and organic carbon-depleted conditions, a favourable environment for the cultivation of nitrifying organisms, at the membrane biofilm interface would support nitrification. If nitrifying bacteria are immobilized to the membrane surface, oxygen can be directly supplied to these bacteria without any formation of bubbles and therefore ammonia can be oxidized effectively [47, 53, 54, 55]; an aerobic heterotrophic layer above this would facilitate carbonaceous pollutant removal, with comparatively high oxygen and organic carbon concentrations conditions, and an anoxic layer close to the biofilm–liquid interface, the region near bulk liquid, would allow denitrification because there would be a favorable condition for heterotrophic denitrification due to organic carbon, nitrite and nitrate-sufficient and oxygen-depleted conditions can be created.

Conventional biofilm reactor is difficult to achieve SND of organic carbon-containing wastewater (Figure 2.1.3). In conventional biofilm reactors, autotrophic nitrifying organisms may be excluded from the oxic layer of the biofilm due to the faster growth of heterotrophs [56]. Oxygen competition between heterotrophic bacteria and nitrifying bacteria near the bulk biofilm interface leads to a decrease of nitrogen removal efficiency [57]. As a result, substantial nitrification only occurs when the carbon substrate loading rate of the wastewater is low. Low rates of nitrification but very high organic carbon oxidation were reported by both [58] and [17] in studies where a washing procedure was employed to detach excess biomass. In both cases, the low rates of nitrification were attributed to the wash-out of slow growing chemoautotrophic nitrifying bacteria.

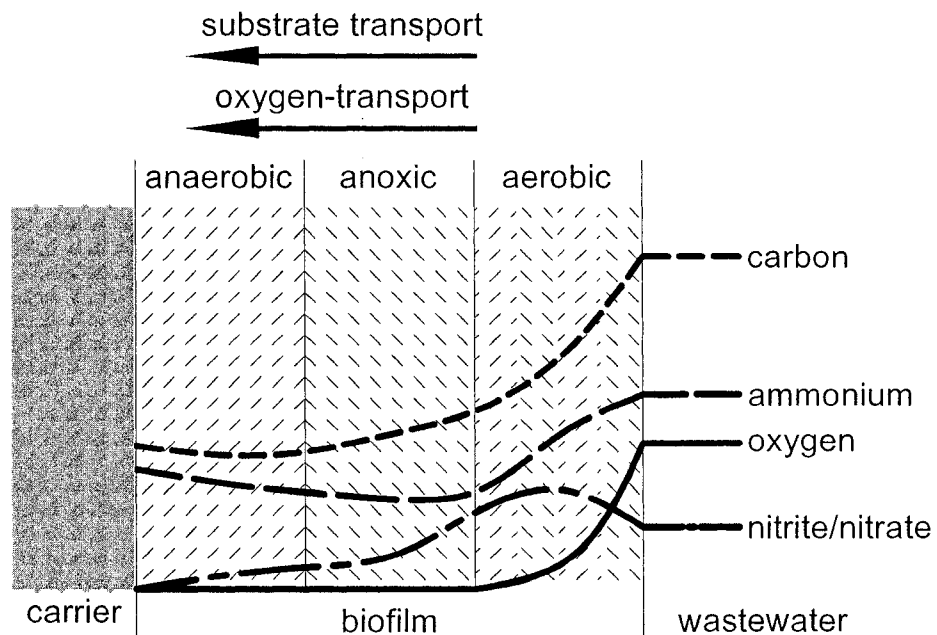


Figure 2.1.3 High organic carbon oxidation but low rates of nitrification in a conventional biofilm reactor [52]

## 2.2 Thermophilic and mesophilic biological treatment processes

Thermophilic aerobic biological treatment (TABT) of industrial wastewaters has gained increasing interest in recent years, especially in the pulp and paper industry. Due to the increasing water system closure and higher process water temperatures, there is a need for efficient thermophilic treatment systems [59]. The advantages of thermophilic biological treatment processes are faster degradation rates, lower sludge yields, and excellent process stability [19-24]. Thermophilic aerobic biological wastewater treatment of several different wastewaters in both pilot and laboratory-scale experiments has been proven to give stable COD removals and tolerate varying operational conditions, such as changes of temperature and volumetric loading rates [59,60]. However, thermophilic aerobic processes, compared to mesophilic processes, have been reported to suffer from poorer effluent quality, typically measured as higher COD values and turbidity [59, 61, 62]. Current literature shows that effluents of thermophilic aerobic wastewater treatment systems are generally more turbid as compared to mesophilic analogues [59, 62]. In particular, a high amount of dispersed particles, such as free bacteria and colloids, increases COD values in thermophilic effluents. In addition, biomass retention is also more difficult under thermophilic conditions. Reasons for this phenomenon are so far unknown [63].

Suvilampi et al [64] compared laboratory-scale mesophilic (20°C ~ 35°C) and thermophilic (55°C) activated sludge processes (ASPs) treating diluted molasses wastewater in aspects of effluent quality, removal of different COD fractions, sludge yield, floc size, and sludge settleability. The results show the thermophilic ASP produced higher COD<sub>sol</sub> removals, which were comparable to those of the mesophilic ASP. However, the COD<sub>fit</sub> and COD<sub>tot</sub> values were markedly higher in the thermophilic than mesophilic effluents. This was due to formation of dispersed particles, such as free bacteria, under thermophilic conditions. The increased amount of dispersed particles was seen in increased COD<sub>col</sub> values.

Vogelaar et al. [65] focused on the thermophilic aerobic post treatment of anaerobically pretreated paper process water which has a relatively high COD concentration but contains few easily biodegradable components. Figure 2.2.1 depicts two diagrams showing the relative distributions of the different wastewater fractions for both temperatures.

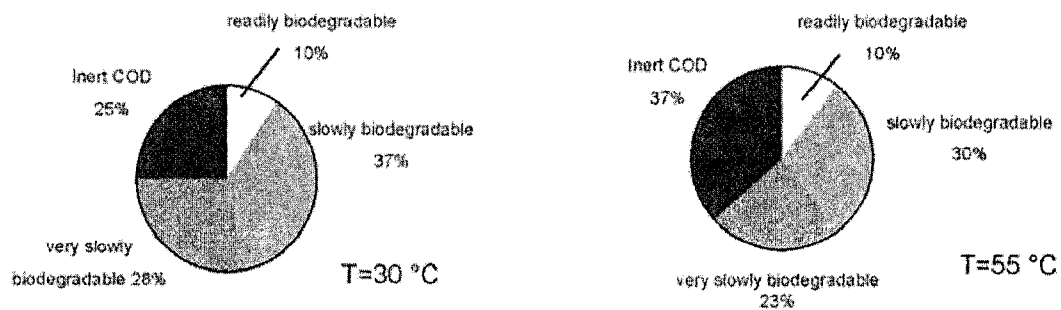


Figure 2.2.1 Wastewater fractions at 30°C and 55°C [65]

It is shown that under thermophilic conditions, the inert COD fraction was higher and slowly and very slowly biodegradable COD fractions were lower as compared to mesophilic conditions. Thermophilic aerobic biomass was not able to degrade the anaerobic effluent to the same extent as the mesophilic biomass resulting in higher at inert COD levels. Under mesophilic conditions colloidal wastewater COD was removed from the liquid phase by a flocculation process. However, under thermophilic conditions, the colloidal fraction remains almost completely stable in the water phase and was washed out in a continuous reactor system, i.e. the colloidal fraction was not removed from the liquid phase.

Juteau et al. [66] applied a self-heating aerobic thermophilic treatment to pig manure (a very high-strength wastewater  $COD_{tot} = 65 \sim 110$  g/L,  $COD_{sol} = 32 \sim 59$  g/L) reaching temperatures up to 75°C (oscillating temperature). The results show that the temperature should be limited to 60°C, which

represents a good compromise to achieve a significant reduction of COD and ammonia and a complete removal of fecal coliforms, *Campylobacter spp.* and *C. perfringens*.

Vogelaar et al. [63] conducted tests to assess the individual role of the mesophilic and thermophilic activated sludge. The results show that they have a very different bioflocculation behavior. Bioflocculation of mesophilic activated sludge and wastewater colloidal particles only occurs when actual aerobic biodegradation takes place. In contrast, hardly any bioflocculation of thermophilic activated sludge and wastewater colloidal particles took place under all circumstances. Thermophilic sludge was found more dispersed, containing a higher volume fraction of small particles and was more sensitive towards shear forces than mesophilic activated sludge. Binding of wastewater colloidal particles on a flat hydrophobic surface did vary with temperature but no general up or downward trend could be observed. Therefore, it is unlikely that changes in the hydrophobic interaction with temperature are causing the large observed differences in bioflocculation behavior. It is expected that the different bioflocculation behavior of mesophilic and thermophilic activated sludge is caused by changes in polymer interactions with temperature and/or by the interplay with exo-enzymes in the activated sludge's.

Some work has been reported on kraft pulp mill foul condensates treatment. Dias et al. [67] treated kraft pulp mill foul condensates under thermophilic and mesophilic conditions (temperature were 35°C, 45°C and 55°C respectively). High COD, total reduced sulphur (TRS) and methanol removals were obtained in the mesophilic temperature range. A decrease in removal efficiency was observed as the temperature increased, although it could still be considered comparatively high. Specifically, a decrease in respiratory activity obtained at 55 °C, followed by a decrease in the TSS concentration in the bioreactor.



Bérubé and Hall [68] treated synthetic condensate, rich in methanol, obtained good methanol removal at temperatures of 55°C and 60°C in a membrane separation bioreactor. Welander et al. [69] obtained high removals of methanol and chemical oxygen demand (COD) using aerobic and anaerobic biological treatment of the kraft mill foul condensate at 55°C. Although anaerobic treatment showed a better operating economy, it was more sensitive to inhibitory compounds and suggested that recovery time after upsets may be long.

Due to the characteristics of thermophilic treatment processes, significant research efforts have been put in development of thermophilic membrane bioreactors and thermophilic biofilm reactors [70] that are less vulnerable to biomass retention problems.

### 2.3 Treatment of pulp and paper mills effluent, kraft mill foul evaporator condensate

Effluents from pulp and paper mills are highly toxic and are a major source of aquatic pollution. The pulping process generates a considerable amount of wastewater, approximately 200 m<sup>3</sup>/tonne of pulp produced [71]. Most of the toxicity in pulp and paper whole mill effluents and process streams is attributed to resin and fatty acids, chlorinated phenols and, to a lesser extent, a broad group of neutral compounds [72]. There is a significant difference in the quality of the wastewaters from pulping and papermaking operations. This is due to the diversity of processes, the chemicals used and the dissolved wood derived substances which are extracted from the wood during the pulping and bleaching processes [73]. Table 2.3.1 shows the wastewater pollution load from individual pulping and papermaking process.

Table 2.3.1 Typical wastewater generation and pollution load from pulp and paper industry [74]

Process	Wastewater (m <sup>3</sup> /adt pulp or paper)	SS (kg/adt pulp)	COD (kg/adt pulp)
Wet debarking	5 -25	Nr	5 – 20
Groundwood pulping	10 – 15	Nr	15 – 32
TMP – unbleached	10 – 30	10 – 40	40 – 60
TMP – bleached	10 – 30	10 – 40	50 – 120
CTMP – unbleached	10 – 15	20 – 50	70 – 120
CTMP – bleached	10 – 15	20 – 50	100 – 180
NSSC	20 – 80	3 – 10	30 – 120
Ca – sulfite(unbleached)	80 – 100	20 – 50	Nr
Ca – sulfite (bleached)	150 – 180	20 – 50	120 – 180
Mg – sulfite (unbleached)	40 – 60	10 – 40	60 – 120
Kraft – unbleached	40 – 60	10 – 20	40 – 60
Kraft – bleached	60 – 90	10 – 40	100 – 140
Paper making	10 – 50	Nr	Nr
Agrobased small paper mill	200 - 250	50 – 100	1000 – 1100

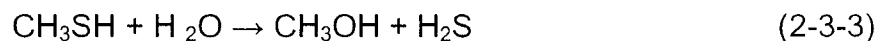
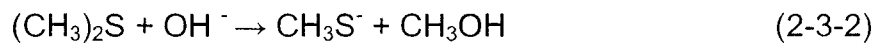
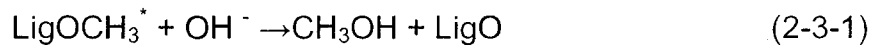
Nr – Not reported; adt – air dry ton; NSSC – neutral sulfite semi-chemicals

The kraft process is the dominant chemical pulping process in Canada and other countries (40%) [6]. In this process, wood chips are digested or “cooked” under pressure with a mixture of hot sodium hydroxide (caustic soda) and sodium sulphide. Lignin and wood extractives are solubilized, leaving the insoluble cellulose fibres as pulp [75]. In an unbleached kraft mill, the product may be pulp or may be processed into unbleached kraft products such as linerboard and paper bags. In a bleached kraft mill, the bleached pulp has a variety of end uses, such as a component of newsprint and other papers [75]. The chemicals are recovered from the spent (strong) black liquor and pulp washings (termed weak black liquor) through a series of involving concentration, combustion, clarification and causticizing. By-

products like Sulphur-containing gases, turpentine and tall oil are produced during digestion and in the chemical recovery system [76].

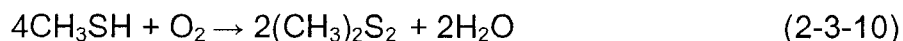
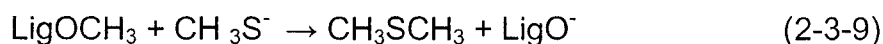
Kraft foul evaporator condensates, produced by the condensation of black liquor vapors from the digesting and pulp washing, are low volume, high strength wastewaters comparing with other kraft mill waste streams. Most of the impurities in kraft foul condensates are volatiles which evaporate from black liquor along with water. One of the main contaminants of concern in foul kraft condensates is methanol which is the most abundant contaminant present in an evaporator condensate, contributing up to 95% of the total organic content, and it is classified as one of the hazardous air pollutants (HAPs) [77]. Other main contaminants of concern are total reduced sulphur compounds (TRS); such as hydrogen sulphide ( $\text{H}_2\text{S}$ ), methyl mercaptan ( $\text{CH}_3\text{SH}$ ), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS). TRS are also classified as HAP and are extremely odorous [6, 76, 78].

Methanol, the main organic in foul condensates, is believed to originate from an alkaline hydrolysis of 4-o-methyl glucuronic acid residues in hemicellulose. These residues are typically greater in hardwoods than in softwoods [6]. Methanol may also be formed by reactions involving dimethyl sulfide/methoxyl groups on lignin or involving methyl mercaptan by the following reactions:



The reduced sulfur compounds (RSCs) in the kraft foul condensates are produced from the  $\text{Na}_2\text{S}$  in the kraft cooking liquor by the following reactions:





\* LigOCH<sub>3</sub> indicates a methoxyl group on lignin.

It appears that RSC concentration is normally the dominant factor in foul condensate toxicity. Envirocon [79] found, using data from several mills, foul condensate toxicity to be highly correlated with RSC concentration, even for stripped condensates. It is also reported that the removal of methyl mercaptan and other organic sulphides was only about 60% in a five-day aerated lagoon. Since organic sulfides are not totally stripped or oxidized in a five day aerated lagoon, should not be rapidly oxidized or air-stripped upon discharge to receiving waters, they will surely tend to linger in receiving waters [6]. Bérubé and Hall [68, 80] indicated that over 99% of the RSC contained in condensate was removed during treatment using an MBR and that the removal was strictly due to abiotic mechanisms. Approximately 33% of the methyl mercaptan was stripped from the MBR by the aeration system. Remaining 67% was abiotically oxidized during treatment. Over 99% of the DNS and DMDS contained in the influent condensate were removed from the MBR by stripping due to the aeration system. The potential importance of RSC in mill effluent toxicity should be taken seriously. The amount of RSC that is released to the atmosphere during aerobic biological treatment can be reduced if the RSC can be rapidly oxidized to non-volatile compounds before having the opportunity to be stripped by the aeration system.

Since the condensate streams have been considered an important pollution hazard, many methods have been utilized for the treatment of condensates. Table 2.3.2 [81] shows the conventional ways that have been investigated for treating kraft foul condensates and their effectiveness.

Table 2.3.2 Foul condensate treatment effectiveness [81]

	RSC Removal	BOD removal	Comments
<b>Selective treatment</b>			
stripping			
5% steam	Excellent	Some	Off-gas incinerated
20% steam	Excellent	Good	Off-gas incinerated
Air	Excellent	Some	Off-gas incinerated
Flue gas	-	Moderate	Off-gas to atmosphere
Chemical Oxidation			
Chlorine	Good	Little	Chlorinated organics
Oxygen	Good	None	Low reaction rate
Air on activated carbon	Good	Poor	No off-gas disposal
Carbon adsorption	Moderate	Moderate	High operating cost
Chemical precipitation	Little	None	Ineffective
Turpentine decantation	None	Some	Turpentine sales
Biological oxidation			
Aerated lagoon, or activated sludge	Good	Good	Ambient odor
Tricking filter	Good	Moderate	Large equipment
Spray irrigation	?	Good	Ambient odor
Anaerobic	Moderate	Moderate	Gaseous fuel
Recycle to process	Some	Some	Possible odor

---

**Combined treatment**

With mill effluent in Some  
aerated lagoon

Good

Ambient odor

---

#### 2.4 Treatment of TMP pressate

The main contaminants in TMP process water are resin acid, fatty acid, and neutral wood extractives. Because TMP processes employ heat and chemical treatment of wood chips prior to refining, the solubilization of wood extractives such as resin acids could be greater than that in other mechanical pulping processes except CTMP [82]. In TMP mills, mechanical processes use steam to soften chips and pressure to refine them, producing a very high yield product, with 85 ~ 95% of the original wood components in the final pulp, including lignin. 2% ~ 5% of the wood material is dissolved, or dispersed as colloidal particles, into the process water [8]. The dissolved and dispersed substances in the process waters of thermomechanical pulping (TMP) system originate from several sources as follows [83]:

- Components of wood dissolved and dispersed during the high-temperature conditions of the defiberization processes (hemicelluloses, pectins, lignin, extractives, and inorganic salts).
- Residuals of processing chemicals possibly applied in mechanical pulping and bleaching.
- Leakages from sealing and lubrication and dissolution of equipment materials in to the process.
- Carryover of residuals of papermaking chemicals with the circulation water that is circulate backward from papermaking to pulping.
- The former possibly including those organic and inorganic substances that came in with fresh water intake and purification.
- Carryover of dissolved and dispersed material from debarking. As the debarking process usually is relatively closed, the concentration of process water becomes high and contaminated water penetrates into wood.

There is a considerable incompatibility for the compositions and the concentrations of substances in process waters due to the different types of the wood which vary largely, and the structure of the water system (Table 2.3.3) [84].

Table 2.3.3 Oxidizable matter in water effluents of various processes [84]

Process	Oxydizable material (kg/t of pulp)
Mechanical	10
Unbleached Kraft	15
Thermo-mechanical	30
Bleached Kraft	50
Chemi-thermomechanical	50
Semi chemical	90
Bisulphite	110

Twice the amount of wood material, measured as BOD, was reported to be released in TMP compared to SGW and RMP pulping (Table 2.3.4) [84].

Table 2.3.4 Dissolved organic substances, BOD, COD and suspended solid discharges from mechanical pulping process [84]

Parameter	Stone groundwood pulping (SGW)	Refiner mechanical pulping (RMP)	Thermo-mechanical pulping (TMP)
Dissolved organic substances (%)	1–2	2	2–5
BOD (kg/t)	10–22	12–25	10–30
COD (kg/t)	22–50	23–55	22–60
Suspended solids (kg/t)	10–50	10–50	10–50

The main components of the dissolved and colloidal substances are hemicelluloses, lipophilic extractives, lignins, and lignin-related substances. Lipophilic wood extractives (LWEs) are nature components of wood, which are liberated into the process water in mechanical pulp production. Chemically LWEs consist of resin and fatty acids, sterols, and triglycerides etc. They are partly present in both soluble, like resin and fatty acids, and non-soluble forms. The non-soluble extractives can be attached to fibres or other particulate matters, or they can be presented in the form of free colloidal droplets making the water typically turbid. Table 2.3.5 [83] gives typical amounts of substances released from TMP of Norway spruce.

Table 2.3.5 Typical amounts of substances released from TMP of Norway spruce [83]

Component group. Kg/ton TMP	Unbleached TMP	Peroxide-bleached TMP
Hemicelluloses	18	8
Galactoglucomannan	16	4
Other hemicelluloses	2	5
Pectins (galacturonans)	2	4
Lignins	2	1
Other lignin-related substances	7	11
Lipophilic extractives (resin)	5	4
Acetic acid	1	20
Formic acid	0.1	4
Inorganic constituents	<1	5

In production of mechanical pulps from wood chips, it is very necessary to remove resin effectively from the pulp because resin is an undesirable component of the final pulp [85]. Resin constitutes a complex mixture of components that are present in the wood chips, such as, steroids, waxes, glycerides, resin acids, terpenes, and fatty acids. To remove resin from mechanical pulps, the pulp is diluted from



the refiner consistency to a concentration of about 3 ~ 5 percent. After dilution the pulp is stored for about 15 ~ 30 minutes in a tank at 50°C ~ 80°C. Thereafter the pulp is pumped to a press where it is pressed to a dryness of about 30 percent. The pressate, which contains resin therein, is separated from the pulp. The pulp is again diluted and again held in another tank for about 15 ~ 30 minutes, and is again pressed. The number of dilution and pressing stages are chosen so that the desired removal of resin from the pulp can be achieved. The pressate, thus, contains various dissolved organic contaminants, e.g. resin and fatty acids, and bleached fines, fibres as well [86].

Although TMP mill effluents tend to be more biodegradable than kraft (chemical pulp) effluents, they are still sufficiently recalcitrant to require very large, expensive biological secondary treatment systems to achieve high effluent quality. For most of thermomechanical pulp mills, traditionally biological treatment is applied to treat the effluents. Resin and fatty acids are reported to be efficiently removed from pulp and paper mill effluents during aerobic treatment (79 ~ 99% removal) [87-90]. The more hydrophilic lignans that also contribute to the acute toxicity from TMP effluents using Norway spruce are removed by 99% during biological treatment [91]. Elliott et al. [92] reported based on their laboratory-scale TMP mill effluent treatment experiments that for a newsprint mill, the level of water reduction did not cause adverse effects on the performance of a secondary biological treatment system (the HRT was set to be proportional to the concentration of reduced volume effluent) as it might be expected. Also, with effluent flow reductions, the feasibility of treatment by non-biological means may become more attractive.

## 2.5 Summary of literature review

Based on a literature survey of past and recent publications, conclusions about the present state of MABR, TABT, and technology of pulp and paper mills effluents treatment can be summarized as follows:

- 1) MABRs have shown potential for removing contaminants from high strength wastewater and a promising commercial potential. However, the inability to control biofilm thickness and overcome mass transport limitations has prevented the commercial application of MABRs in wastewater treatment. Novel methods to conquer the weakness require to be developed.
- 2) In spite of significance to properly control MABRs, there are only few reports which discuss operational parameters affecting reactor performance, i.e. air pressure, air flow rate, concentration of oxygen for the aeration, and substrates loading rate etc. Therefore the effects of operational factors on biodegradation of carbonaceous organic compounds in MABRs needs to be further investigated.
- 3) Understanding of the microbial reaction and diffusion processes is necessary for the scale-up of MABRs. However, to date, no comprehensive study has been reported on the oxygen and substrate mass transfer characteristics in MABRs. What is more, the effects of particular MABR operating conditions on the spatial locations of active organisms have not yet been resolved. Thus, further study is needed.
- 4) The MABR appears to be a promising system for one stage organic carbonaceous pollutant removal, nitrification and denitrification. However, further investigations on the fundamentals of the interacting layers that exist in such biofilms need to be carried out.

5) Thermophilic aerobic biological wastewater treatment systems are generally known as more turbid as compared to mesophilic analogues in activated sludge processes. In addition, biomass retention is also more difficult under thermophilic conditions. However, research efforts can be put in development of the membrane aerated biofilm reactors that are less vulnerable to biomass retention problems to gain the benefits of the thermophilic biological processes, e.g. energy saving, biomass thickness control improving. The performance of thermophilic SBRs, which have a complete different operating manner (cyclic operation) from the ASP, has not been explored for kraft evaporator condensate and TMP pressate treatment.

6) Kraft foul evaporator condensate and TMP mills pressate are of high temperature, high strength of carbonaceous organic compounds, hazardous air pollutants and toxicity, accounting for significant amount (about 40%) of the total BOD discharged while constituting only 5% of the total mill effluent volume. Endeavor to explore the in-mill novel biological treatment technology for afore mentioned waste streams rather than using steam stripping and/or conventional biological wastewater treatment processes is completely required. The potential of SBRs and MABRs for the treatment of these two types of wastewaters has not been explored yet.

## 2.6 Significance of this study

The literature review has shown that development of MABRs in conjunction with TABT, for the treatment of high strength industrial VOCs wastewater, has not been explored yet.

Although MABRs have shown a potential for removing the contaminants from the high strength industrial VOCs wastewater, - an indication of a promising commercial potential, its inherent lack of ability to control the thickness of biofilm, and hence the mass transportation across the membrane during heavy biofilm formation has prevented its commercial application. As for TABT, the turbidity and biomass retention problems remaining in a conventional aerated biological treatment process has brought the challenge to its application to industrial strength wastewater treatment regardless its unique characteristics TABT possesses, such as; elevated operational temperature, rapid biodegradation rates, low sludge yields, and excellent process stability.

Keeping in view of the potentials of MABRs and TABT and to overcome their intrinsic limitations, combining the two (e. g. thermophilic MABRs) makes a plausible step towards gaining the benefits from both in terms of energy saving and improvement in biomass thickness control.

This study deals with the application of novel biological wastewater treatment technologies – MABRs and SBR, for high strength industrial effluent treatment under thermophilic condition ( $55 \pm 0.5^\circ\text{C}$ ) and evaluation of the efficiency of above novel approaches (MABRs and SBRs) of wastewater treatment against the conventional mesophilic biological treatment processes.

In order to examine and compare the wastewater treatment efficiency of MABRs and SBRs under different conditions (thermophilic vs. mesophilic), parameters including influent and effluent chemical oxygen demand, concentrations of effluent suspended solids, mixed liquor suspended solids, are monitored and adjusted. Different levels of influent methanol COD (750 mg/L, 1500 mg/L, 3000 mg/L) were tested at an HRT of 12 hours. The TMP pressate at an influent COD of 3700 ~ 4100 mg/L was

treated at different HRTs (6 hours, 12 hours, 24 hours). The results from this study have the potential for full-scale applications in pulp and paper mills.

In addition, the settleability and flocculating ability of sludge under thermophilic and mesophilic conditions were evaluated in terms of sludge volume index (SVI) and effluent suspended solids (ESS), respectively. To further understand the factors that affect settleability and flocculating ability of sludge, morphology of sludge is studied under different microscopes and floc size distribution and zeta potential of sludge flocs were determined.

My study could offer a tremendous technical support and beneficial application in treating foul kraft evaporator condensate and/or TMP mill pressate in an environmentally friendly way along with economical benefits to the relevant pulp and paper mills, if the combination of above two technologies (thermophilic MABRs) and the thermophilic SBR technology were found to have a good performance with respect to the treatment efficiency and the biofilm control properties, unlike the predecessors technologies such as MABRs and TABT.

### 3. Experimental Materials and Methods

Described in this chapter are the experimental materials and methods used in the present study. The subsections are outlined in the following sequence: laboratory-scale sequencing batch reactor (SBR) system; laboratory-scale membrane aerated biofilm reactor (MABR) system; synthetic kraft evaporator condensate; TMP pressate; inoculum and acclimation of thermophilic bacteria; control strategies of the bioreactors; standard wastewater analyses (COD, MLSS, ESS, SVI, DO); Analysis of ammonia, nitrate and nitrite; microbiology; floc size distribution; zeta potential; and statistical methods.

#### 3.1 Experimental system

##### 3.1.1 Laboratory-scale sequencing batch reactor system

The experimental system, as illustrated in the schematic diagram (Figure 3.1.1), is composed of the following elements: four SBRs operated in parallel for treating wastewaters and producing biomass; a refrigerator for storing the synthetic kraft evaporator condensate or TMP pressate feed at 4°C; two preheating tanks that increased the temperature of the synthetic feed from 4°C to 30°C and 55°C respectively before it entered the SBRs; two water baths that circulated water at different constant temperatures through the jacket of SBRs, resulting in each two SBRs operating at a certain constant temperature ( $30 \pm 0.5^\circ\text{C}$ ,  $55 \pm 0.5^\circ\text{C}$  respectively); four on-line pH controllers (one per SBR); and four timers for controlling the cyclic operation such as feeding pumping, aeration diffusing and mixing, withdrawing pumping, pH measurement of each SBR.

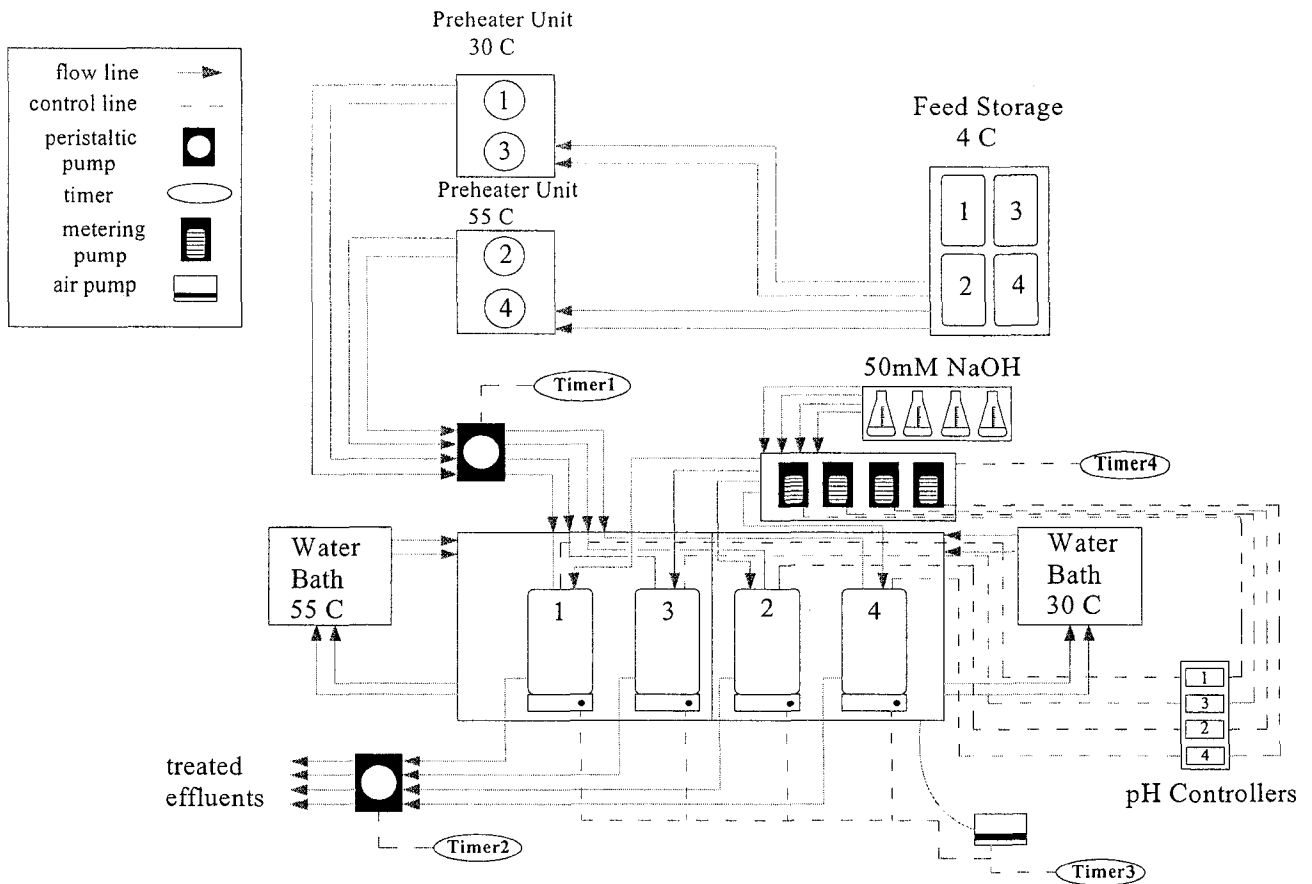


Figure 3.1.1 Schematic diagram of the laboratory-scale SBR system

A general description of the laboratory-scale SBR system is presented in the following sections:

Feed storage refrigerator: The feed was prepared by diluting the stock solutions (methanol,  $\text{NH}_4\text{NO}_3$  +  $\text{KH}_2\text{PO}_4$ , other inorganic salt nutrients) to the desired concentration in four autoclavable rectangular polypropylene carboys (volume: 8 L each) (Nalgene Company, Rochester, NY) and then stored in a bar sized refrigerator (Danby Products Limited, ON, Canada). The purpose of using a refrigerator was to minimize the potential biodegradation of the feed by maintaining the feed at a low temperature ( $4^\circ\text{C}$ ) during storage.

Preheating units: The purpose of the preheating system was to increase the feed temperature from 4°C to 30°C (for mesophilic SBRs) and 55°C (for thermophilic SBRs) respectively before it entered the SBRs. Four silicone tubes (length: 8 meter each) connecting the four carboys and the pump with four pump heads (Masterflex Standard Pump Drive and Masterflex L/S size 18 Pump head, Cole-Parmer Instrument, CO., Niles, Illinois, USA) were suspended in two preheating water baths (two in each bath) (29in×15in×15in Sheldon Manufacturing Inc., Cornelius, OR). One of the preheating water baths was maintained at 32°C (for mesophilic SBRs) and the other was maintained at 55°C (for thermophilic SBRs).

Sequencing batch reactors: Each SBR was made of glass with an operating diameter of 127 mm and a height of 340 mm. It was enclosed within a 25.4 mm annular thickness glass jacket for temperature control and had a volume of 2 L (Figure 3.1.2). Four outlet ports were positioned on each SBR, corresponding to volumes of 0, 0.5, 0.8 and 1L from the bottom. The 0 L port was used for wasting mixed liquor and washing purpose. The 0.8 L port was used for discharging the treated effluent, and the 1.0 L port was designed for collecting mixed liquor samples. The 0.5 L port was sealed with rubber septa. The aeration diffuser, feed tube, pH buffer tube and pH probe, put into SBR, were held by a wooden stopper at the top of each SBR.



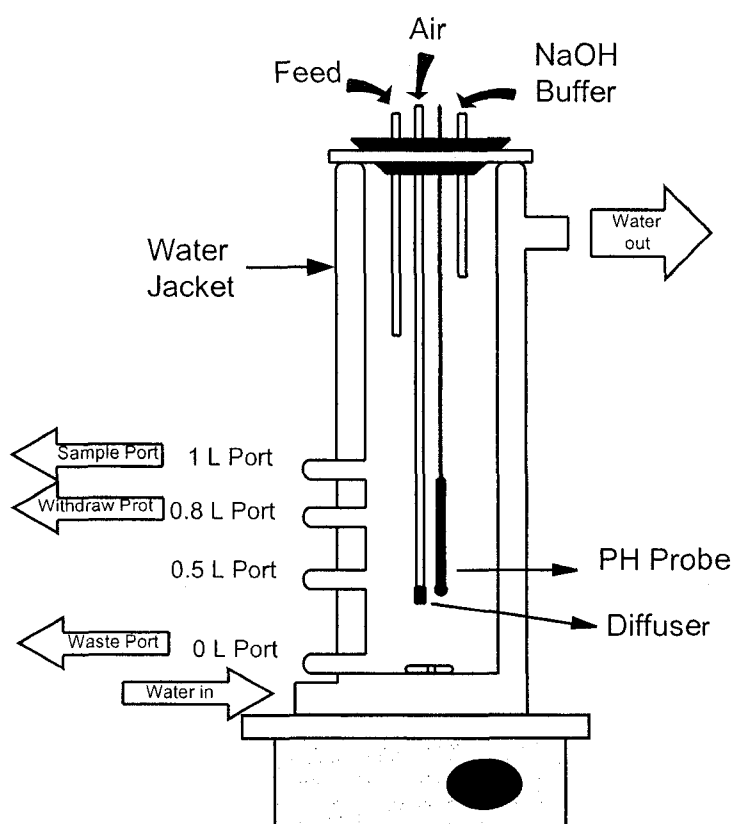


Figure 3.1.2 Schematic diagram of a laboratory-scale SBR

The sludge suspension was continuously stirred in the reaction phase with a magnetic stirring bar (0.7 cm × 0.7 cm × 5 cm) placed at the bottom of each SBR. The mixing intensity was maintained by appropriate adjustment of each magnetic stirrer at mixing level 4 (rate: 120 ~ 150 r/min) and by controlling the flow rate of air (1.5 L/min). The air, which served as an oxygen supply, was introduced in the SBR through a stone air diffuser positioned at a level corresponding to approximately the 0.4 L reactor volume. The SBRs were housed and secured in a wooden frame shown as photograph (Figure 3.1.3).

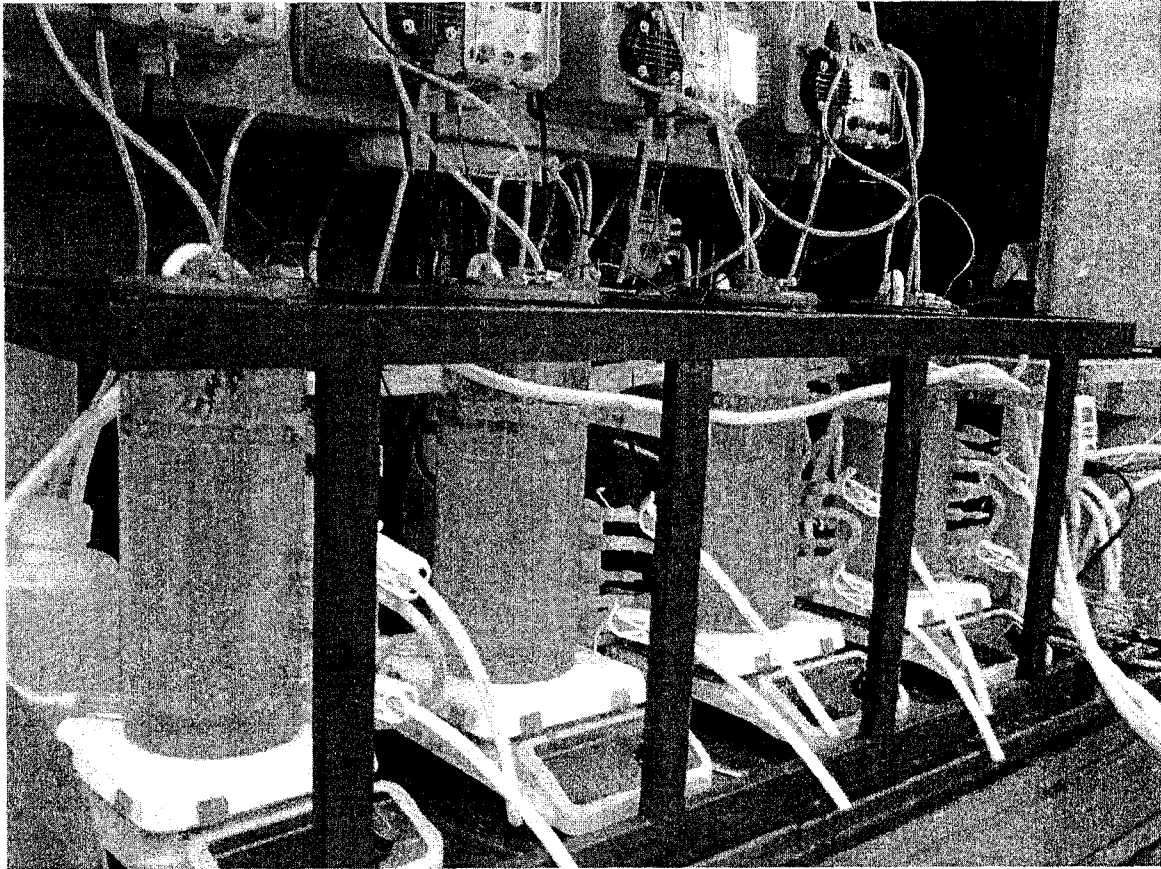


Figure 3.1.3 Laboratory-scale sequencing batch reactors set-up

Cyclic operation of the sequencing batch reactors: The SBR is a fill - and - draw activated sludge system. All SBRs have four operating steps in each cycle that are carried out in a time sequence as follows: 1) fill; 2) reaction (aeration); 3) sedimentation/clarification; and 4) draw. The operating sequence is illustrated in Figure 3.1.4. Sludge samples were collected for characterization at the end of reaction phase.

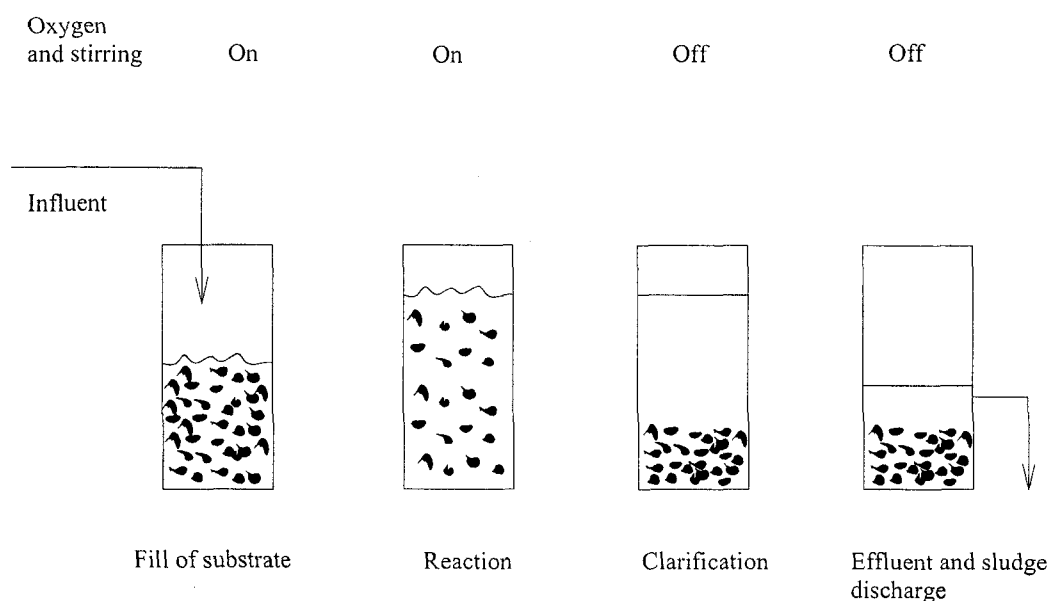


Figure 3.1.4 Process flow diagram in the operating sequence of the SBR

Temperature controller: The operating temperatures of the SBRs were maintained at 30°C and 55°C by circulating water at constant temperatures through the SBRs jacket. The water baths were maintained at 32°C and 68°C, respectively, to achieve a bioreactor temperature of 30°C and 55°C, respectively, due to a loss of heat in delivering the recirculation water from the water bath to the jacket of the SBRs. The water was circulated through the jacket of the SBRs using a variable speed peristaltic pump driving with four pump heads (Masterflex Standard Pump Drive and Masterflex L/S size 18 Pump head, Cole-Parmer Instrument, CO., Niles, Illinois, USA).

On-line pH controller and buffer: Control of the pH was achieved by immersing a pH electrode, which was connected to an on-line pH controller (LED pH/ORP controller, Cole-Parmer Instrument Co., Niles, Illinois, USA) at the 0.4 L reactor volume level in each of the four SBRs. A 0.05 - 0.1 N NaOH solution

was used as a buffer and was introduced in the SBRs by the online pH controllers to maintain the pH at the desired value ( $7.2 \pm 0.4$ ).

Timers: Control of the cyclic operation of the SBRs was achieved through the use of four on-and-off programmable timers (Sper Scientific Model 810030, Sper Scientific Ltd., Scottsdale, Arizona, USA). The four programmable timers were used to control the transfer of the feed to the SBRs (the cold feed passed through the preheating unit to warm up first then entered SBRs at a constant temperature); pH controllers' working time; the aeration and mixing time; and the discharge of the treated effluent, respectively. Control was achieved by switching the electric equipment on and off at predetermined times. The operating conditions of the SBR system are shown in Table 3.1.1

Table 3.1.1 Operating conditions of the SBR system

Parameters	Units	Value
Cycle length	Hours	12 ( Evaporator Condensate ) 12, 24, 6 ( TMP Pressate)
Filling period	Minutes	10
Aeration (reaction) period	Minutes	660 ( Evaporator Condensate ) 660, 1380, 300 ( TMP Pressate)
Settling period	Minutes	40
Withdrawing period	Minutes	10
Sludge retention time (calculated)	Days	4-10 (Thermophilic Reactors), 2-5 (Mesophilic Reactors)
Effective volume of each SBR	Liters	1.8

Operating temperature	°C	30, 55
Operational pH	-	7.2 ± 0.4

All tygon extended-life silicone tubes for transferring the feed to the SBRs were cleaned at times, in order to prevent the accumulation of biomass in the tubes.

Control of the concentration of mixed liquor suspended solids:

The concentrations of Mixed liquor suspended solids (MLSS) in SBRs were controlled at a similar level (about 2000 mg MLSS/ L) by wasting a fitting amount of activated sludge per day to minimize the influence of biomass concentration on the COD removal efficiency, flocculating ability and compressibility of sludge flocs in SBRs. for the parallel processes. MLSS and effluent suspended solids (ESS) were monitored every 2 or 3 days. These measurements gave the information necessary for determining the change in the amount of sludge wasted per day to achieve better control of the MLSS concentration. The equation for the calculating is as follows:

$$\text{SRT} = \frac{\text{Sludge in Reactor (gVSS)}}{\text{Sludge Waste (g/day)}} = \frac{V_o X}{(Q_w X + Q_E X_E)}$$

Where SRT is the sludge retention time, [day] (4 ~ 10 days for thermophilic reactors, and 2 ~ 5 days for mesophilic reactors were maintained in this research);  $V_o$  is the volume of each SBR, [L] ;  $X$  is the MLSS concentration measured at the end of one cycle, [mg/L];  $Q_w$  is the amount of the sludge wasted per day from each SBR, [L];  $Q_E$  is the amount of discharged effluent per day from each reactor, [L]; and  $X_E$  is the ESS concentration in treated effluent, [mg/L].

Experimental procedures: At the start of this study, the SBR system was inoculated with biomass from an activated sludge plant treating kraft mill effluent of a local pulp and paper mill. Initially, all four SBRs were operated at a temperature of 30°C. Then, the temperature in two of them (thermophilic SBRs) was gradually changed to 55°C within about one month (temperature increasing was about 1°C/day). The influent COD was increased from 750 mg/L at the beginning to 1500mg/L after 25 days of operation and then finally to 3000 mg/L after 64 days' operation. Two of the SBRs (1-thermophilic SBR and 1-mesophilic SBR) were converted into MABRs at the operational day of 138 (more detailed description of the MABRs was provided later). After 238 days operation of the SBR and MABR systems, the synthetic kraft evaporator condensate was switched to the real TMP pressate (Table 3.1.2).

Table 3.1.2 Wastewater experimented Vs. operational time

Operational days	Feed COD [mg/L]
June17 ~ July 5, 2006	750, Synthetic kraft evaporator condensate
July 06 ~ Aug. 30, 2006	1500, Synthetic kraft evaporator condensate
Aug 31,2006 ~ Feb.06,2007	3000, Synthetic kraft evaporator condensate
Feb 07 ~ June 01, 2007	3700-4100 mg/L, TMP pressate from a local mill*

\* The COD for TMP pressate, real wastewater from a local pulp and paper mill was measured, as described in Table 3.1.4.

### 3.1.2 Laboratory-scale membrane aerated biofilm reactor system

Two hydrophobic membrane modules were placed into a thermophilic SBR (maintained at 55°C) and a mesophilic SBR (maintained at 30°C) respectively to form the sequencing batch membrane aerated biofilm reactors (MABRs) at the 138<sup>th</sup> operating day with an initial biomass dosage that could form a biofilm thickness of about 100  $\mu\text{m}$ . The schematic diagram is shown in Figure 3.1.5.

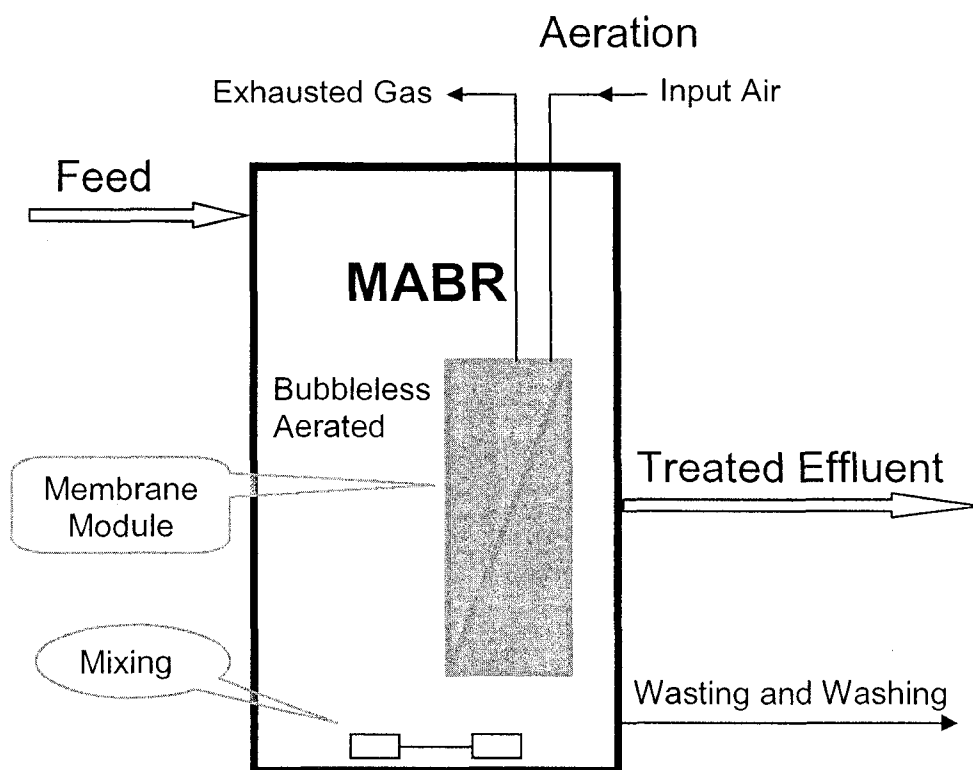


Figure 3.1.5 Schematic diagram of membrane aerated biofilm reactor

The membrane module (Model: M60-130W-200L-FC8, 13cm wide  $\times$  20cm length, supplied by Nagayanagi Co., Ltd, Japan) installed in each reactor is woven fabric silicone hollow fiber membranes (outer diameter: 320  $\mu\text{m}$ ; inner diameter: 200  $\mu\text{m}$ ; 8 layers and 1600 fibers/ each module) having a total

surface area of  $0.26 \text{ m}^2$  and provided a specific surface area of  $173.3 \text{ m}^2/\text{m}^3$  in each batch MABR (Figure 3.1.6 the photo of the membrane module).

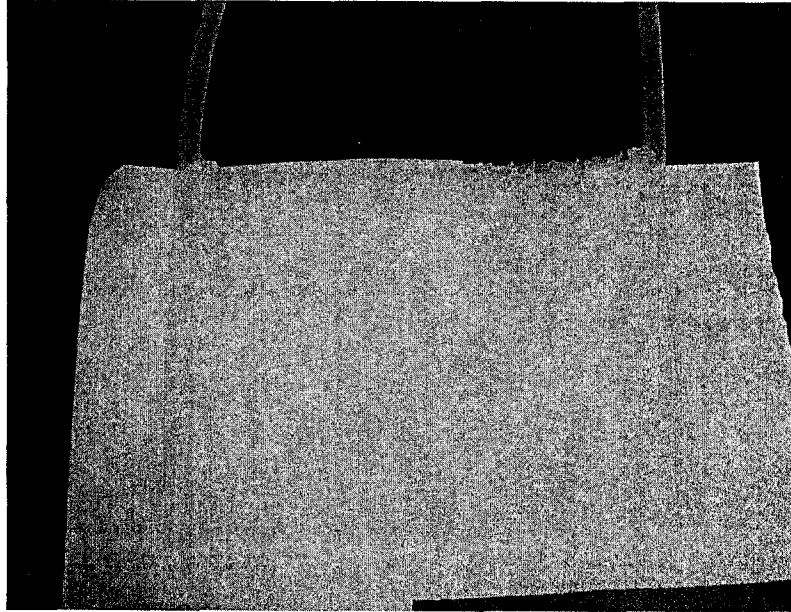


Figure 3.1.6 Woven fabric silicone hollow membrane module

The same as SBRs, mixing of wastewater was provided by a magnetic stirring bar (120 ~ 150 rpm) in each batch MABR. Compressed air was supplied to the inside of silicone hollow fiber membranes via a gas regulator at 4 or 6 psi at a flow rate of 0.75 to 1.0 L/min. At this air flow rate, the supplied oxygen is 50 to 80 times of the COD loading (3000 mg/L) to the MABRs.

The membrane modules were placed in the two batch reactors at 138<sup>th</sup> operational day with an initial suspended biomass concentration of 1500 mg/L for thermophilic MABR, 1300 mg/L for mesophilic MABR (biomass dry weight: 2.25 g in thermophilic MABR, 2.0 g in mesophilic MABR), considering the lower growth rate of thermophilic biofilm, more thermophilic suspended biomass concentration



(0.3g thermophilic biomass) was put in the thermophilic MABR for the immobilization at day 3. Four days were allowed to immobilize bacteria on silicone hollow fiber membranes with an initial biomass dosage that could form approximately a biofilm thickness of 100  $\mu\text{m}$ . The operational parameters during the acclimation were the same as those for treating synthetic evaporator condensate.

### 3.1.3 Synthetic kraft evaporator condensate

The chemical composition and concentration of the synthetic kraft evaporator condensate was adapted from Bérubé and Hall [93], simulating the foul fraction of the evaporator condensate from a kraft pulp mill. The synthetic kraft evaporator condensate contained methanol, dimethyl sulphide, dimethyl disulphide and inorganic salts and was diluted to the desired influent COD using tap water (Table 3.1.3).

Table 3.1.3 chemical composition of the synthetic evaporator condensate

Chemicals	Does (mg/L)	Grade and source of chemicals
Methanol	500, 1000, 2000	Analytical (Sigma-Aldrich )
Dimethyl sulphide	37	Analytical (Sigma-Aldrich )
Dimethyl disulphide	25	Analytical (Sigma-Aldrich )
$\text{NH}_4\text{NO}_3$	1000	Analytical (Sigma-Aldrich )
$\text{KH}_2\text{PO}_4$	165	Analytical (Sigma-Aldrich )
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1280	Analytical (Sigma-Aldrich )
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	270	Analytical (Sigma-Aldrich )
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	70	Analytical (Sigma-Aldrich )
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	20	Analytical (Sigma-Aldrich )
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	1.8	Analytical (Sigma-Aldrich )

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	4.5	Analytical (Sigma-Aldrich)
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.22	Analytical (Sigma-Aldrich)
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.05	Analytical (Sigma-Aldrich)
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.03	Analytical (Sigma-Aldrich)

### 3.1.4 TMP pressate

The TMP pressate treated in this study was from a local pulp and papermill. The soluble chemical oxygen demand (COD) of this wastewater was illustrated in Table 3.1.4. The ratio of the soluble COD to the total COD was about 0.9 ~ 0.95.

Table 3.1.4 Chemical oxygen demand of the TMP pressate

Date	Operational time interval	Chemical Oxygen Demand (COD) (mg/L)				
		Barrel 1	Barrel 2	Barrel 3	Barrel 4	Barrel 5
0207-07	0207	4102				
0223-07	-0226	4038				
0227-07	0227-0319		3937			
0416-07	0320-0430			3843		
0510-07	0501-0514				3708	
0530-07	0515-0601					3937

### 3.1.5 Inoculum and acclimation of thermophilic bacteria

At the start of this study, the SBR system was inoculated with biomass from an activated sludge plant treating kraft pulp mill effluent of a local pulp and paper mill. Initially, all four SBRs were operated at a

temperature of 30°C. Then, the temperature in two of them was gradually changed to 55°C within about one month (in about 1°C/day temperature increasing manner).

### 3.2 Measurement and analytical methods

#### 3.2.1 Standard wastewater analyses (COD, MLSS, ESS, SVI, DO)

General characterization of wastewater and biomass followed standard methods described by the American Public Health Association (APHA, 1992) [94]

Mixed liquor suspended solids: Mixed liquor suspended solids (MLSS) were measured at the end of the reaction phase in accordance with Standard Methods [94].

Chemical oxygen demand: The closed reflux colorimetric method (Section 5220D, APHA, 1992) [94] was used to determine COD of the feed and the treated effluent. The treated effluent was filtered through a 0.45 µm pore size filter paper (Gelman Sciences Filter Paper, diameter 25 mm) before COD measurement. Culture tubes with desired effluent (2.5 mL), digestion solution ( $K_2Cr_2O_7 + HgSO_4 + H_2SO_4$ ), and reagents ( $Ag_2SO_4 + H_2SO_4$ ) were heated in a Hach COD reactor ( Model 45600-00, Hach Co., Loveland, CO, USA ) for 2 hours at 150°C. The cooled samples were then measured spectrophotometrically (Bausch & Lomb Spectronic 20D with Hach 19230-00 Adapter) at 600 nm. Potassium hydrogen phthalate (KHP) was used as a COD standard. All chemical reagents used for COD measurements were from BDH Chemicals Inc., and were of analytical grade.

Dissolved oxygen: The dissolved oxygen (DO) levels in the SBRs were frequently monitored using a DO meter (Model 600 Oxygen Analyzer, Engineered Systems & Design, Newark, DE, USA). The DO

levels during the reaction phase were maintained at 1.8 ~ 3.1 for the thermophilic SBRs and 4.6 ~ 7.0 for the mesophilic SBRs.

Sludge volume index: The compressibility of sludge was evaluated by the sludge volume index (SVI). The SVI is the volume in mL occupied by one gram of MLSS after 30 minutes of compaction. The SVI measurement was carried out by placing the well-mixed liquor into 500 mL graduated cylinders at the end of the cyclic operation in the SBRs. The concentration of the mixed liquor for the SVI measurement was fluctuated with the system upset or the property changing of the biomass at times. The average MLSS concentration for treating synthetic kraft evaporator condensate in thermophilic SBR was  $1445 \pm 429$  mg/L, and that in mesophilic SBR was  $2004 \pm 365$  mg/L. For treating TMP pressate, that in thermophilic SBR was  $2616 \pm 1248$  mg/L, and that in mesophilic SBR was  $3018 \pm 1370$  mg/L.

$$\text{SVI} = \frac{\text{Volume in mL after 30 minutes of compaction in a 500 mL graduated cylinder} \times 2}{\text{Biomass concentration (g/L)}}$$

Effluent suspend solids: The flocculating ability of sludge flocs in the SBR system was evaluated by the effluent suspended solids (ESS) measurement as described in Standard Methods (Method 2540D, APHA, 1992) [94]. The level of ESS was determined after a 40-minute compaction of the mixed liquor.

### 3.2.2 Analysis of ammonium-N, nitrate-N and nitrite-N

Ammonium (NH<sub>4</sub>-N): NH<sub>4</sub>-N is determined by colorimetry using the Skalar autoanalyzer system. The automated procedure for the determination of ammonia nitrogen is based on the modified Berthelot reaction: ammonium is chlorinated to monochloramine which reacts with salicylate to form 5-

aminosalicylate. The absorption of the formed complex is measured spectrophotometrically at 660nm. The method detection limit (MDL) and calibration range are given in Table 3.2.1.

Table 3.2.1 The method detection limit (MDL) and calibration range of ammonium

Component	Parameter CODE	MDL (mg/L)	Calibration Range (mg/L)		Upper Limit (mg/L)
Ammonium (NH <sub>4</sub> -N)	WNH <sub>3</sub>	0.25	1.0	10.0	10.0

#### Nitrate and nitrite (Anions NO<sub>3</sub>-N, NO<sub>2</sub>-N)

The LUEL method code, WICA, is suitable for drinking waters and waste waters. It is based on the EPA300 Method A for anions but uses a Dionex AS14 anion column (4×250mm) with an AG14 guard column.

A sample is introduced into a stream of 3.5 mM carbonate / 1.0 nM bicarbonate eluent and passed via high pressure through a highly basic ion exchange column where anions are separated based on their relative affinity to the column. The analytical system is set up with a self-regenerating micro-membrane suppressor which reduces the baseline effects from the effluent. The conductivity of individual peaks is then measured with a conductivity cell. The method detection limit (MDL) and calibration range are given in Table 3.2.2.

Some other analytical parameters are:

Flow rate = 1.0 mL/minute

Temperature = ambient

Detection = Suppressed conductivity using a CD25

Applied current= 100mA

Injection volume=100uL

Samples are diluted 1/10 in order to fall within the calibration range.

Table 3.2.2 The MDL and calibration range of nitrate and nitrite

Component	Parameter CODE	MDL (mg/L)	Calibration Range (mg/L)		Upper Limit (mg/L)
Nitrate (NO <sub>3</sub> -N)	WICNO <sub>3</sub>	0.005	0.025	25.0	25.0
Nitrite (NO <sub>2</sub> -N)	WICNO <sub>2</sub>	0.005	0.025	25.0	25.0

### 3.2.3 Microbiology

Morphology of sludge flocs were observed and recorded with a light microscope (Olympus, BH2-RFCA) at a magnification of X 100 at the same time for filamentous microorganisms quantification. 3 measurements were conducted for each SBR in each week of the experimental time. The number of filamentous microorganisms was classified into levels 1 to 6 according to Jenkins et al. [95]. A lower level corresponds to a fewer filamentous microorganisms.

### 3.2.4 Floc size distribution

Floc size distribution of mixed liquor suspended solids and effluent suspended solids in treated effluent (after 40 minutes settling) was determined by using a Mastersize 2000E (measuring range 0.04 ~ 1000 µm) made by Marvin Instrument. One drop of MLSS or 5 mL of treated effluent was diluted in distilled water with the same ionic strength in the feed before floc size distribution. The Malvern instrument uses light scattering and the data is given as frequency by volume. Three measurements were taken for each SBR in each week of the experimental time.

### 3.2.5 Zeta potential

Zeta potential of the non-settleable fraction of sludge flocs in the treated effluent as ESS was measured by Zetacompact Z8000 model (CAD Instrumentation). The Smoluchowski equation was chosen in the software to calculate the zeta potential of the non-settleable fraction of sludge flocs. The electric field added on the solution containing non-settleable flocs was controlled by a cell voltage of Zetacompact Z8000 and was fixed at 80 V. The pH of the treated effluent was in the range of  $7.3 \pm 0.4$ . The ionic strength in the feed was constant during the measurement.

### 3.2.6 Floc ultrastructure

Nanoscale observations of floc extracellular polymeric substances (EPS) were made on ultra-thin sections of whole flocs (to compare SRTs of 4 and 20 days), which were prepared for transmission electron microscopy (TEM) by the multi-method technique of Liss et al. [96]. Measurements were made from preparations derived from flocs fixed initially in glutaraldehyde plus ruthenium red [96]. After the double fixation (designed to minimize extraction and shrinkage), the flocs were embedded in Spurr's epoxy resin, and then sectioned with an RMC Ultramicrotome MT-7 (Boeckeler Instruments, Tucson, AZ). The 70 nm sections were mounted on formvar-covered copper TEM grids, and then counterstained [96]. The searches of TEM views of flocs, to select representative images of ultrastructural features, were done systematically according to the protocol of Leppard et al. [97]. Documentation was performed with a JEOL 1200 EXII TEMSCAN scanning transmission electron microscope (JEOL, Peabody, MA) operated in transmission mode at 80 kV.

### 3.2.7 Fourier transfer infrared spectroscopy

Sludge samples were first washed with deionized distilled water at 2000 x g for 5 minutes and filtered to remove the major part of water, and then dried in a freezer dryer at -30°C for three days. To get the infrared (IR) spectrum, the prepared pellets were scanned for 100 cycles in a wavelength range of 4000 to 400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , using a Bruker Tensor 37 Fourier transform infrared (FTIR) spectrophotometer [98, 99].

## 3.3 Statistical methods

The statistical (version 1.7) software package (StatistiXL, Australia), run on a personal computer, was used for all statistical analyses. Basically, two types of statistical analyses were used in this study: analysis of variance (ANOVA) and correlation. The significance of the influence of operational temperature on the properties and settleability of sludge flocs and effluent quality was evaluated by ANOVA, while the significance of correlations between sludge flocs properties and bioflocculating and settling properties was tested by Pearson's product-momentum correlation [100, 101].

### 3.3.1 Analysis of variances

Analysis of variance (ANOVA) is a method for testing two or more treatments to determine whether their sample means could have been obtained from populations with the same true mean. This is done by estimating the amount of variance within treatments and comparing it to the variance between treatments. The Type I error rate was set at 0.05 for all tests performed in this study. Once differences between means were identified by ANOVA, a least significant difference test was performed to estimate the means and to determine the magnitude of the differences.



### 3.3.2 Correlation

The potential correlation between two variables was evaluated by the Pearson's product moment correlation coefficient ( $r_p$ ). experimental data measured within three days was used for correlation analyses [102, 95]. The statistical significance of a calculated correlation coefficient was determined with the t-test. The correlations between variables were considered to be significant at a 95% confidence level. The relationships were checked graphically in order to avoid situations where dispersion around the regression line was high.

## 4. Results and Discussion

In this chapter, the results and discussion are organized and presented in four sections in the following orders: 1.) treatment of synthetic kraft fowl evaporator condensate using thermophilic and mesophilic SBRs; 2.) treatment of synthetic kraft fowl evaporator condensate using thermophilic and mesophilic MABRs; 3.) comparison on floc structures and characteristics between thermophilic and mesophilic sludge; and 4.) treatment of TMP pressate using thermophilic and mesophilic SBRs and MABRs. The details of each section are described as below.

### 4.1 Treatment of synthetic kraft fowl evaporator condensate using thermophilic and mesophilic sequencing batch reactors

The purpose of this study was to compare the COD removal efficiency, sludge settleability and flocculating ability between thermophilic and mesophilic SBRs for synthetic kraft evaporator condensate treatment.

#### 4.1.1 COD removal efficiency

Figure 4.1.1 shows COD removal efficiency for treating the synthetic kraft evaporator condensate in thermophilic and mesophilic SBRs during the 240 days operational time. Three feed concentrations (750, 1500 and 3000 mg COD/L) were tested. Under tested conditions, a COD removal efficiency of 90 ~ 98% was achieved for both of the SBRs at all three organic loading rates. However, a decrease in the COD removal efficiency was occasionally observed, particularly for the thermophilic SBR. This might be due to a change in microbial community which caused the upset of the SBRs. The COD removal efficiency from this study is consistent with that from a thermophilic membrane bioreactor reported by

Bérubé and Hall [68, 103]. These results suggest that treatment of synthetic kraft condensate is feasible in terms of COD removal at both thermophilic and mesophilic SBR.

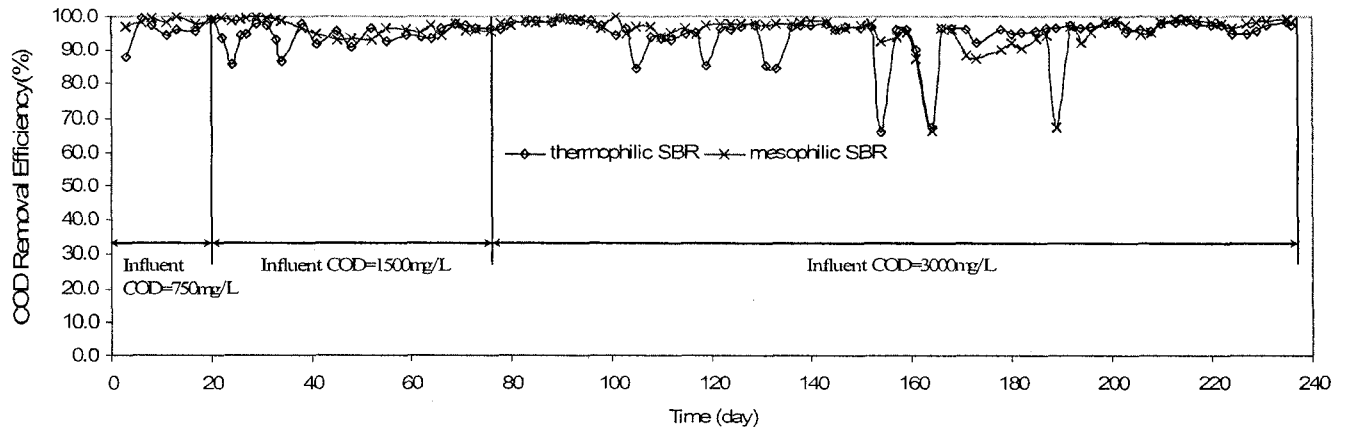


Fig 4.1.1 Soluble COD removal efficiency versus operating time for treating synthetic kraft evaporator condensate in thermophilic and mesophilic SBRs (HRT=12 Hours)

It is also interesting to note that the COD removal efficiency did not change for different influent COD stages, only with some variations (mainly occurred in the thermophilic reactor) when the influent COD was increased from 750 to 3000 mg/L. This phenomenon can be understood by referring to Figure 4.1.2. Figure 4.1.2 shows the decrease in the concentration of effluent COD with reaction time in one operational cycle. Most of the consumable COD was removed within either a three-hour period for mesophilic condition or a six-hour period for thermophilic condition. Because methanol is easily biodegradable and could be totally removed within the reaction time [7, 44, 103], the presence of 40mg/L COD (mesophilic SBR) and 70mg/L COD (thermophilic SBR) in the treated effluent strongly suggests that compounds other than methanol could be responsible for the COD remaining in the treated effluent. The compounds remaining in treated effluent could be from cell lysis or soluble microbial products [104].

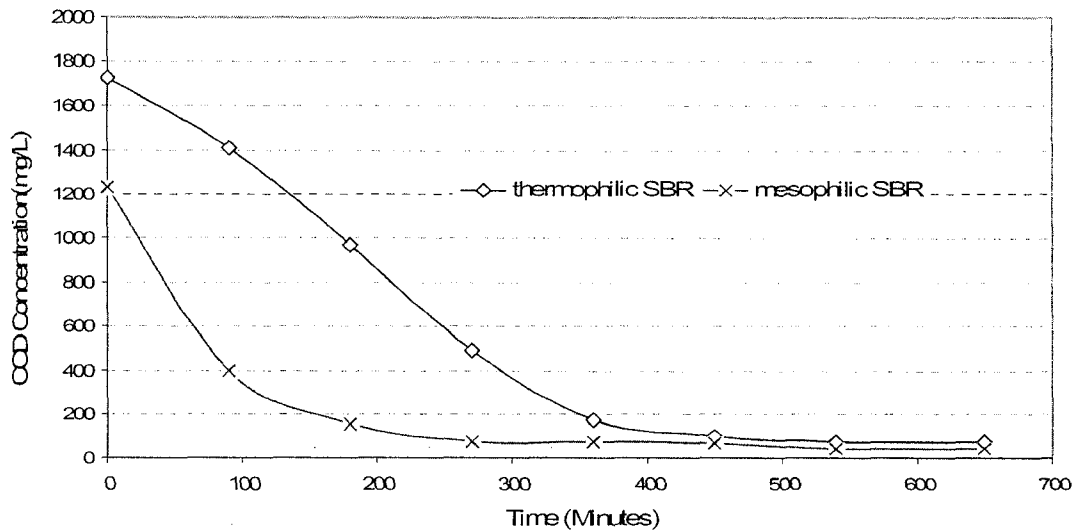


Figure 4.1.2 Soluble COD concentration versus time during one operational cycle for treating synthetic kraft evaporator condensate in thermophilic and mesophilic SBRs (Influent COD= 3000 mg/L, HRT=12 Hours) in Jan 18-07

A calculation of the COD removal rate from Figure 4.1.2 suggests that the COD removal rate between the thermophilic (4.4 g COD/g MLSS.day) and mesophilic (3.5 g COD/g MLSS.day) sludge was comparable. As compared to the mesophilic SBR, the longer reaction time of the thermophilic sludge could be due to a lower biomass concentration, which was caused by the difficulty of maintaining biomass concentration due to sludge bulking. Although some studies suggest a higher reaction rate was associated with thermophilic sludge [21, 105, 106], other studies found similar or even smaller reaction rate of the thermophilic sludge [59, 62, 107]. This might not be surprising, as the thermophilic sludge is a mixture of microorganisms. The change in microbial composition would affect the reaction rate of sludge. The big difference of dissolved oxygen (DO) concentrations in both thermophilic SBR and mesophilic SBR was another reason that caused the lower reaction rate for thermophilic condition. Figure 4.1.3 shows the concentrations of DO in thermophilic and mesophilic SBRs for one operational cycle at the same experimental day with the COD cycle test. The DO concentration in thermophilic SBR

was much lower than that in mesophilic SBR due to the low saturation concentration of oxygen and high oxygen uptake rate at the thermophilic condition [19, 108].

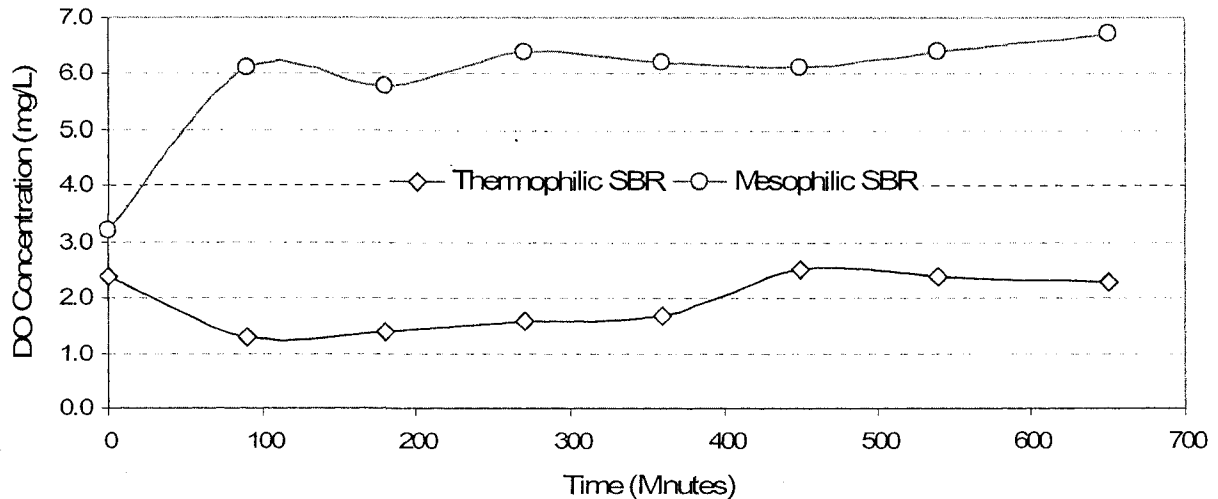


Figure 4.1.3 Dissolved oxygen (DO) concentration versus time during one operational cycle for treating synthetic kraft evaporator condensate in thermophilic and mesophilic SBRs (HRT=12 Hours) at Jan 18-07

#### 4.1.2 Sludge settleability and flocculating ability

Figure 4.1.4 shows the changes in settleability of sludge, as measured by sludge volume index (SVI), versus time in thermophilic and mesophilic SBRs. At the lower organic loadings (750 and 1500 mg COD/L), there was no bulking of both the thermophilic and mesophilic sludge. However, a further increase in the feed COD to 3000 mg/L promoted the growth of filamentous microorganisms in thermophilic sludge and thus led to filamentous bulking situation, while the mesophilic sludge was still in a good settleability under this organic loading rate. There was a statistically difference between SVIs in thermophilic SBR and mesophilic SBR at a influent COD of 3000 mg/L. Much larger SVI values (poorer compaction) and a higher frequency of filamentous bulking situations were observed at the thermophilic condition (ANOVA,  $p < 0.05$ ). These results are generally in agreement with previously

reported results [25, 109]. The difference in sludge settleability at the high organic loading rate could be related to the difference in the DO level under thermophilic and mesophilic conditions. A number of studies have found that a minimum of 2.0 ppm DO is required to suppress the overgrowth of filamentous microorganisms in activated sludge system [49, 110]. A higher organic loading rate requires a higher oxygen transfer rate for biodegradation. The lower level of DO (1.0 ~ 1.7 ppm) under thermophilic condition could promote the overgrowth of filamentous microorganisms. While the DO level (6 ~ 7 ppm) under mesophilic condition was well above the minimum DO level (2.0 ppm) that minimizes the growth of filamentous microorganisms.

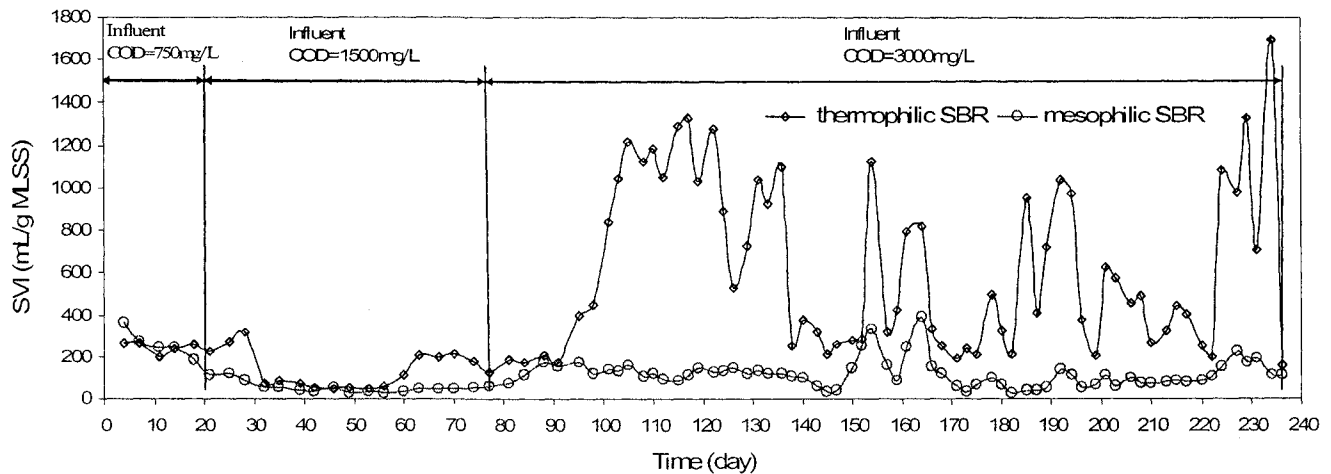


Figure 4.1.4 Sludge volume index (SVI) versus time for treating synthetic kraft evaporator condensate in thermophilic and mesophilic SBRs (HRT = 12 Hours)

The variation in effluent suspended solids (ESS), an indication of flocculating ability, of thermophilic and mesophilic SBRs is shown in Figure 4.1.5. Statistical analysis indicates that there was a significant difference in the level of ESS between thermophilic and mesophilic SBRs. The level of ESS in the treated effluent of the thermophilic SBR was much higher than that of the mesophilic SBR (ANOVA,

$p < 0.05$ ). The results suggest that the flocculating ability of thermophilic sludge was poorer than that of the mesophilic sludge. These results are generally in agreement with previously reported results in that thermophilic sludge has a poorer flocculating ability (higher ESS level) than that of mesophilic sludge [59, 62, 111].

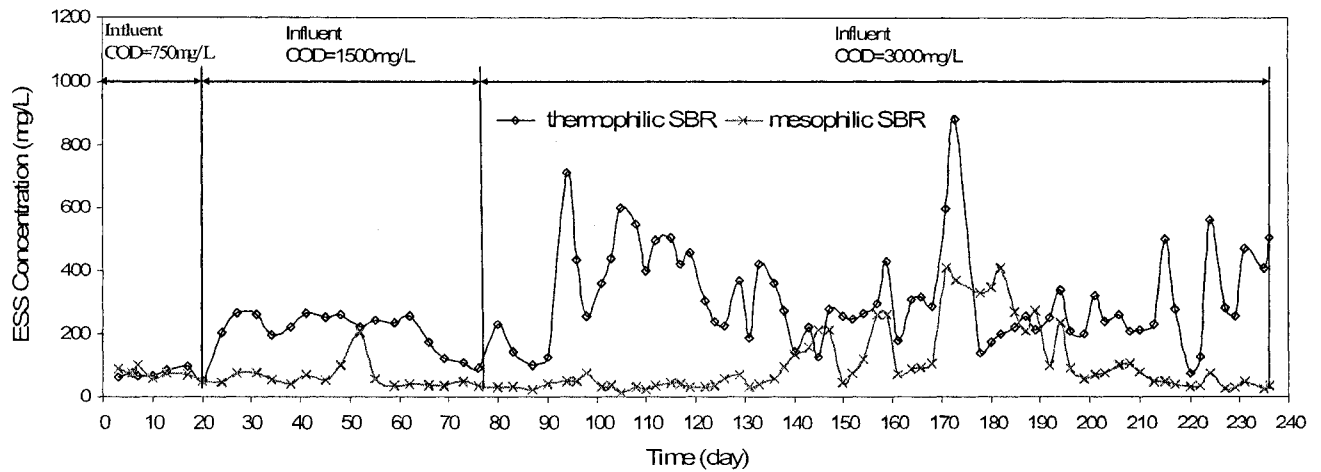


Figure 4.1.5 Concentration of effluent suspended solids (ESS) versus time for treating synthetic kraft evaporator condensate in thermophilic and mesophilic SBRs (HRT = 12 Hours)

From the COD, SVI and ESS data, it is clear that treatment of synthetic kraft evaporator condensate is feasible using mesophilic SBR but faces challenges in biomass separation using thermophilic SBR. One way to overcome the biomass separation problems caused by a low DO level in thermophilic SBR can be the use of pure oxygen rather than air for aeration to increase the DO level in thermophilic temperatures. An economic analysis should be conducted to compare the cost of cooling wastewater to mesophilic temperature and reheating the treated wastewater to reuse it as process water for mesophilic treatment and the cost of using pure oxygen in thermophilic treatment to determine the optimal treatment scenarios. Another way can be the use of membrane separation bioreactor (MBR) to replace

SBR to eliminate sludge bulking problems. However, the presence of a larger amount of fine colloidal particles in the treated effluent could cause a membrane fouling problem [112,113].

#### 4.2 Treatment of synthetic kraft foul evaporator condensate using thermophilic and mesophilic membrane aerated biofilm reactors

The purpose of this study was to compare the COD and N removal efficiencies of treating the synthetic kraft evaporator condensate (Table 3.1.3) using thermophilic and mesophilic MABRs under well-controlled conditions. Two silicon hollow fibre membrane models were put into the thermophilic and the mesophilic SBR at 138<sup>th</sup> operational day of the two SBRs to form thermophilic and mesophilic MABR respectively. At the beginning, the dosage of biomass for biofilm formation on membrane surfaces was controlled approximately at a biofilm thickness of 100  $\mu\text{m}$  by adding in adequate amount of biomass (3.1.2).

##### 4.2.1 COD removal efficiency and flocculating ability

Figure 4.2.1 shows soluble COD removal efficiency for treating the synthetic kraft evaporator condensate in the thermophilic and mesophilic SBRs and MABRs with respect to experimental time. Under the tested conditions with an influent COD concentration of 3000 mg/L, a soluble COD removal efficiency of 80-90% for thermophilic MABR and 90 ~ 95% for mesophilic MABR were achieved except the upset period of the system (mainly under the mesophilic condition). There was a large fluctuation regarding the performance of the mesophilic MABR for COD removal during the operational day 150 to day 165. This phenomenon might be related to the transition of pure aerobic COD removal (thinner biofilm thickness) to the establishment of anaerobic and aerobic COD and N removal (thicker biofilm thickness), due to an increase in biofilm thickness. It was observed that the



color of the membrane biofilm in the mesophilic MABR was changed from yellow brown to black and gas bubbles were observed during this period of time.

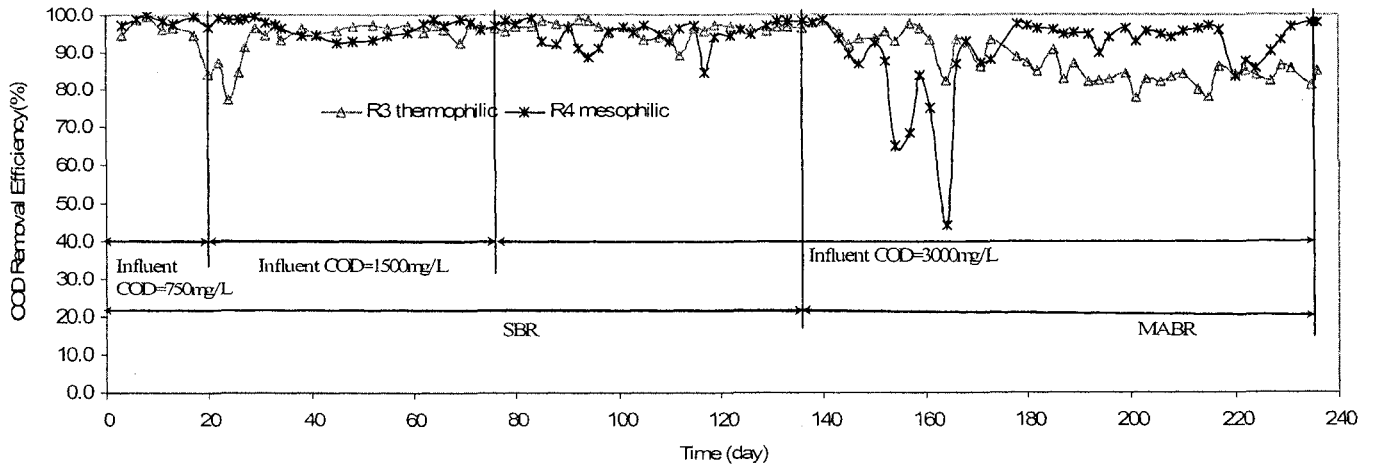


Fig 4.2.1 Soluble COD removal efficiency versus operating time for treating synthetic kraft evaporator condensate in thermophilic and mesophilic MABRs (HRT=12 Hours)

The COD removal efficiency of thermophilic MABR was basically lower than that of mesophilic MABR. This is inconsistent with previous studies [108]. Liao and Liss [108] showed that the thermophilic MABR had better performance than the mesophilic MABR with respect to the COD removal due to its lower growth rate of biofilm, resulting in a proper biofilm thickness close to the optimal one (in the order of a few hundred  $\mu\text{m}$ ) [114,115]. This difference could be explained by the contribution of anaerobic COD removal (denitrification) in the mesophilic MABR in this study, which was not observed in the previous study of Liao and Liss [108].

A comparison on the COD removal efficiency between SBRs and MABRs, as shown in Figure 4.1.1 and Figure 4.2.1, indicate that a slightly higher COD removal efficiency was obtained in the SBRs.

However, the COD removal could be mainly attributed into two categories: biodegradation and stripping in the SBRs and the relative contribution of biodegradation and stripping is not clear. In the MABRs, the COD removal was mainly attributed into biodegradation, as the use of bubbleless aeration led to a minimum stripping effect. A GC-MS analysis of the exhausted air from the MABRs showed that there was no methanol or only trace-amount of methanol in the outlet air. From the stripping point of view, the advantages of MABRs over SBRs for kraft evaporator condensate treatment are obvious.

Figure 4.2.2 shows the decrease in the concentration of treated effluent COD with respect to operating time in one cycle for treating synthetic kraft evaporator condensate in thermophilic and mesophilic MABRs. From the profiles in Figure 4.2.2, the consumable COD was removed gradually during the whole reaction period. More COD concentration was remained at the end of the reaction for thermophilic MABR than that in mesophilic MABR. However, from the trend of the thermophilic profile, it would be likely that COD reduced to a further extent to the equal level with that of mesophilic SBR if HRT were set longer.

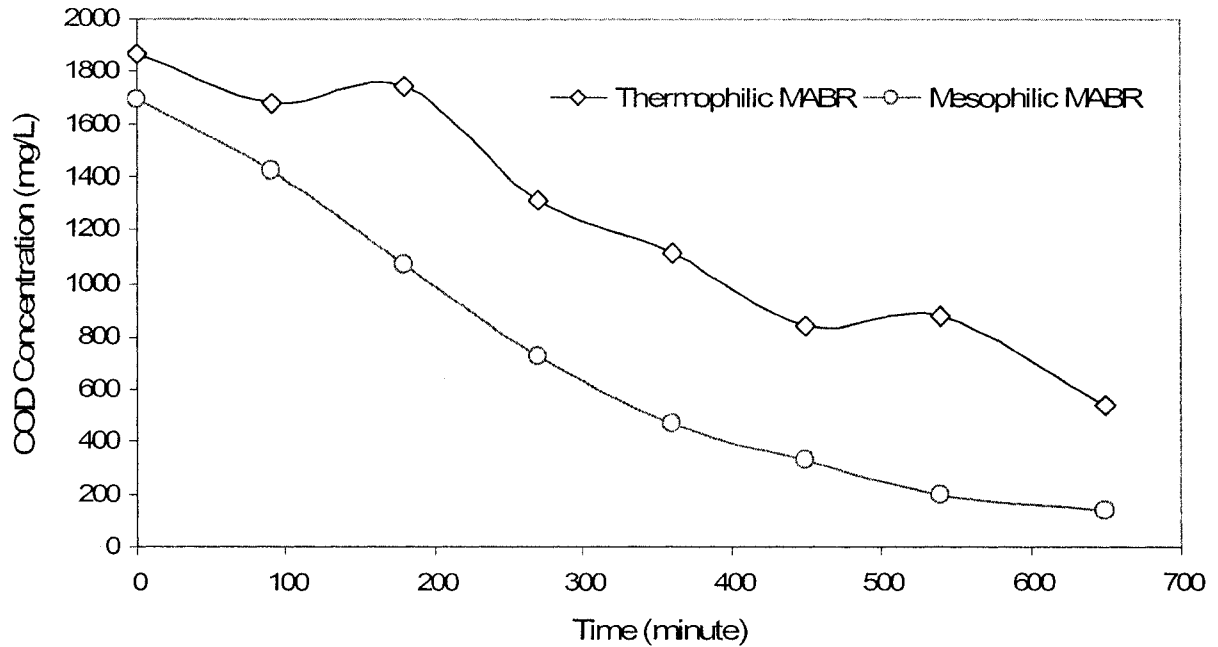


Fig 4.2.2 Soluble treated effluent COD concentration versus operating time during one operational cycle for treating synthetic kraft evaporator condensate in thermophilic and mesophilic MABRs (Influent COD= 3000 mg/L, HRT=12 Hours) at Jan 07-07

Concentration of effluent suspended solid (ESS), one of the indicators for treated effluent quality, for treating synthetic kraft evaporator condensate using thermophilic and mesophilic MABRs is shown in Figure 4.2.3. The ESS concentration for thermophilic MABR was much lower (reduced from 250 mg/L average to 90 mg/L) than that in thermophilic SBR after the stabilization period. ESS level for mesophilic MABR remained almost the same (a slightly lower) as it in mesophilic SBR but was more stable. The statistical analysis indicates that there was a significant difference in the level of ESS between thermophilic SBR and MABR. The concentration of ESS existed in the treated effluent in thermophilic MABR (90mg/L) was much lower than it in thermophilic SBR (250 mg/L) but was still a bit higher than that in mesophilic MABR (60mg/L) (ANOVA,  $p < 0.05$ ). It suggests that thermophilic MABR has an outstanding performance regarding the separation of the treated effluent from the

suspended solids, as compared to the thermophilic SBR. This is probably not surprising that most of biomass was attached on the membrane surface thus lightened the poor settleability effect of thermophilic sludge on ESS level as that in thermophilic SBR. Pankhania et al [17] reported the ESS concentration increased immediately after the biomass detachment when treated synthetic sewage using MABR. This result indicates that thermophilic MABR has advantages than thermophilic SBR in terms of the ESS level in treated effluent.

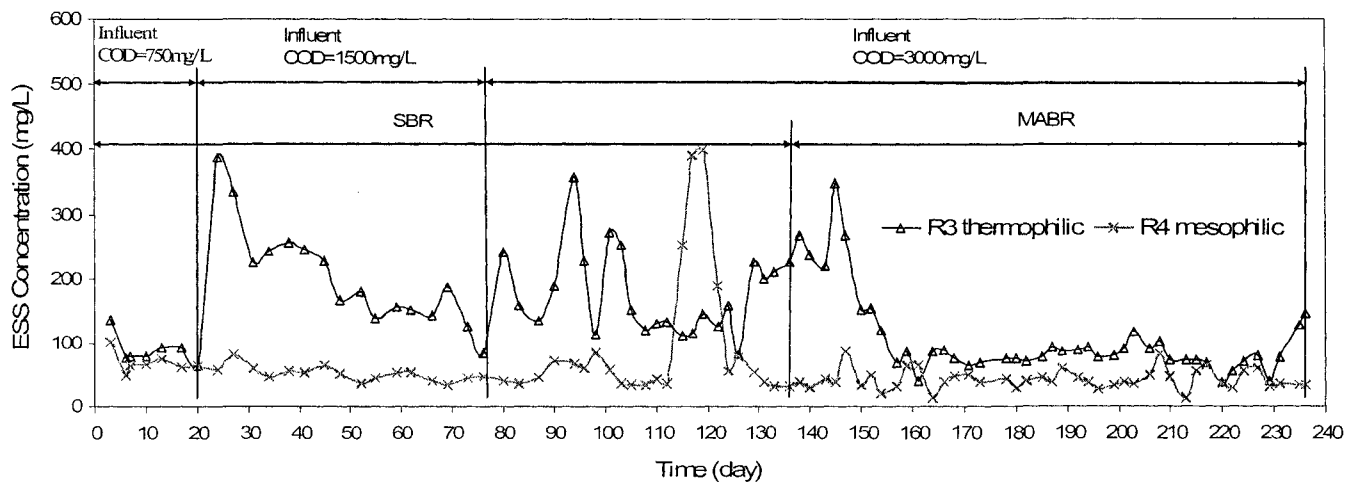


Figure 4.2.3 Concentration of effluent suspended solids (ESS) versus operating time for treating synthetic kraft evaporator condensate in thermophilic and mesophilic MABRs (HRT=12 Hours)

#### 4.2.2 Nitrification and denitrification

The nitrogen composition in the synthetic evaporator condensate was introduced by addition of nutrients. Three hundreds mg/L of total N (150 mg/L  $\text{MH}_4\text{-N}$ , 150  $\text{NO}_3\text{-N}$ ) was added in the synthetic wastewater influent in the form of  $\text{NH}_4\text{NO}_3$  (1000 mg/L). Figure 4.2.4 and Figure 4.2.5 are the nitrogen (Ammonium-N, Nitrate-N, and Nitrite-N) concentrations in thermophilic and mesophilic MABRs with

respect to operating days respectively. A large amount of N was removed by the biodegradation from mesophilic MABR than that in thermophilic MABR. Total N concentration was reduced to 150 ~ 240 mg-N/L for the thermophilic MABR and 80 ~ 140 mg-N/L for the mesophilic MABR. Nitrification process generates hydrogen ions thus causes significant reductions in pH which may inhibit nitrification in return [49,116]. Grunditz et al. [116] reported optimum pH was 8.1 for *Nitrosomonas* and 7.9 for *Nitrobacter*, nitrification activities decreased 40 ~ 80 % when pH was among 6 ~ 7. But it is not the case in this study. On the contrary, once the reaction started, the pH usually increased, especially, in the beginning 2 ~ 3 hours of the reaction and the pH values in mesophilic MABR were 0.3 ~ 0.8 higher than those in thermophilic MABR. It shows that there would be denitrification in the mesophilic MABR occurring at the same time which consumed the hydrogen ions and produced alkalinity.

From Figure 4.2.4, it is clear that the removal efficiency of  $\text{NH}_4\text{-N}$  fluctuated a lot, while the  $\text{NO}_3\text{-N}$  concentration decreased with time, a simultaneous increase in  $\text{NO}_2\text{-N}$  was observed. The results indicate that nitrification at the thermophilic temperature is not stable. This is in agreement with the result that nitrification is inhibited at the reaction temperature larger than 45 °C [117]. There is a very obvious trend for the variation of concentration of nitrate-N and nitrite-N. Nitrate-N concentration reduced to zero gradually with the nitrite-N concentration increasing from zero to 95 mg/L from 138<sup>th</sup> ~ 236<sup>th</sup> operating day. It suggests that at the beginning reaction of MABR, there was no denitrification occurring in thermophilic MABR and with the reaction going on and the biofilm on the membrane surface was getting thicker, an increasing denitrifying reaction occurred. However, due to the high temperature (55°C) in thermophilic MABR, the nitrite-N accumulated, suggesting that denitrification was not complete which is not desirable. It should be noted that nitrate-N concentration decreased only can be

caused by denitrification because nitrate-N is unlikely consumed as nitrogen nutrient for bacteria growth with presence of ammonium -N [117].

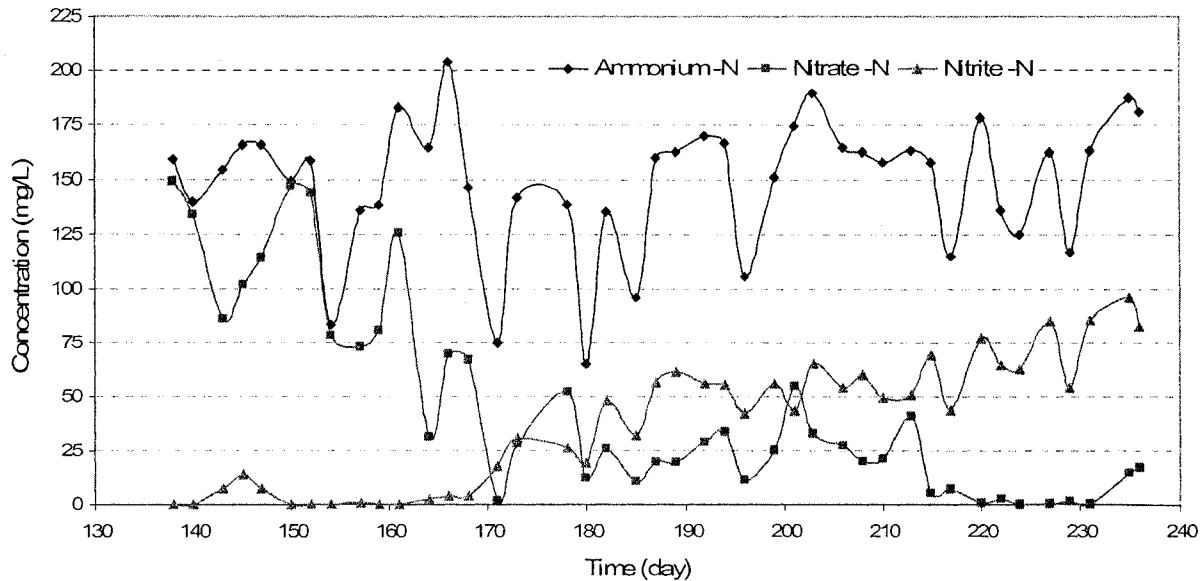


Figure 4.2.4 Concentration of Ammonium-N, Nitrate-N, and Nitrite-N versus time for synthetic kraft evaporator condensate in thermophilic MABR (Influent COD= 3000 mg/L, influent total N = 300 mg/L HRT=12 Hours)

It was also observed that much lower level of nitrate-N and nitrite-N was found in mesophilic MABR (Figure 4.2.5) than that in thermophilic MABR (Figure 4.2.4). It suggests that some nitrification and very effective denitrification were occurring in the mesophilic MABR rather than thermophilic MABR. This is not surprising because the biofilm thickness in the mesophilic MABR could be much thicker (the weight of the mesophilic MABR was much higher than that of the thermophilic MABR) than that in the thermophilic MABR, which could lead to the development of three layers biofilm (aerobic, anoxic, anaerobic) to facility simultaneous nitrification and denitrification (SND) in the mesophilic MABR. Similar results were found in previous studies [41, 118, 119]. Terada et al [119] indicated that there was

no simultaneous nitrogen removal until a minimum biofilm thickness ( $450\ \mu\text{m}$ ) was attained. This phenomenon suggests that a more integrated SND biofilm structure existed in mesophilic MABR during the reaction.

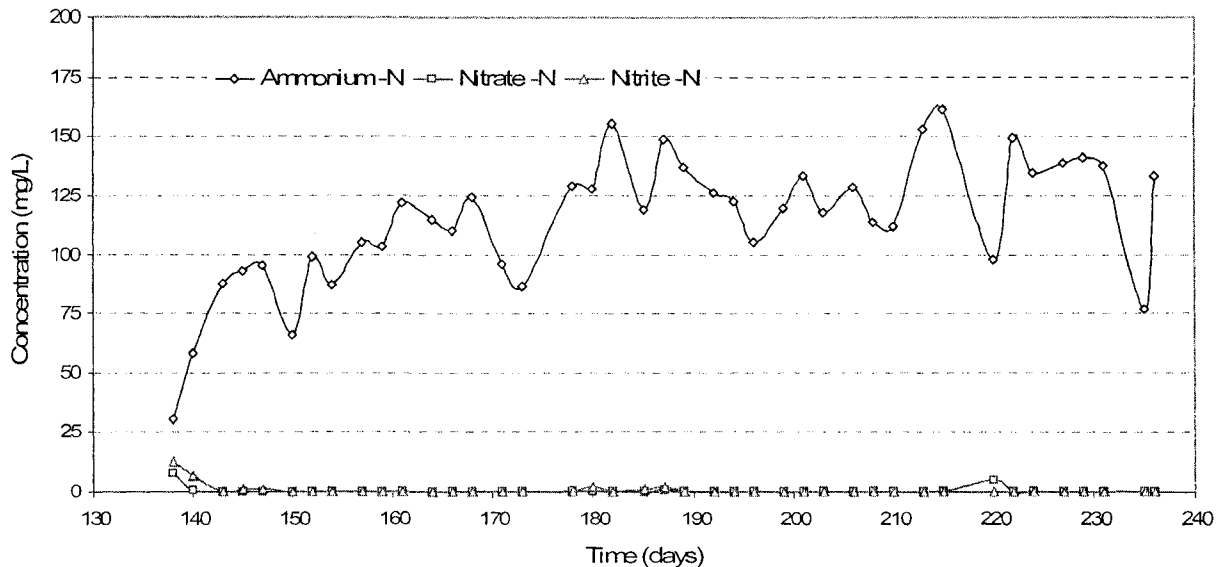


Figure 4.2.5 Concentration of Ammonium-N, Nitrate-N, and Nitrite-N versus time for synthetic kraft evaporator condensate in mesophilic MABR (Influent COD= 3000 mg/L, influent total N = 300 mg/L HRT=12 Hours)

Figure 4.2.5 suggests that nitrifying reaction was much less effective than denitrification in mesophilic MABR even though the reaction temperature was within the optimal temperature range ( $28^{\circ}\text{C} \sim 32^{\circ}\text{C}$ ) for nitrification [117], which may be caused by the inhibition of high concentration of ammonia produced by ammonium ion in a higher pH environment [117, 120]. In addition, the high COD concentration (3000 mg/L) might favor the growth of heterotrophs and suppress the growth of autotrophs, which requires a low COD level for nitrifiers growth, and thus led to a poor simultaneous nitrification in the present study [57]. From Figure 4.2.5, the residual ammonium-N concentration increased with experimental time and the Nitrate-N concentration decreased with experimental time.

This could be explained by the change in biofilm thickness. In the first few days of the mesophilic MABR operation, the biofilm thickness was in the optimal range of a few hundred  $\mu\text{m}$ , which gave a good nitrification efficiency. With an increase in biofilm thickness with experimental time, the nitrification efficiency decreased and at the same time denitrification efficiency was improved.

The results, as shown in Figures 4.2.6 and 4.2.7, of further analyses of ammonium-N, nitrate-N, and nitrite-N concentrations in an operating cycle support the observations of the long-term experimental results (Figures 4.2.4 and 4.2.5). In one operational cycle, sometimes ammonium -N decreased with the operating time (results not reported here) while the other times ammonium-N did not change significantly from the beginning to the end of the reaction cycle (Figure 4.2.6). These results indicate that ammonium-N removal was not stable in the thermophilic MABR. It suggests that there was no stable nitrification occurring under the thermophilic condition. Denitrification in thermophilic MABR was not complete, and the nitrite-N accumulated up to 50 mg/L which might be caused by the high operating temperature. In mesophilic MABR, concentration of ammonia-N decreased by about three times of that in thermophilic MABR (50 mg/L) during all operating cycle (Figure 4.2.7). The drop in the amount of ammonium-N could be due to two factors: (1) some of ammonium ions were removed as a nitrogen nutrient for COD removal; and (2) some of the ammonium ions were oxidized to nitrite by *Nitrosomonas*, and then oxidized to nitrate ions by *Nitrobacter* (no adverse operational condition developed in mesophilic MABR). Figure 4.2.7 suggests that a complete denitrification occurred in mesophilic MABR. The reaction included, (1)  $\text{NO}_3^-$  reduction occurred immediately after the feed  $\text{NO}_3^-$ -N was added; (2)  $\text{NO}_3^-$  reduction occurred immediately after  $\text{NO}_3^-$  was produced by nitrification from ammonium-N; and (3)  $\text{NO}_2^-$  was directly reduced to  $\text{N}_2$  gas without the reverse reaction by changing to  $\text{NO}_3^-$ . There was no  $\text{NO}_2$ -N built-up in the mesophilic MABR. All of these results suggest that there was



a big difference in nitrification and denitrification behaviour between thermophilic and mesophilic MABR. The mesophilic MABR had a higher efficiency in N removal than the thermophilic MABR.

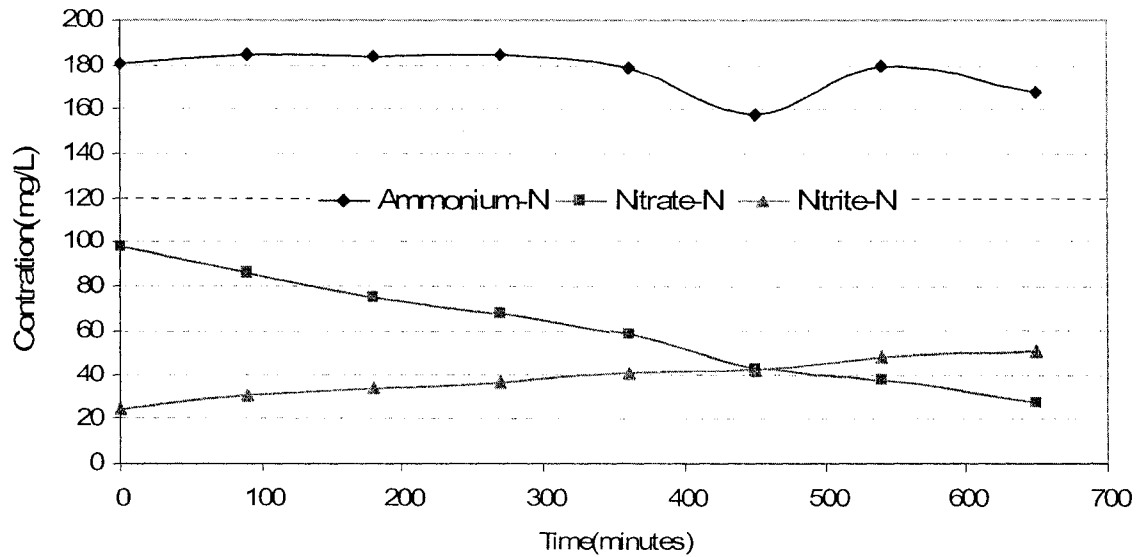


Fig 4.2.6 Concentration of ammonium -N, nitrate-N, and nitrite-N versus time for synthetic kraft evaporator condensate in thermophilic MABR during one operating cycle on Jan 07, 2007  
(Influent COD= 3000 mg/L, influent total N = 300 mg/L HRT=12 Hours)

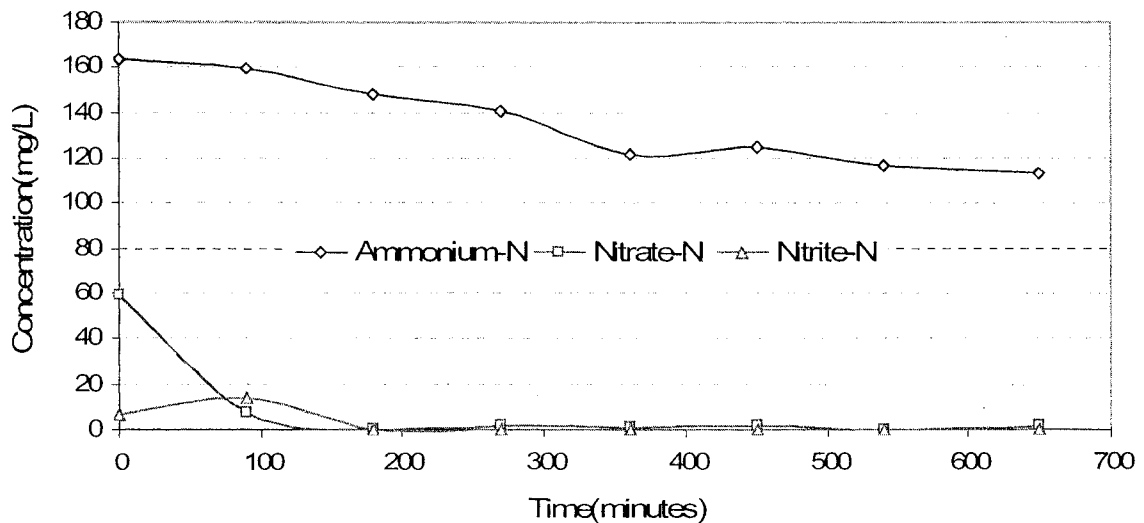


Fig 4.2.7 Concentration of ammonium -N, nitrate-N, and nitrite-N versus time for synthetic kraft evaporator condensate in mesophilic MABR during one operating cycle on Jan 07, 2007  
(Influent COD= 3000 mg/L, influent total N = 300 mg/L HRT=12 Hours)

### 4.3 Characterization of sludge flocs and biofilms

Study of flocculating ability, settleability, and compressibility of sludge flocs has been one of the most important tasks in biological wastewater treatment researches due to its crucial role in effective separation of biomass from treated effluent to achieve a high quality of receiving water. In this part, a comparison on floc structure and characteristics between thermophilic and mesophilic sludge was conducted.

#### 4.3.1 Floc morphology, ultrastructure, and filamentous microorganisms

Figure 4.3.1 shows the typical morphology of the thermophilic and mesophilic sludge. An examination of sludge morphology over a period of 8 months' experimental time suggests that both types of sludge flocs were irregular in shape. Cells that are growing rapidly and under nutrient rich conditions could give rise to more complex microcolony and colony morphology [121]. The thermophilic sludge contained a significant portion of filamentous microorganisms, while the mesophilic sludge contained no or very few filamentous microorganisms. Three different types of filamentous microorganisms, including *Haliscomenbacter hydroxsis*, *Thiothrix* I and Type 1863, were identified (Figure 4.3.2), according to the methods presented in Jenkins et al. [95], in thermophilic sludge.

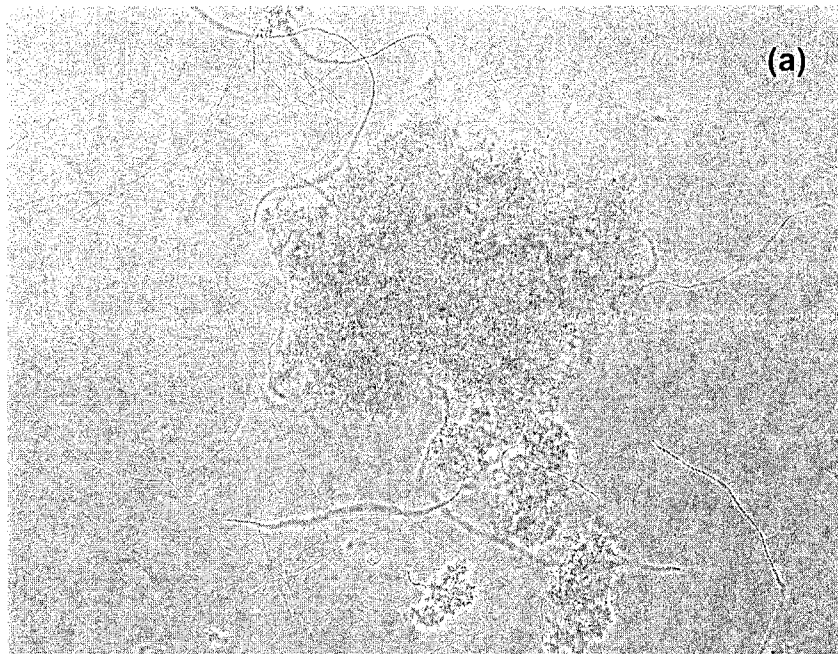


Figure 4.3.1 Typical morphology of (a) thermophilic and (b) mesophilic sludge

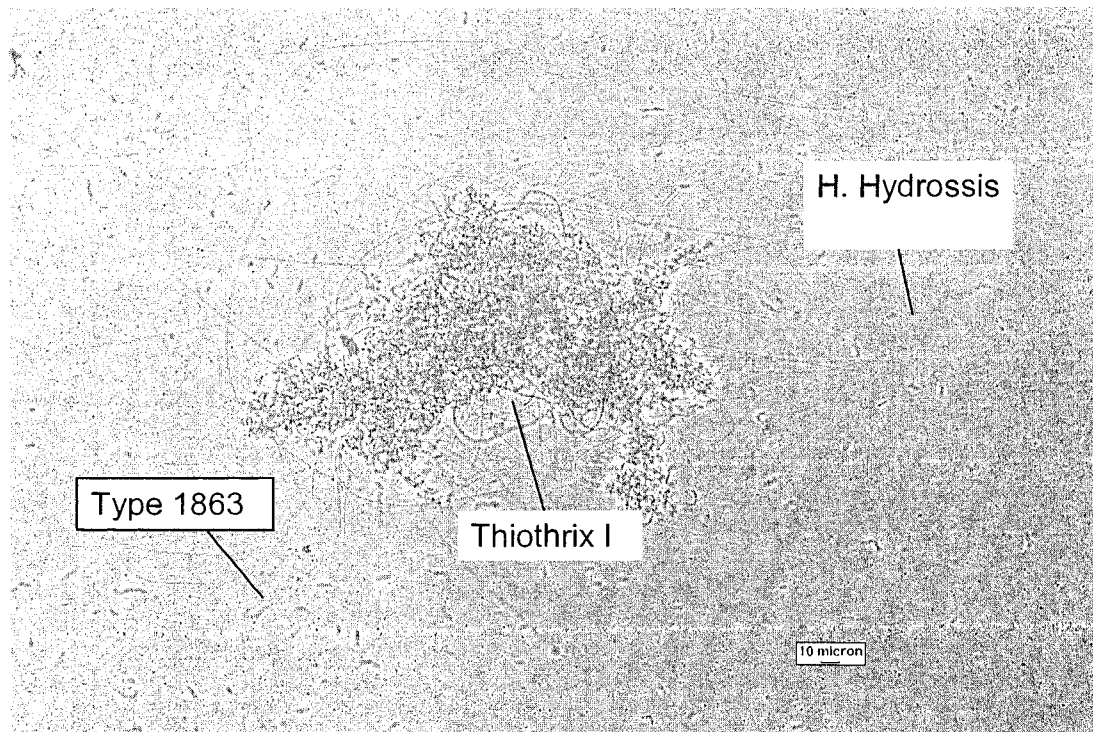
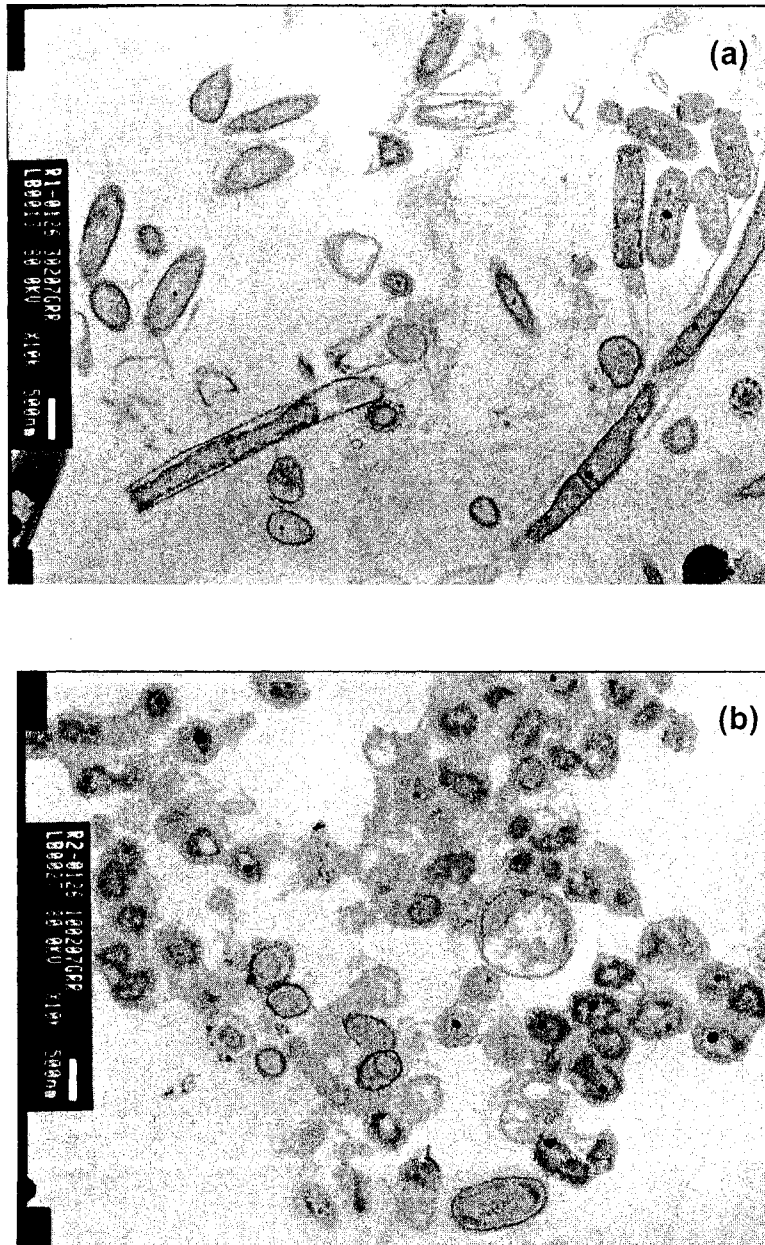


Figure 4.3.2 Three different types of filamentous microorganisms identified in thermophilic sludge

The growth of filamentous microorganisms was related to the organic loading of COD in the thermophilic SBR. There were no or fewer filamentous microorganisms at an influent COD of 1500 mg/L. Filamentous microorganisms started to show up in a large quantity when the influent COD was increased from 1500 mg/L to 3000 mg/L in the thermophilic SBR.

While the conventional optical microscopy (COM) provides information on cross morphology of sludge flocs, detailed information on ultrastructure needs the use of transmission electron microscope (TEM). The ultrastructure of sludge flocs observed TEM is shown in Figure 4.3.3 (a) and (b). There are considerable differences in the floc surface roughness and micro-conolies. The populations of the thermophilic and mesophilic sludge showed some diversity in morphology, but a significant difference

between populations in surface roughness is observed by nanoscale resolution. Figure 4.3.3 reveals the presence of patches of a nanoscale surface layer of filamentous microorganisms which is present commonly on flocs of thermophilic sludge, but rarely on flocs of mesophilic sludge.



4.3.3 Ultrastructure of a portion of a floc (a) from thermophilic SBR, and (b) from mesophilic SBR. The marker represents 500 nm.

The change in the level of filamentous microorganisms with respect to experimental time is shown in Figure 4.3.4. Obviously, the level of filamentous microorganisms in thermophilic sludge was much higher than that of the mesophilic sludge all the time. The difference in the level of filamentous microorganisms between thermophilic and mesophilic sludge explains the difference in settleability of thermophilic and mesophilic sludge (Figure 4.3.5). From Figure 4.3.5, The average SVI levels  $\pm$  standard deviations were  $653 \pm 117$  mL/g MLSS in the thermophilic SBR and  $391 \pm 66$  mL/g MLSS in mesophilic SBR from 61 sample tests for each SBR during an influent COD of 3000 mg/L for treating synthetic kraft evaporator condensate. It is clear, from Figures 4.3.4 and 4.3.5, that the poorer settleability of thermophilic sludge was associated with a higher level of filamentous microorganisms. This finding is generally consistent with a number of previous studies [122, 123] in that the presence of a large portion of filamentous microorganisms in sludge causes sludge bulking problem.

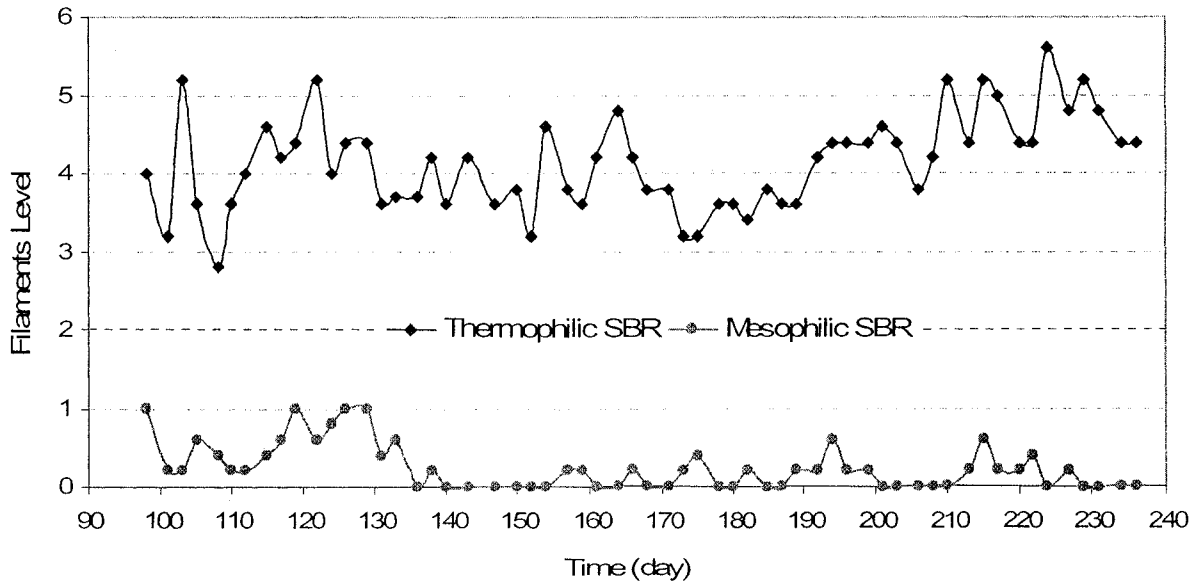


Figure 4.3.4 Level of filamentous microorganisms in thermophilic and mesophilic sludge versus experimental time for treating synthetic kraft evaporator condensate (Influent COD = 3000 mg/L, HRT = 12 Hours)

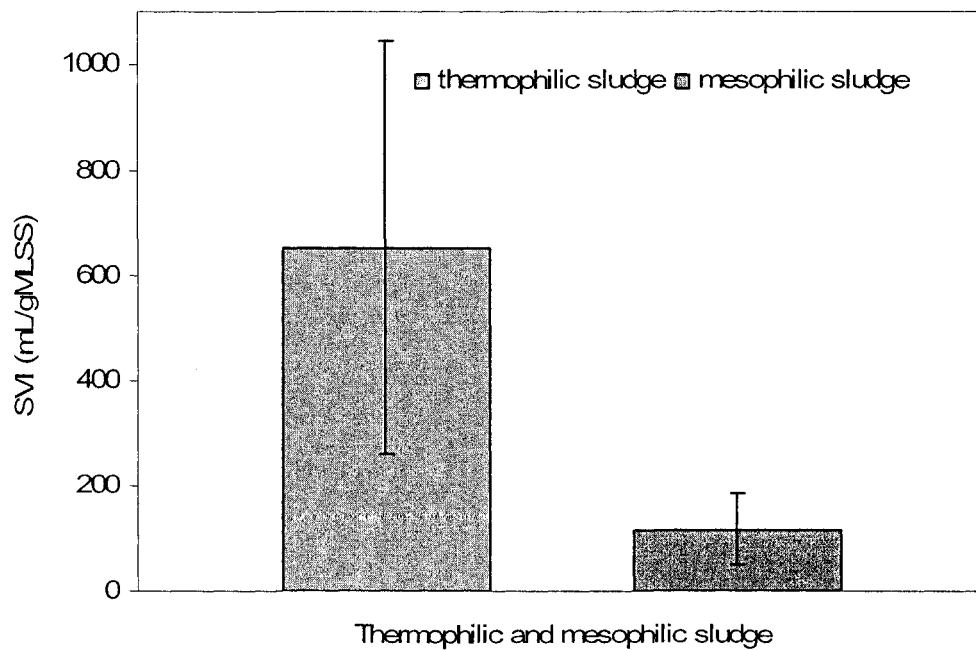


Figure 4.3.5 A comparison on settleability of thermophilic and mesophilic sludge for treating synthetic kraft evaporator condensate. Results are expressed as the average  $\pm$  standard deviation (Influent COD = 3000 mg/L, HRT = 12 Hours)

The difference in the level of filamentous microorganisms could be related to the difference in the DO level and influent organic loading in the thermophilic (1.0 ~ 1.5 ppm) and mesophilic SBR (5.5 ~ 6.5 ppm). It is generally believed that a minimum of DO at 2.0 ppm should be maintained in the bulk solution to prevent the overgrowth of filamentous microorganisms [49, 110]. The low DO (1.0-1.7 ppm) in the thermophilic sludge caused oxygen diffusion limitation into sludge flocs and thus promoted the overgrowth of filaments [124]. The overgrowth of filamentous microorganisms was also related to the influent COD level in the thermophilic SBR. With a higher influent COD level (3000 mg/L), an even larger transfer rate of oxygen was desired to biodegrade the COD, which further worsen the oxygen limitation problems in the thermophilic SBR. One way to solve the thermophilic sludge bulking problem

is to use pure oxygen for aeration. The use of pure oxygen can significantly increase the DO level in thermophilic temperatures and thus minimize the growth of filamentous microorganisms caused by oxygen limitation. Another approach to solve the thermophilic biomass separation problems is the use of membrane separation bioreactor (MBR) technology. The use of MBR can retain all sludge flocs with a size larger than the pore size of membrane, no matter sludge is bulking or not. Further studies should focus on the impact of pure oxygen on thermophilic sludge settleability and the use of MBR to eliminate biomass separation problems.

#### 4.3.2 FTIR spectrum

Fourier transfer infrared spectroscopy (FTIR) technique was used to distinguish the microbial community between thermophilic and mesophilic sludge. As shown in Figure 4.3.6, the FTIR spectrum was generally similar except for a characteristic peak at  $1080\text{ cm}^{-1}$  existing in the thermophilic sludge but not showing in the mesophilic sludge. The unique characteristic peak at  $1080\text{ cm}^{-1}$  corresponds to the sugar groups in polysaccharides [125]. This result might suggest that the thermophilic sludge was richer in polysaccharides.

The similarity of the FTIR spectrum was due to the fact that both the thermophilic and mesophilic sludge contain proteins, polysaccharides, DNA, RNA and lipids as their molecular composition. The characteristic peak near  $1654$  and  $1542\text{ cm}^{-1}$  corresponds to the primary amino group (Am I) and the secondary amino group (Am II) in proteins, respectively. The characteristic peak near  $1460\text{ cm}^{-1}$  may also come from the secondary amine and is resulted from the  $\text{CH}_2$  group of aliphatic chains [126]. The deformation vibration of  $(\text{CH}_3)_2$  or  $(\text{CH}_3)_3$  may contribute to the characteristic peak near  $1400\text{ cm}^{-1}$ . The phosphate group (PI) and primary alcohol connected with saturated and unsaturated organic backbones in sludge leads to a deformation vibration near  $1240$  and  $1035\text{ cm}^{-1}$ , respectively [126].



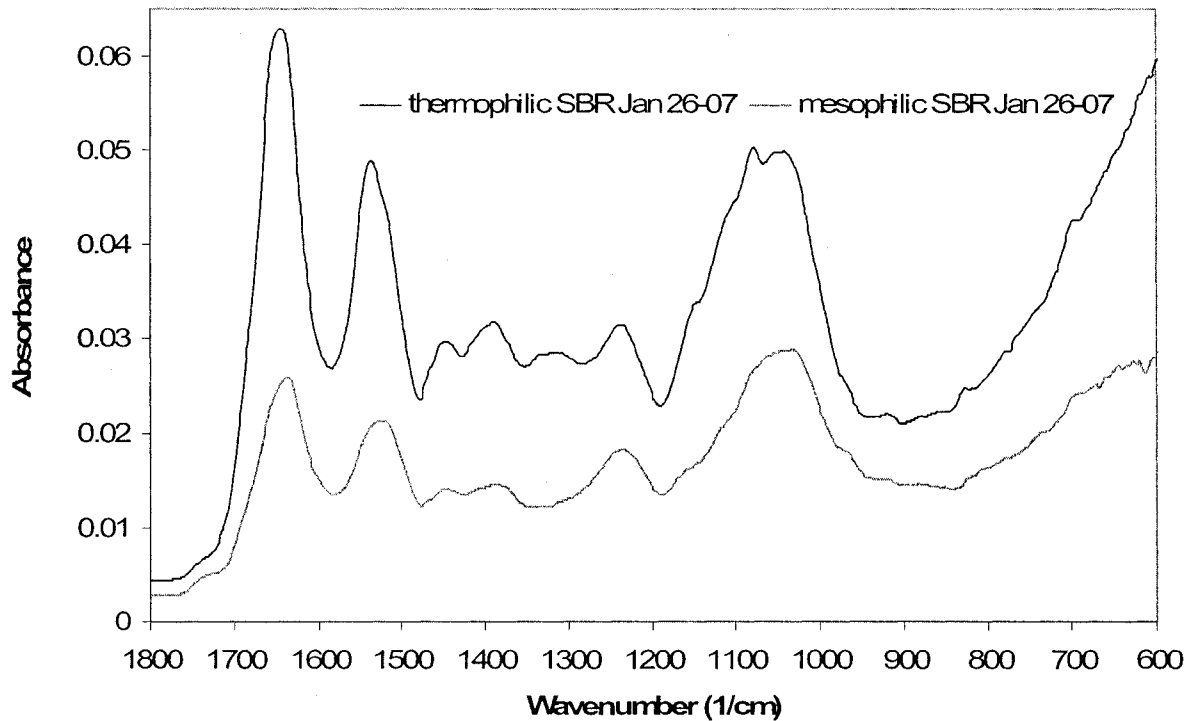


Figure 4.3.6 FTIR spectrum for thermophilic and mesophilic sludge for treating synthetic kraft evaporator condensate (Influent COD = 3000 mg/L, HRT = 12 Hours)

The differences illustrated by the presence or absence of unique characteristic peak at  $1080\text{ cm}^{-1}$  suggest that FTIR spectroscopy can be used to recognize differences in microbial community structure. The results suggest that there were some differences in microbial community structure between thermophilic and mesophilic sludge.

#### 4.3.3 Floc size distribution

Floc size distribution of the non-settleable fraction of sludge flocs in treated effluent and the MLSS is shown in Figures 4.3.7 and 4.3.8. A significant larger portion of fine colloidal particles in the size range of 0.1 to 10 $\mu\text{m}$  was observed in the treated effluent of the thermophilic SBR, as shown in Figure 4.3.7. However, there was a larger fraction of large particles (400 ~ 1000 $\mu\text{m}$ ) in the thermophilic MLSS

(Figure 4.3.8). This may not be surprising, as the presence of filamentous microorganisms in the thermophilic sludge provides the backbones of formation of large flocs.

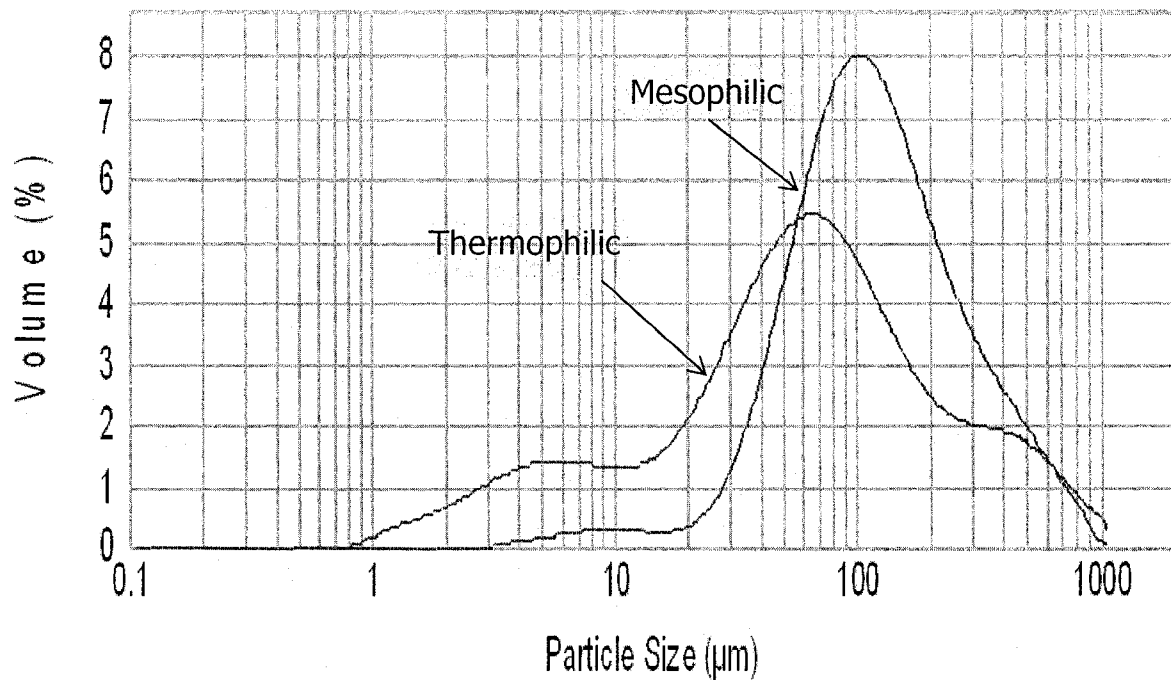


Figure 4.3.7 Floc size distribution (Volume %) Vs. particle size of thermophilic and mesophilic ESS for treating synthetic kraft evaporator condensate (Influent COD = 3000 mg/L, HRT = 12 Hours)

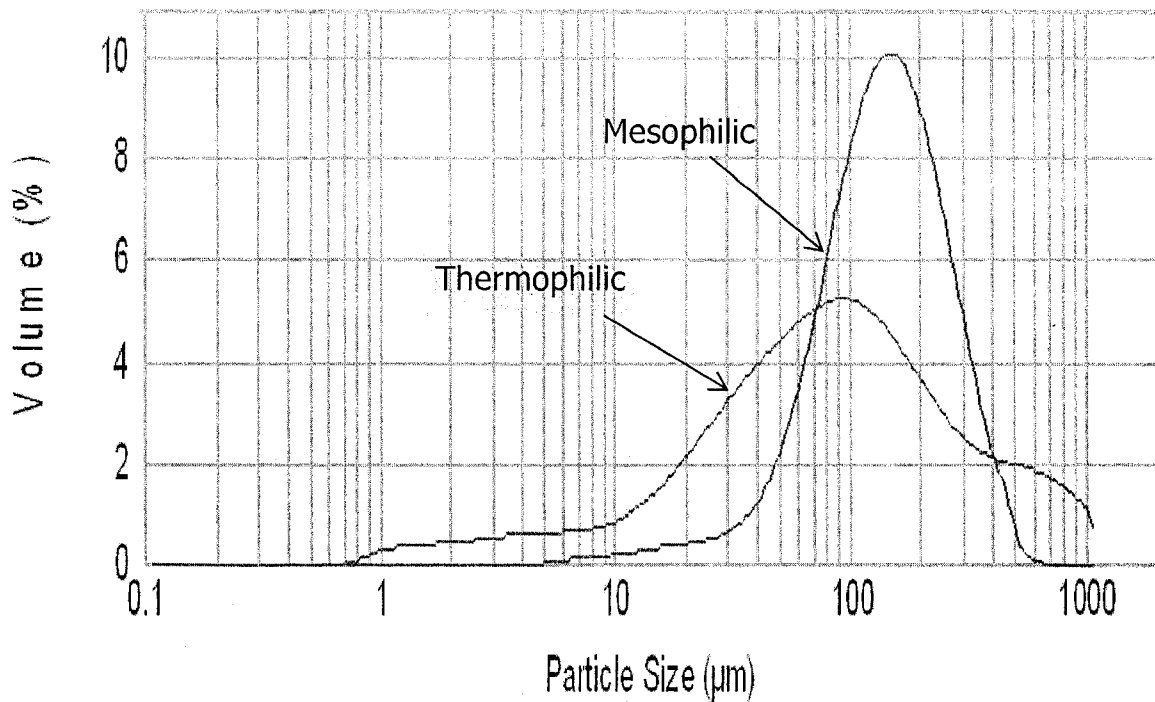


Figure 4.3.8 Floc size distribution (Volume %) Vs. particle size of thermophilic and mesophilic MLSS for treating synthetic kraft evaporator condensate (Influent COD = 3000 mg/L, HRT = 12 Hours)

The larger portion of non-settleable fraction of colloidal particles in thermophilic sludge was related to a higher level of ESS (Figure 4.3.9). From Figure 4.3.8, The average ESS concentrations  $\pm$  deviations were  $328 \pm 152$  mg/L in the thermophilic SBR and  $109 \pm 105$  mg/L in mesophilic SBR from 61 sample tests for each SBR during an influent COD of 3000 mg/L for treating synthetic kraft evaporator condensate. The significant difference of ESS levels between thermophilic and mesophilic SBRs is probably not surprising, as the ESS concentration is related to the level of the non-settleable fraction of particles.

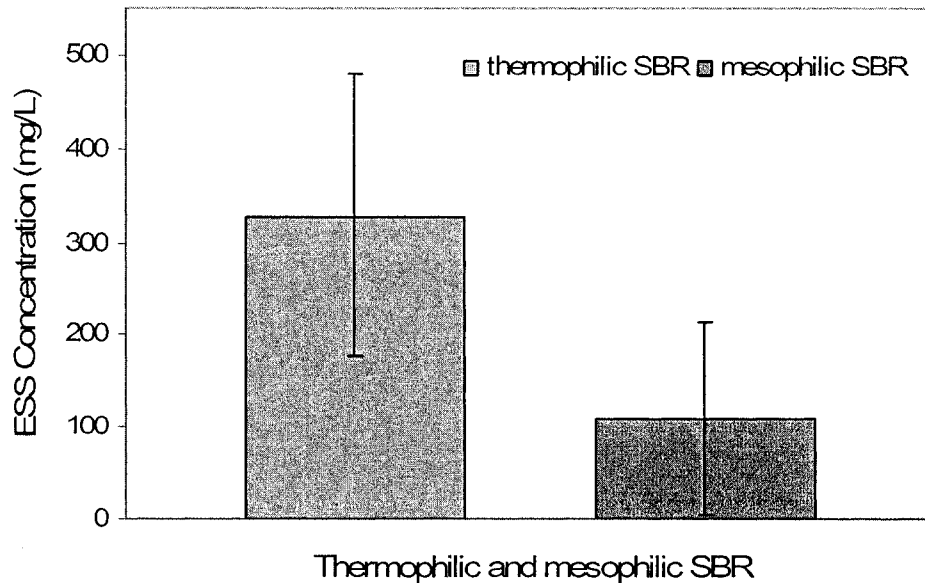
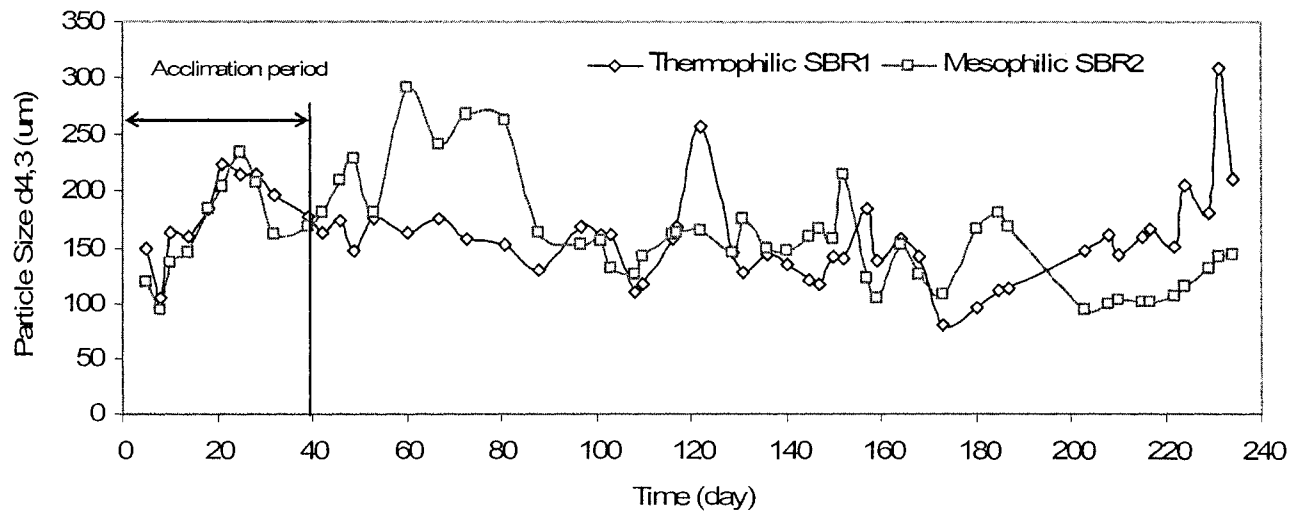


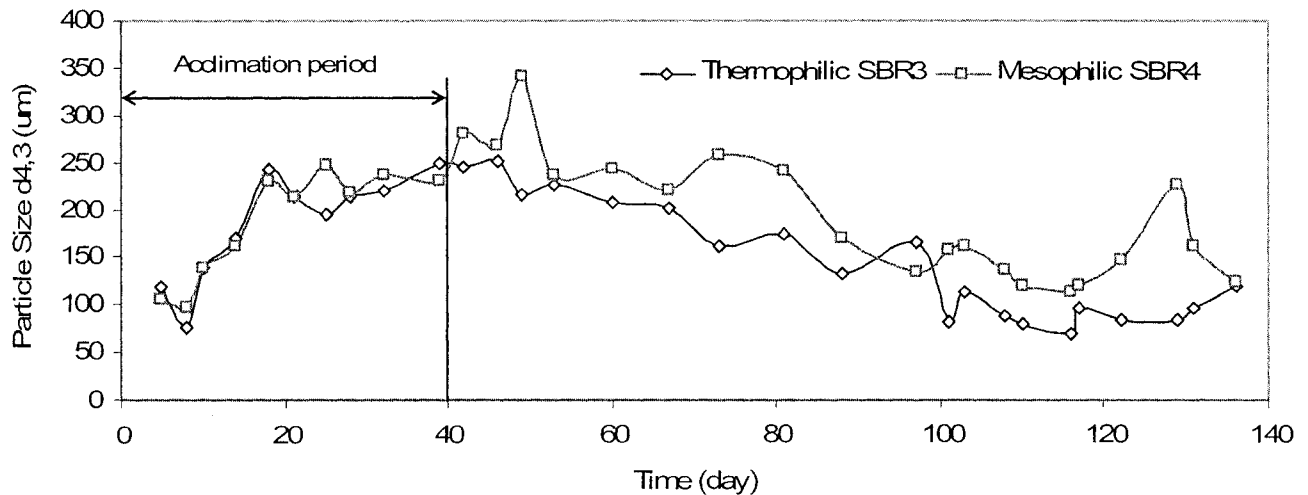
Figure 4.3.9 A comparison on the ESS level between thermophilic and mesophilic SBRs for treating synthetic kraft evaporator condensate. Results are expressed as the average  $\pm$  standard deviation (Influent COD = 3000 mg/L, HRT = 12 Hours)

A comparison on the average diameter ( $d_{4,3}$ ) between thermophilic sludge and mesophilic sludge with experimental time is shown in Figures 4.3.10 (a) and 4.3.10 (b). The average diameter was similar in these two sludges during the acclimation period of time. This is not surprising, as all the SBRs were seeded with the same seed sludge and operated under similar conditions. However, significant differences in the average diameter were observed once the thermophilic SBRs reached at the thermophilic temperatures. The average diameter of the thermophilic sludge was usually smaller than that of the mesophilic sludge. This was attributed to the larger portion of non-settable fraction of colloidal particles in the thermophilic sludge. A reversal in the average diameter of flocs was observed at the end of the experiment. The larger average diameter of thermophilic sludge could be attributed to the formation of a large portion of large filamentous microorganisms-backbone flocs. A comparison between the average diameter of sludge flocs (Figures 4.3.10(a)-(b)) and the settleability of sludge

(Figure 4.3.5) suggests that a smaller SVI was usually related to a larger average diameter of flocs. Similarly, a lower level of ESS was usually related to a larger average diameter of flocs (Figure 4.3.9). This is consistent with the previous findings of Liao et al. [127]. Therefore, a large and dense floc is desirable for effective biomass separation. From this point of view, thermophilic sludge faces challenges of biomass separations.



(a) MLSS average particle diameter versus experimental time for thermophilic-SBR1 and mesophilic-SBR2



(b) MLSS average particle diameter versus experimental time for thermophilic-SBR3 and mesophilic-SBR4

Figure 4.3.10 MLSS average particle diameter with respect to experimental time for treating synthetic kraft evaporator condensate (Influent COD = 3000 mg/L, HRT = 12 Hours)

#### 4.3.4 Zeta potential

Figure 4.3.11 shows the average zeta potential in the thermophilic ESS ( $-10.44 \pm 2.44$  mV) and mesophilic ESS ( $-10.84 \pm 2.53$  mV). The average values and standard deviations of zeta potential were calculated from 80 sample tests for each of both thermophilic ESS and mesophilic ESS for treating synthetic kraft evaporator condensate. In contrast to the significant difference in ESS concentration and SVI level between thermophilic and mesophilic sludge, there was no significant difference in zeta potential between the thermophilic and mesophilic sludge. The results of statistical analysis among the zeta potential, SVI and ESS data suggest that there is no correlation either between SVI and zeta potential or between ESS and zeta potential ( $p > 0.05$ ). This result is consistent with the findings of Vogelaar et al. [63] in that the DLVO (Derjaguin, Landau, Verweij and Overbeek) theory is not valid in explaining the difference in bioflocculation and settleability between thermophilic and mesophilic sludge. It is likely the biopolymer bridging mechanism by extracellular polymeric substance (EPS) plays a more important role in controlling bioflocculation [63]. Further studies should focus on the quantity and composition of EPS from thermophilic and mesophilic sludge.

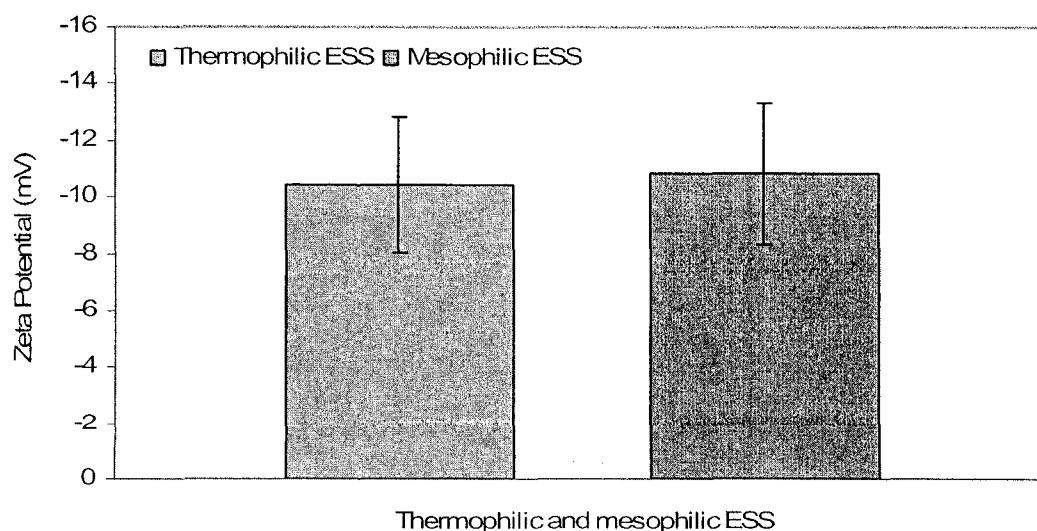


Figure 4.3.11 A comparison on zeta potential of thermophilic and mesophilic ESS for treating synthetic kraft evaporator condensate. Results are expressed as the average  $\pm$  standard deviation (Influent COD = 3000 mg/L, HRT=12 Hours)

#### 4.4 Treatment of TMP pressate using thermophilic and mesophilic SBRs and MABRs

In this part of experiments, the main goal was to conduct a comparative study of the soluble chemical oxygen demand (COD) removal efficiencies, sludge settleability and flocculating ability of thermomechanical pulp (TMP) pressate treatment (Table 3.4) using thermophilic and mesophilic SBRs and MABRs under well-controlled conditions. The two SBRs were operated at 30°C (mesophilic temperature) and 55°C (thermophilic temperature), respectively. The same was for the two MABRs. The soluble COD of the TMP pressate from a local pulp and paper mill was in the range of 3700 ~ 4100 mg/L. Nutrients added in the influent wastewater were adjusted to:  $\text{NH}_4\text{NO}_3 = 570$  mg/L, and  $\text{KH}_2\text{PO}_4 = 175$  mg/L (others remained the same as shown in Table 3.1.3) according to the ratio of COD: N: P = 100: 5: 1. Parametric evaluations (residual COD, SVI, ESS, particle size distribution, and zeta potential) with time were performed in order to investigate the performance of biomass to remove the organic contaminants. The influent COD levels were shown in Table 3.1.4. Each barrel contained about 170 liter TMP pressate. The performance of the MABRs was monitored and evaluated by taking the same means except abandoning the SVI measurements.

##### 4.4.1 COD removal efficiency

Figures 4.4.1 and 4.4.2 show soluble COD removal efficiencies for the TMP pressate in thermophilic and mesophilic SBRs and MABRs, respectively, during the 236<sup>th</sup> ~ the 350<sup>th</sup> day operational time under tested conditions with an influent COD of 3700 ~ 4100 mg/L (Table 3.1.4). From Figure 4.4.1, a soluble COD removal efficiency of 75 ~ 85 % was achieved for the thermophilic SBR and 80 ~ 90 % was achieved for the mesophilic SBR when the HRT was set at 12 and 24 hours. And a very stable performance regarding soluble COD removal was observed. However, when the HRT was changed to 6 hours from 325<sup>th</sup> to 334<sup>th</sup> day, the soluble COD removal efficiency reduced dramatically and much less

stable for both thermophilic and mesophilic conditions (worse for thermophilic than mesophilic condition). Then, when the HRT was changed back to 12 hours from 335<sup>th</sup> to 350<sup>th</sup> day, the soluble COD removal efficiency was getting improved (50 ~ 85 %) under both thermophilic and mesophilic conditions. What is more, it was observed that the MLSS concentration in thermophilic SBR was very low (600 ~ 1100 mg/LMLSS) during the period of the HRT was set to 6 hours (325<sup>th</sup> to 334<sup>th</sup> day) even with none MLSS wasted, which was another reason to cause the very low COD removal efficiency besides the shorter HRT. It suggests that the HRT of 6 hours was not sufficient for the biodegradation to accomplish for both thermophilic and mesophilic SBRs and the intensity of high feed frequency under the HRT of 6 hours might greatly inhibit activated sludge growth due to an increase in the loading of toxic compounds in TMP pressate.

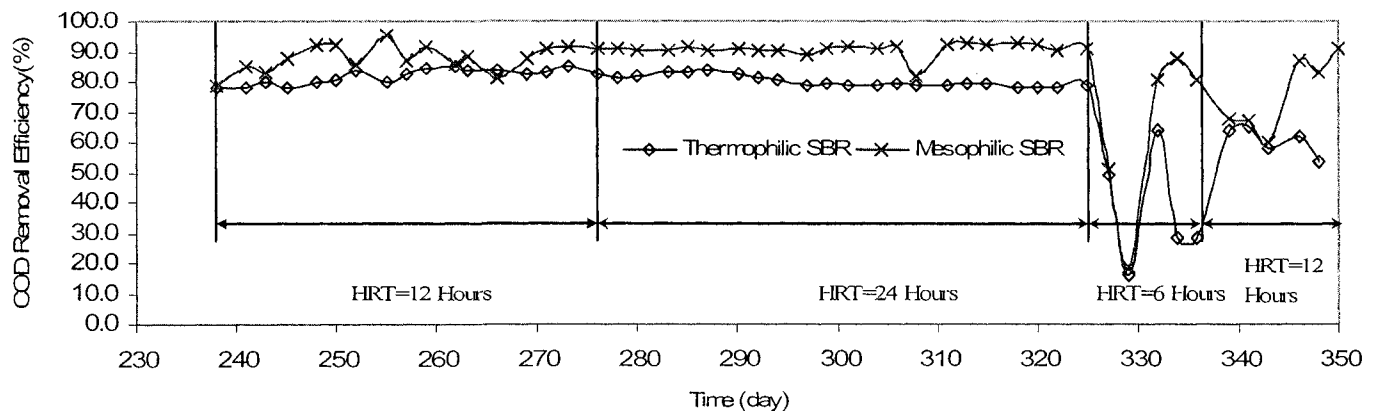


Fig 4.4.1 COD removal efficiency versus operating time for treating TMP pressate in thermophilic and mesophilic SBRs (Influent COD = 3700 ~ 4100 mg/L)



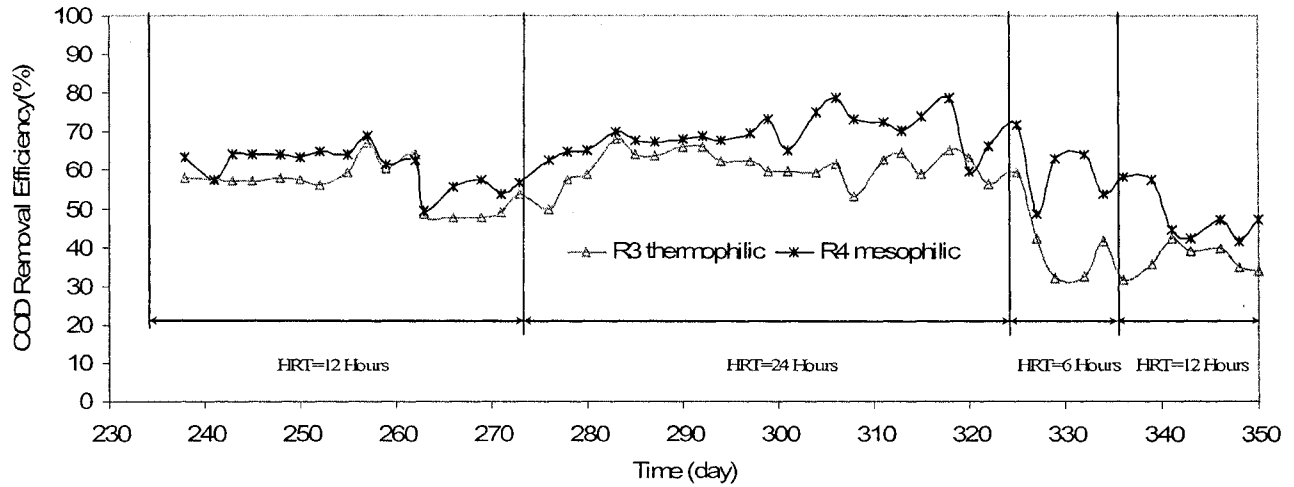


Figure 4.4.2 COD removal efficiency versus operating time for treating TMP pressate in thermophilic and mesophilic MABRs (Influent COD = 3700 ~ 4100 mg/L)

From Figure 4.4.2, the COD removal efficiency for thermophilic MABR (45 ~ 65 %) and mesophilic MABR (55 ~ 80 %) was lower than that for thermophilic and mesophilic SBRs respectively. An increase in the HRT from 12 hours to 24 hours led to a slightly increase in the COD removal efficiency of both the thermophilic and mesophilic MABRs. In addition, the soluble COD removal efficiency deteriorated when the HRT was changed to 6 hours. A little bit higher soluble COD removal efficiency obtained after the HRT was changed to 12 hours. It is obvious that the HRT of 6 hours was not sufficient for the reaction for thermophilic and mesophilic MABRs either. As compared to the MABRs, the higher COD removal efficiencies in the SBRs could be at least partially attributed to the stripping of VOC by conventional bubble aeration.

The reason that soluble COD removal efficiency of treating TMP pressate was generally lower than that of treating synthetic kraft evaporator condensate might be related to the composition and the

concentration of the feed. There might be a portion of toxic and/or non-biodegradable organic compounds that affected the bacteria (especially, thermophilic bacteria) performance with respect to removing COD occurring in the TMP pressate. It is well known that the TMP pressate contains toxic compounds, notably the resin and fatty acids and soluble lignin-like material [128-130]. Similar results were reported by the previous study [88, 130]. Magnus et al. [130] reported a large portion of unidentified extractives, both extractable by MTBE and water-soluble, were non-biodegradable. The analysis of the influent TMP pressate, such as BOD measurement and some main contaminants identification, are being conducted in this research group.

Figure 4.4.3 and Figure 4.4.4 show the reduction of the soluble COD concentration versus operating time in one operating cycle for thermophilic and mesophilic SBRs and MABRs respectively. Most of the consumable COD was removed within the first six hours period for thermophilic and mesophilic SBRs. However, the portions of about 600 mg/L and 400 mg/L COD were remaining without being biodegraded in thermophilic SBR and mesophilic SBR respectively. Much higher COD concentration remaining was found, from Figure 4.4.4, for thermophilic and mesophilic MABR. It suggests that great amount of non-biodegradable contaminants and/or microbial culture inhibition may occur in the wastewater treatment system. The significant difference in the COD removal efficiency between MABRs and SBRs could be at least partially attributed to the stripping effect of bubble aeration and adsorption onto biosolid [131] in SBRs.

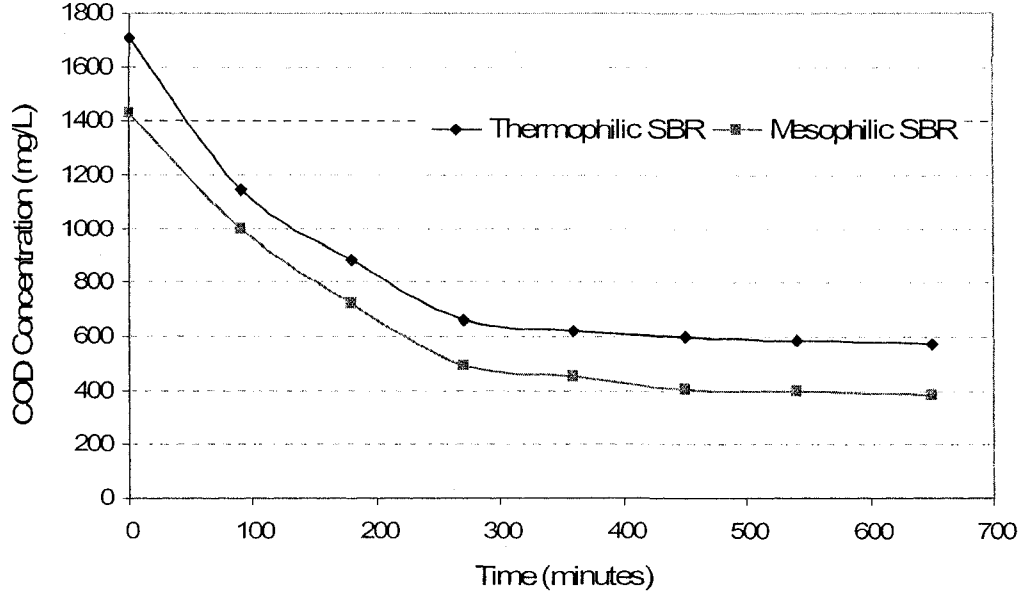


Fig 4.4.3 COD concentration versus time during one operating cycle for treating TMP pressate in thermophilic and mesophilic SBRs (Influent COD = 3700 ~ 4100 mg/L, HRT = 12 Hours) at March 06-07

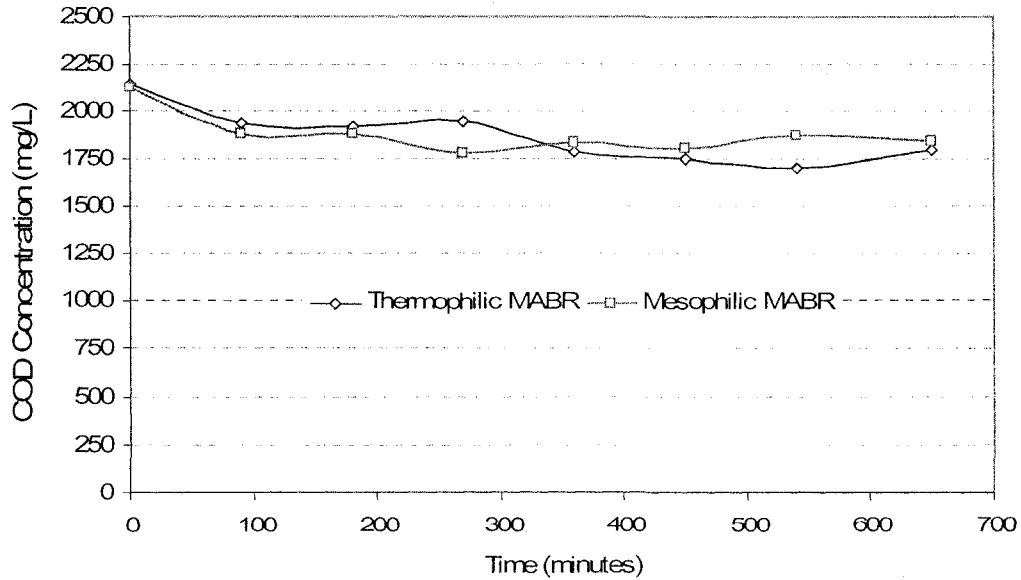


Fig 4.4.4 COD concentration versus time during one operating cycle for treating TMP pressate in thermophilic and mesophilic MABRs (Influent COD = 3700 ~ 4100 mg/L, HRT = 12 Hours) at March 06-07

#### 4.4.2 Settleability and flocculating ability

Figure 4.4.5 shows the settleability of sludge - sludge volume index (SVI) in the thermophilic and mesophilic SBRs for TMP pressate treatment. It is obvious that there was not so significant and consistent disparity in SVIs between the thermophilic and mesophilic SBR for TMP pressate treatment (ANOVA,  $p > 0.05$ ). This was different from the results of synthetic kraft evaporator condensate treatment. It was found that the SVI level was still larger for thermophilic SBR than those for mesophilic SBR at the beginning of the feed switching to TMP pressate from synthetic kraft evaporator condensate, then SVI values for thermophilic sludge gradually reduced and after about 30 days' stabilizing period, the SVI level of thermophilic sludge were even lower than those of mesophilic sludge. This is probably not surprising because at the beginning the level of filaments decreased gradually with experimental time, and finally much less filaments were observed morphologically for thermophilic flocs treating TMP pressate (Figure 4.4.6). From Figure 4.4.6 (a) – (d) (241<sup>th</sup> ~ 334<sup>th</sup> operational day) the amount of filaments were decreasing gradually. This observation also suggests that the TMP pressate inhibited the growth of filaments.

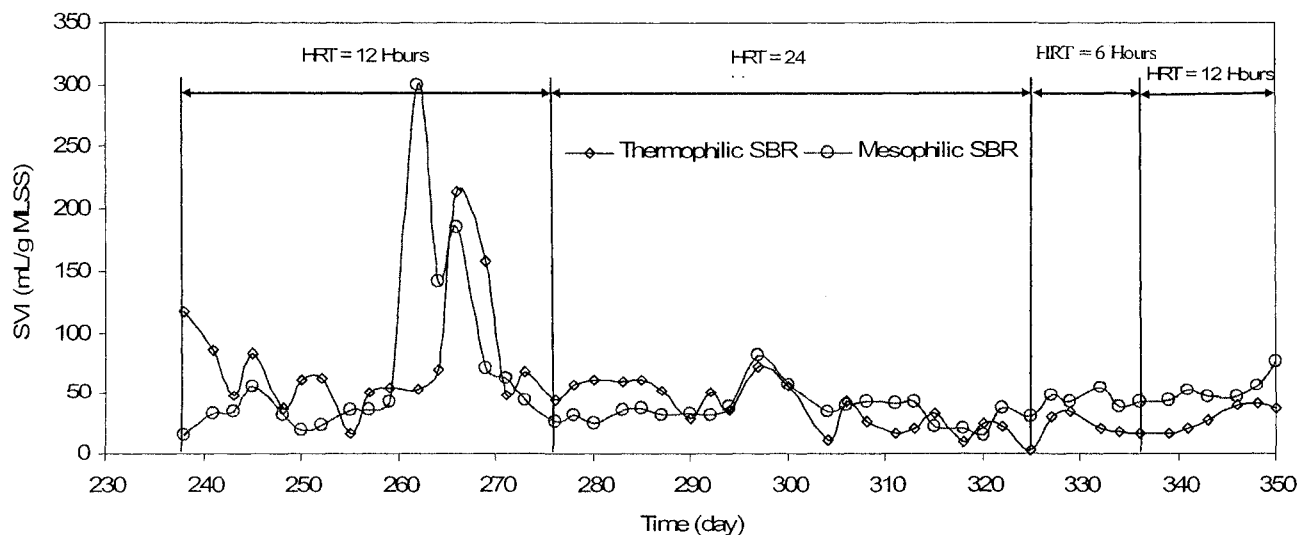


Figure 4.4.5 SVI versus time for treating TMP pressate in thermophilic and mesophilic SBRs (Influent COD = 3700 ~ 4100 mg/L)

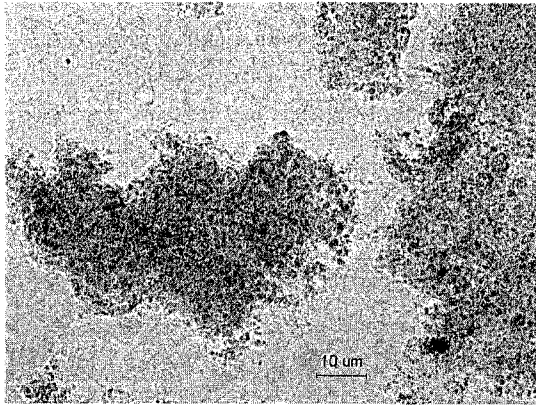
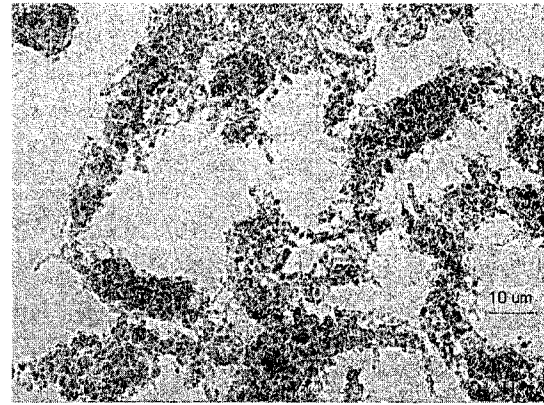
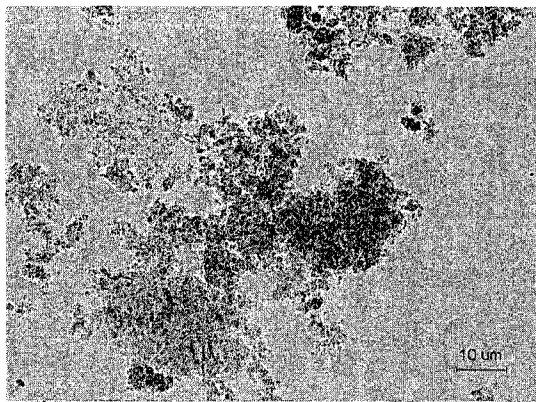
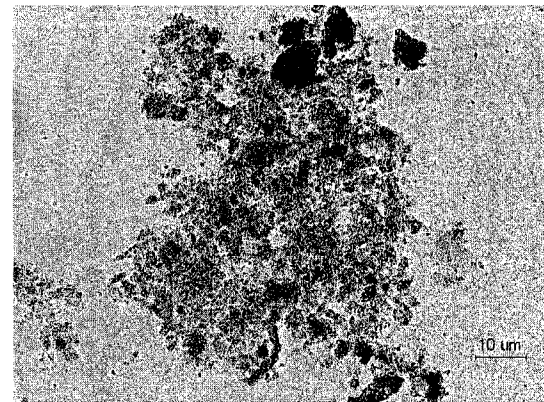
a) Thermophilic Sludge 0212-07 (241<sup>th</sup>)b) Thermophilic Sludge 0305-07 (262<sup>th</sup>)c) Thermophilic Sludge 0409-07 (297<sup>th</sup>)d) Thermophilic Sludge 0516-07 (334<sup>th</sup>)

Figure 4.4.6 Microscopical images of thermophilic activated sludge for treating TMP pressate in thermophilic SBR at different operational days (Influent COD = 3700 ~ 4100 mg/L, HRT = 6 ~ 24 Hours)

The effluent suspended solid (ESS) concentrations with respect to operational time for TMP pressate in thermophilic and mesophilic SBRs and MABRs are shown in Figure 4.4.7 and 4.4.8 respectively. ESS for thermophilic sludge in SBR was low (100 ~ 240 mg/L) during first two operating months, but increased (400 ~ 600 mg/L) after. The change in the flocculating ability as indicated by the ESS level

was probably due to a decrease in the filamentous level in the thermophilic sludge. At the beginning of treating TMP pressate, the filaments level might be decreased to a level that favor the formation of filament-backbone flocs [95] and minimized the non-settleable colloidal particles. However, with a further decrease in the filaments level and until complete disappear of the filaments, the filaments-backbones disappeared and thus dispersed growth might occur, which explained the significant increase in the ESS level after two months operation.

A significant detachment of both thermophilic and mesophilic biofilms in the MABRs was observed (Figure 4.4.8), as compared to the membrane attached biofilms that treated synthetic kraft evaporator condensate. This would indicate that the TMP pressate might contain toxic compounds that cause the detachment of membrane attached biofilms. The high level of ESS in the treated effluent of MABRs may suggest the need of a solids separation stage after the MABRs to remove the detached biofilms.

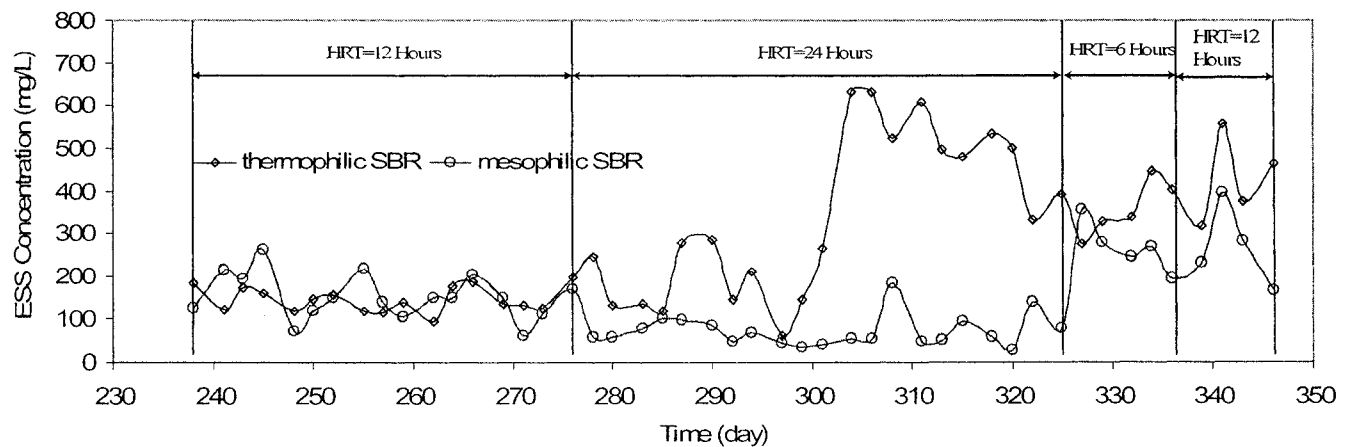


Figure 4.4.7 ESS concentration versus time for treating TMP pressate in thermophilic and mesophilic SBRs (Influent COD = 3700 ~ 4100 mg/L)

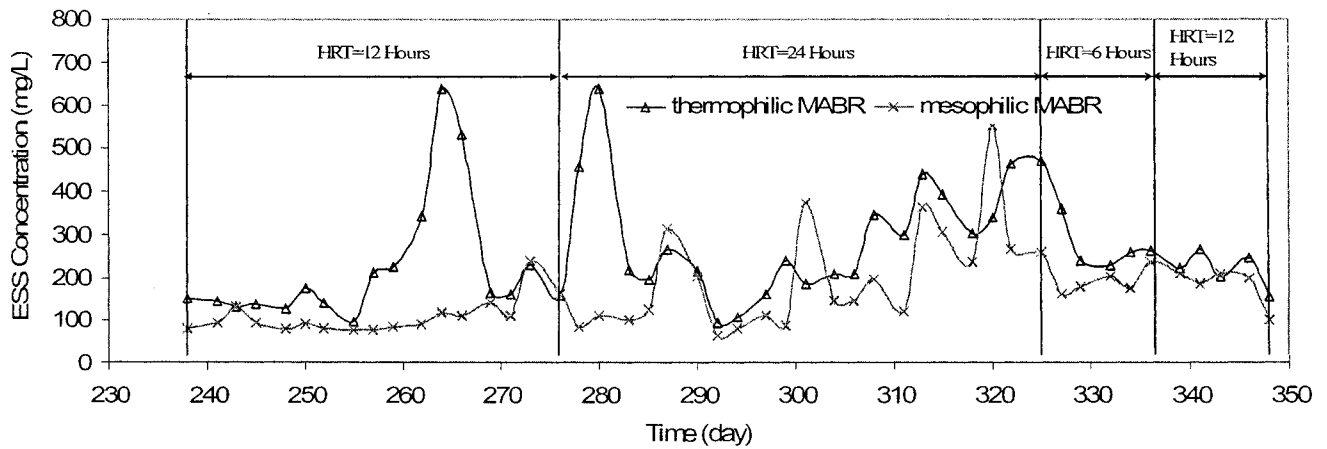
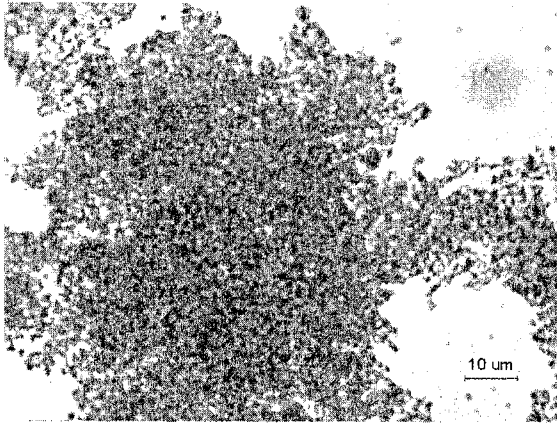


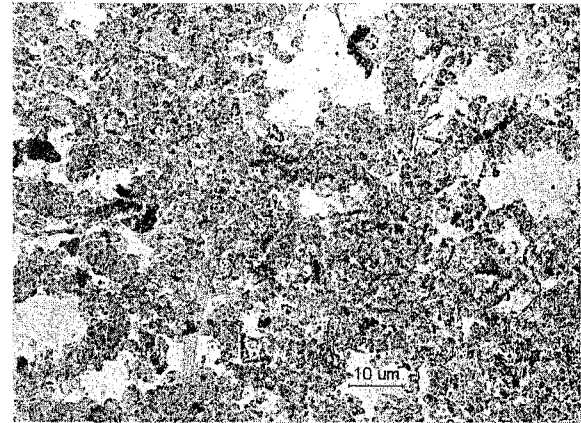
Figure 4.4.8 ESS concentration versus time for treating TMP pressate in thermophilic and mesophilic MABRs (Influent COD = 3700 ~ 4100 mg/L)

The better flocculating ability of mesophilic SBR during an HRT of 24 hours, might probably due to the effect of overabundance of protozoa in mesophilic sludge by their grazing upon effluent turbidity. Protozoa are known to graze upon activated sludge flocs and feed up on free-swimming bacteria [132]. Figure 4.4.9 shows microscopical images of mesophilic activated sludge for TMP pressate treatment in mesophilic SBR at different operational days. At the beginning of treating TMP pressate (HRT = 12 hours), almost no protozoa was observed, and then the number of protozoa increased gradually, and an abundance of protozoa (free ciliates) were observed after the HRT was changed to 24 hours (Figure 4.4.9-c). This is not surprising because Ciliates are usually found under conditions of good floc formation and generally indicate satisfactory activated sludge operation [95]. However, under operated temperature above 40°C, protozoa and other higher life forms are generally absent from activated sludge systems [95], which is why there were no protozoa observed in thermophilic SBR which might be another reason to cause high ESS level in thermophilic SBR. When the HRT was set to 6 hours, the population of protozoa in the mesophilic SBR reduced greatly, which resulted in ESS level went much

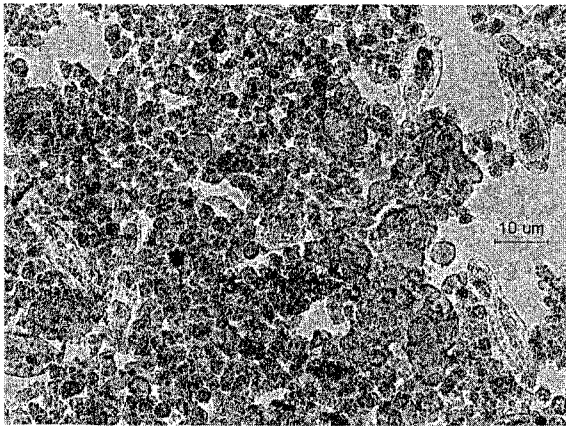
higher in mesophilic SBR (Figure 4.4.7). LaPara et al [19] reported that the absence of protozoa and other higher life forms is a possible cause for high turbidity and ESS level of treated effluent.



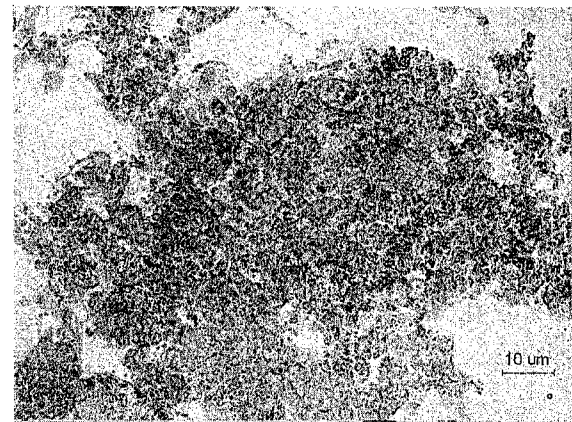
a) Mesophilic Sludge 0212-07 (241<sup>th</sup>)  
(Beginning of HRT = 12 Hours)



b) Mesophilic Sludge 0305-07 (264<sup>th</sup>)  
(HRT = 12 Hours)



c) Mesophilic Sludge 0409-07 (297<sup>th</sup>)  
(HRT = 24 Hours)



d) Mesophilic Sludge 0516-07 (334<sup>th</sup>)  
(HRT = 6 Hours)

Figure 4.4.9 Microscopical images of mesophilic activated sludge for treating TMP pressate in mesophilic SBR at different operational days (Influent COD = 3700 ~ 4100 mg/L, HRT = 6 ~ 24 Hours)



#### 4.4.3 Particle size distribution

Floc size distribution of the non-settleable fraction of sludge flocs in treated effluent and the MLSS is shown in Figures 4.4.10 and 4.4.11. A significant larger portion of fine colloidal particles in the size range of 0.1 to 10 $\mu$ m was observed in the treated effluent of the thermophilic SBR, as shown in Figure 4.4.10. There was a larger fraction of large particles (70 ~ 300  $\mu$ m) in the mesophilic MLSS (Figure 4.4.11).

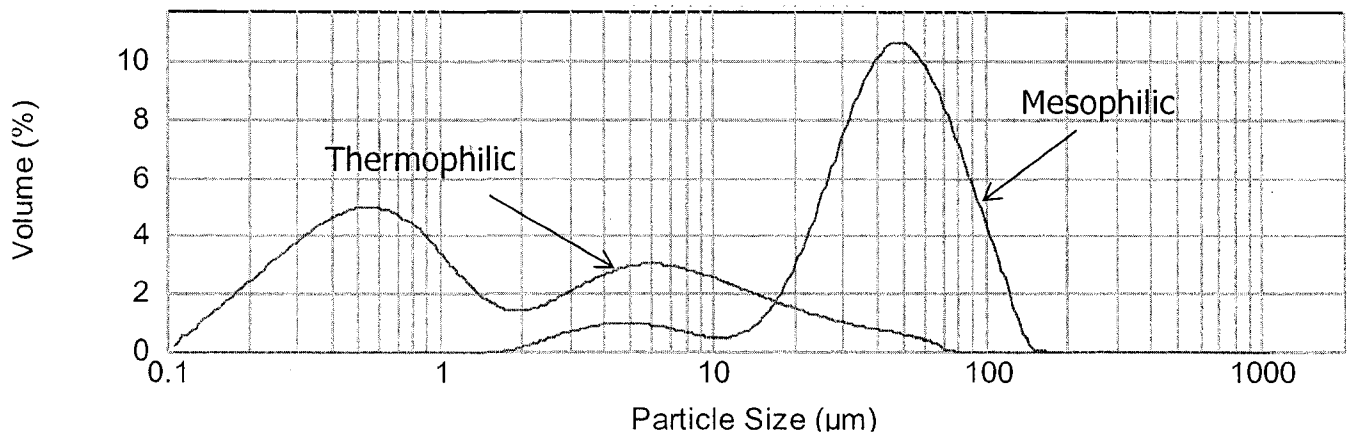


Figure 4.4.10 Floc size distribution (Volume %) Vs. particle size of thermophilic and mesophilic ESS for treating TMP pressate

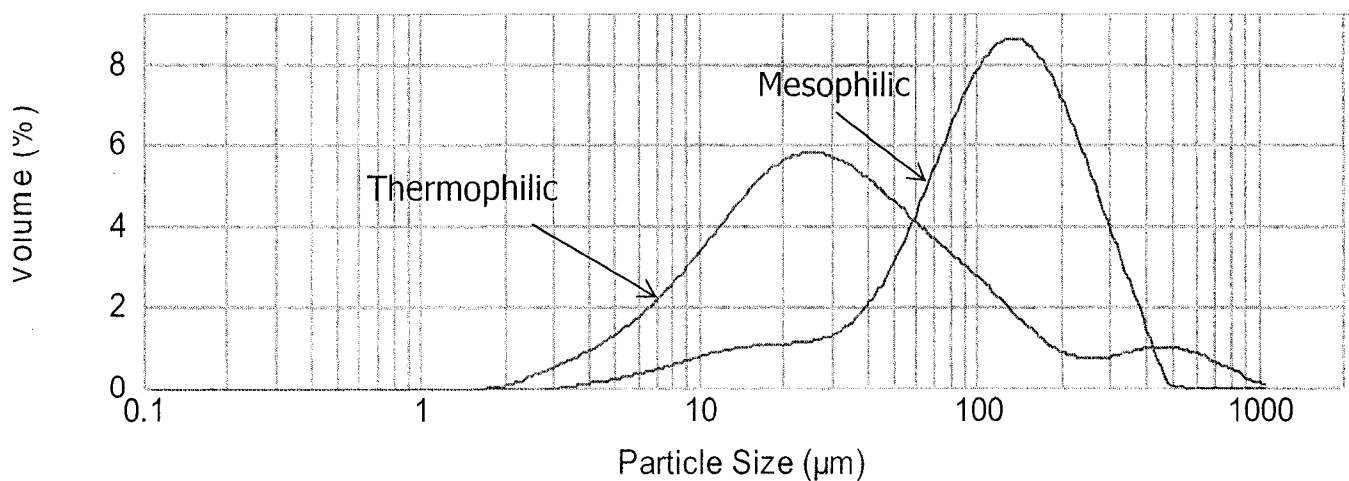


Figure 4.4.11 Floc size distribution (Volume %) Vs. particle size of thermophilic and mesophilic MLSS for treating TMP pressate

The average diameter ( $d_{4,3}$ ) of thermophilic sludge and mesophilic sludge with experimental time for treating TMP pressate is shown in Figures 4.3.12. The average diameter of the thermophilic sludge was greatly larger (100 ~ 270  $\mu\text{m}$ ) than that of the mesophilic sludge (50 ~ 110  $\mu\text{m}$ ) when the HRT = 12 Hours. Then, when the HRT = 24 hours, the average diameter of both the thermophilic and mesophilic sludge stayed in a very close level (50 ~ 100  $\mu\text{m}$ ). The average diameter of the mesophilic sludge went higher (100 ~ 150  $\mu\text{m}$ ) while that of thermophilic sludge stayed in the same level when the HRT changed to 6 hours. The results of particle size changing might reflect the variation of microbial cultures due to the toxic quality of real wastewater (TMP pressate), especially for the thermophilic sludge as the filaments disappearing. There was no obvious correlation between the Particle size and ESS, SVI respectively for treating TMP pressate under the experimental conditions of this study.

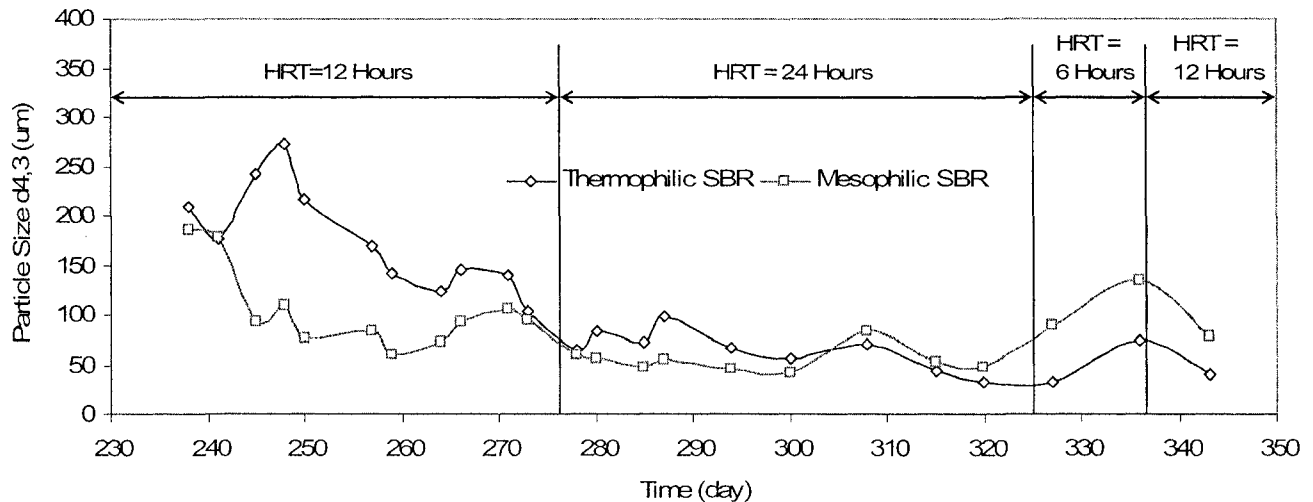


Figure 4.4.12 MLSS average particle diameter with respect to experimental time for treating TMP pressate (Influent COD = 3700 ~ 4100 mg/L, HRT = 6 ~ 24 Hours)

#### 4.4.4 Zeta potential

Figure 4.4.13 shows the average zeta potential in the thermophilic ESS ( $-17.23 \pm 5.81$  mV) and mesophilic ESS ( $-17.76 \pm 6.38$  mV). The average values and standard deviations of zeta potential were calculated from 30 sample tests for each of both thermophilic ESS and mesophilic ESS for treating TMP

pressate. Similarly, there is no significant difference in zeta potential between the thermophilic and mesophilic sludge. The results of statistical analysis among the zeta potential, SVI and ESS data suggest that there is no correlation either between SVI and zeta potential or between ESS and zeta potential ( $p>0.05$ ). This result is consistent with the findings of our study in treating synthetic kraft evaporator condensate (section 4.3.3) and Vogelaar et al. [63] that the DLVO theory can not explain the difference in flocculating ability of thermophilic and mesophilic sludge. Other mechanisms, such as hydrophobic interaction and polymer bridging may be responsible for the difference. Further studies on the role of extracellular polymeric substances (EPS) in flocculation are under going by other graduate students in this research group.

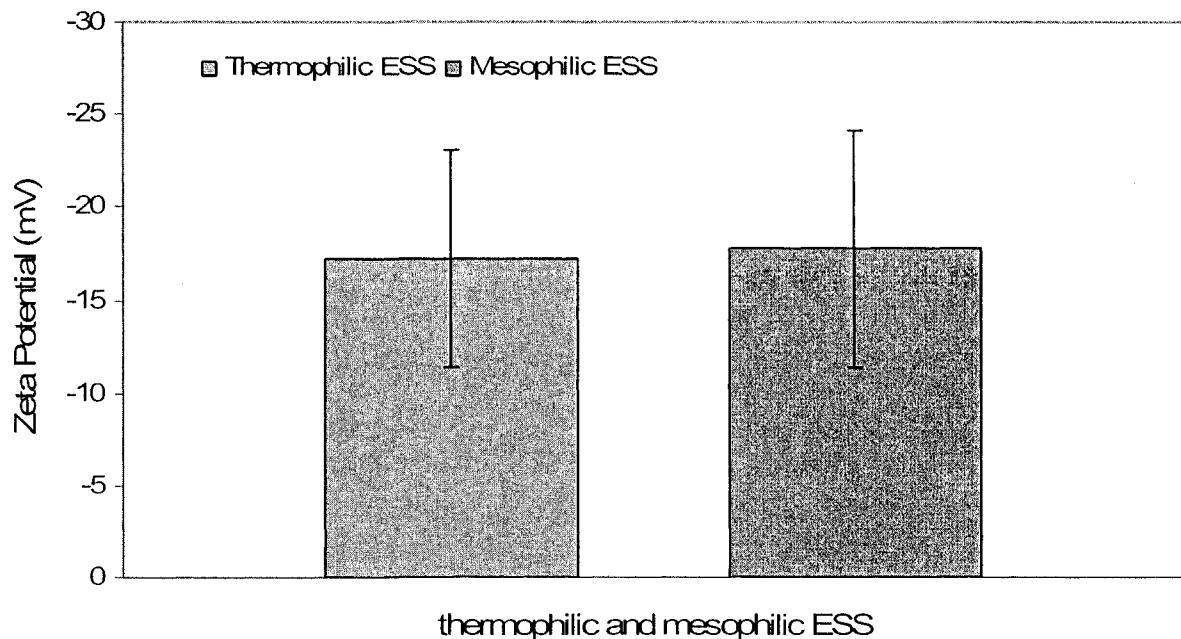


Figure 4.4.13 A comparison on zeta potential of thermophilic and mesophilic ESS for treating TMP pressate. Results are expressed as the average  $\pm$  standard deviation (Influent COD = 3700 ~ 4100 mg/L, HRT = 6 ~ 24 Hours)

#### 4.4.5 MLSS level

Figure 4.4.14 shows MLSS concentration versus operating time for TMP pressate in thermophilic and mesophilic SBRs. A proper amount of sludge was wasted after the reaction period every two days according to the monitoring data of MLSS concentrations and the relevant calculation to try to maintain a similar MLSS level ( $2000 \pm 300$  mg/L) at each SRT. However, the MLSS level fluctuated due to an operational difficulty in dealing with the accumulation of sludge on the wall of SBRs at the water-air interface. The accumulated sludge could fall down back the mixed liquor randomly. The MLSS in thermophilic SBR grew slowly comparing with that in mesophilic SBR. This might not be surprising, as the yield of thermophilic sludge was generally much lower than that of the mesophilic sludge [19]. It was also noticed that the growth of biomass was under the lowest level with an HRT of 6 Hours. This suggests that the loading of toxic contaminants was too higher, as compared to that at an HRT of 12 and 24 hours, at an HRT of 6 hours that inhibited the growth of biomass [133].

Figure 4.4.15 shows the average MLSS concentration  $\pm$  standard deviation in the thermophilic SBR ( $2616 \pm 1248$  mg/L) and mesophilic SBR ( $3018 \pm 1370$  mg/L). The average concentration of thermophilic sludge for TMP pressate was higher than that for synthetic kraft evaporator condensate treatment. This was mainly due to the improvement of thermophilic sludge settleability in TMP pressate treatment, which eliminated the wasting of biomass in treated effluent.

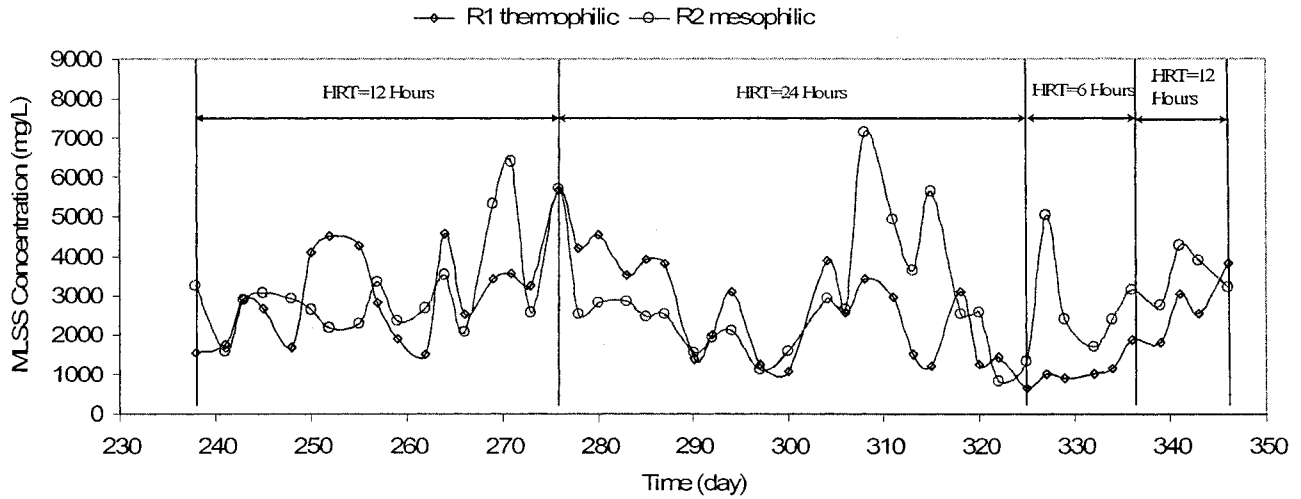


Figure 4.4.14 MLSS concentration versus operational time for treating TMP pressate in thermophilic and mesophilic SBRs (Influent COD = 3700 ~ 4100 mg/L)

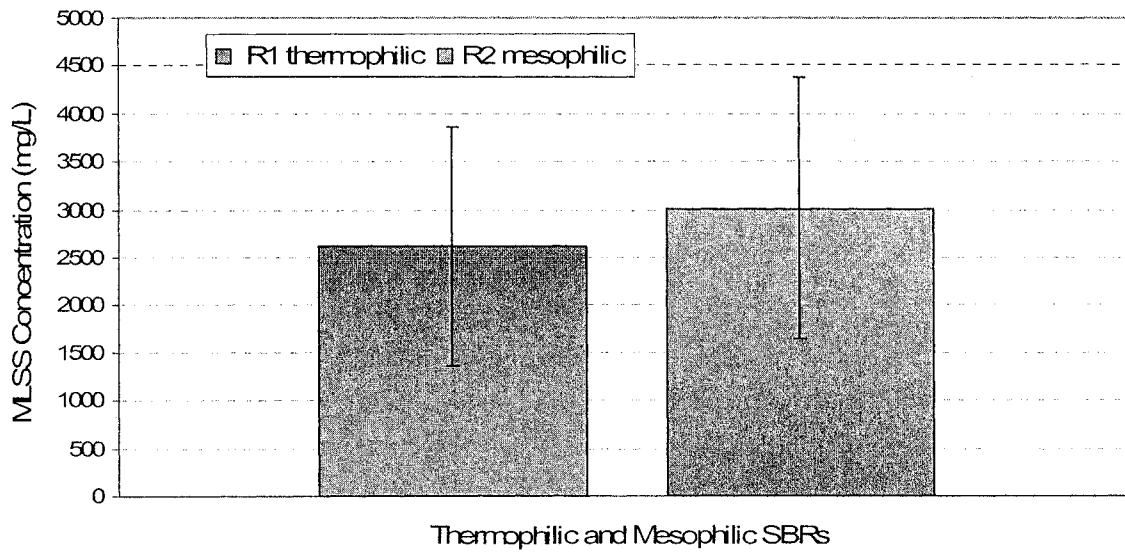


Figure 4.4.15 MLSS average concentration for treating TMP pressate in thermophilic and mesophilic SBRs. Results are expressed as the average  $\pm$  standard deviation. (Influent COD= 3700 ~ 4100 mg/L, HRT= 6 ~ 24 Hours)

## 5. Conclusions and Recommendations

### 5.1 Conclusions

A comparative study was conducted to evaluate and compare the performance between thermophilic and mesophilic treatment processes using two types of bioreactors - MABRs and SBRs and characterize structure and properties of microbial flocs and biofilms for synthetic kraft evaporator condensate and TMP pressate treatment. The main conclusions are summarized below.

1.) For synthetic kraft evaporator condensate: Treatment of synthetic kraft evaporator condensate at both thermophilic (55°C) and mesophilic (30°C) temperature was feasible in MABRs and SBRs; Under normal operation, soluble COD removal between thermophilic and mesophilic SBR (90 ~ 98%) was comparable; When compared with SBR, the soluble COD removal efficiency of MABR (80 ~ 95%) was slightly lower; The soluble COD removal efficiency of thermophilic MABR (80 ~ 90%) was slightly lower than mesophilic MABR (90 ~ 95%); Settleability of thermophilic sludge was poorer when compared with that of mesophilic sludge; The level of ESS in the thermophilic process was higher than that in the mesophilic process for synthetic evaporator condensate. These results suggest that treatment of synthetic kraft evaporator condensate in thermophilic SBR was feasible in terms of COD removal but faces challenges of biomass separation. The thermophilic MABR showed the advantages in overcoming stripping of VOC (methanol) and biomass separation problems, as compared to thermophilic SBR.

2.) For TMP Pressate: Treatment of TMP pressate at both thermophilic (55°C) and mesophilic (30°C) temperature was feasible for MABRs and SBRs; The soluble COD removal efficiency of thermophilic SBR (75 ~ 85%) was slightly lower than that of mesophilic SBR (80 ~ 90%); The soluble COD removal

efficiency of thermophilic MABR (40 ~ 65%) was slightly lower than that of mesophilic MABR (50 ~ 80%); The soluble COD removal efficiency of MABR (40 ~ 80%) was lower than that (60 ~ 90%) of SBR ; Settleability of thermophilic sludge was comparable to that of mesophilic sludge; The level of ESS in thermophilic process was higher than that in mesophilic process for TMP pressate. These results suggest that treatment of TMP pressate is feasible in thermophilic SBR. The lower COD removal efficiency and higher ESS of MABRs needs further investigation.

3.) For the characteristics and structure of thermophilic and mesophilic sludge treating synthetic evaporator condensate, there are significant differences in floc morphology, ultrastructure, filaments, surface functional groups, floc size distribution, bioflocculating ability and settleability between thermophilic and mesophilic sludge. The poorer settleability of thermophilic sludge was related to a higher level of filaments, which could be caused by a low DO level at the thermophilic temperature (55°C). The poorer bioflocculating ability of thermophilic sludge could not be explained by the conventional DLVO theory, pointing to other mechanisms, such as polymer bridging and hydrophobic interactions. Treatment of evaporator condensate under thermophilic condition faces the challenge of biomass separations and requires further studies on pure oxygen and MBR technology to solve biomass separation problems.

## 5.2 Recommendations

Although this thesis explores a novel biological treatment technology – thermophilic MABR for kraft evaporator condensate treatment, and provides a long-term (one year) experiment on a bench-scale to prove its feasibility, a number of questions raised by this study still require further investigation. Specific recommendations for future studies are outlined below.

- Optimization of the performance of MABR. Significant attention has to be paid to uniformly distributing the aeration gas, simultaneously provide effective contact between the biofilm and the wastewater.
- developing of mechanism for optimally controlling biofilm thickness. Optimizing the operating conditions, such as, pure oxygen aeration, gas flow rate and gas pressure etc.
- Further membrane development for bubble-free aeration under higher temperature (55°C).
- Bioreactors application for closed cycle operation of pulp and paper mills to solve biomass separation problems.
- Pilot-scale studies of TMP pressate treatment using SBR and/or MABR.



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**Appendix A Effluent Chemical Oxygen Demand Data [mg COD/L]**

Day	Date	thermophilic SBR1	mesophilic SBR2	thermophilic SBR3/MABR	mesophilic SBR4/MABR
3	June 19-06	90	21.9	40	21
6	June 22-06	3	11.4	8.9	8.9
8	June 24-06	18	3.9	4	1
11	June 27-06	43	11.6	28.2	11.5
13	June 29-06	28	1.3	25.6	16.6
17	July 03-06	31	16.8	39.7	3.8
20	July 06-06	5	6.4	117	21.6
22	July 08-06	97	6.4	187	10.2
24	July 10-06	216	19.2	336.6	15.4
26	July 12-06	85	15	230.3	15
27	July 13-06	80	4	128	10
29	July 15-06	33	2	53	5
31	July 17-06	41	9	80	27
33	July 19-06	101	16	37	38
34	July 20-06	199	22	95	50
38	July 24-06	32	51	52	78
41	July 27-06	124	78	72	81
45	July 31-06	67	105	62	112
48	Aug 03-06	136	99	48.2	102.8
52	Aug 07-06	51	104.1	40.6	100.3
55	Aug 10-06	109	50	50	81
59	Aug 14-06	86	58	39	71
62	Aug 17-06	88	69	71	33
64	Aug 19-06	99	40	38	18
66	Aug 21-06	52	81	55	38
69	Aug 24-06	34	34	109	18
71	Aug 26-06	38	63	33	29
73	Aug 28-06	52	57	42	59
76	Aug 31-06	54	63	50	40
78	Sep 02-06	110	61	121	46
80	Sep 04-06	55	82	95	74
83	Sep 07-06	52	38	92	27
85	Sep 09-06	43	53	50	204
88	Sep 12-06	47	44	70	226
90	Sep 14-06	17	19	83	102
92	Sep 16-06	20	28	38	265
94	Sep 18-06	41	28	43	329
96	Sep 20-06	40	62	90	270
98	Sep 22-06	75	103	142	121
101	Sep 25-06	170	5	88	92
103	Sep 27-06	109	152	104	136
105	Sep 29-06	460	96	197	76
108	Oct 02-06	185	95	174	148
110	Oct 04-06	198	175	120	211
112	Oct 06-06	207	147	323	106
115	Oct 09-06	156	102	107	86

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117	Oct 11-06	148	161	132	462
119	Oct 13-06	445	79	86	173
122	Oct 16-06	102	65	92	161
124	Oct 18-06	119	64	101	113
126	Oct 20-06	95	62	99	149
129	Cct 23-06	77	66	121	85
131	Oct 25-06	440	83	87	50
133	Oct 27-06	471	64	91	46
136	Oct 30-06	87	66	108	50
138	Nov 01-06	74	53	58	58
140	Nov 03-06	72	41	52	34
143	Nov 06-06	68	49	133	182
145	Nov 08-06	110	110	228	315
147	Nov 10-06	94	100	187	390
150	Nov 13-06	105	79	187	223
152	Nov 15-06	96	59	131	367
154	Nov 17-06	1027	214	205	1049
157	Nov 20-06	120	176	72	938
159	Nov 22-06	111	143	101	484
161	Nov 24-06	299	374	191	747
164	Nov 27-06	985	1014	524	1678
166	Nov 29-06	106	99	193	385
168	Dec 01-06	99	120	220	201
171	Dec 04-06	120	345	411	379
173	Dec 06-06	235	376	201	359
178	Dec 11-06	116	296	333	65
180	Dec 13-06	158	238	377	78
182	Dec 15-06	147	286	453	100
185	Dec 18-06	130	188	277	117
187	Dec 20-06	105	169	514	149
189	Dec 22-06	103	985	387	137
192	Dec 25-06	80	96	538	150
194	Dec 27-06	97	227	526	297
196	Dec 29-06	88	148	519	173
199	Jan 01-07	64	46	466	102
201	Jan 03-07	52	34	664	210
203	Jan 05-07	143	72	512	124
206	Jan 08-07	118	160	546	150
208	Jan 10-07	132	140	491	173
210	Jan 12-07	67	50	466	129
213	Jan 15-07	46	25	595	100
215	Jan 17-07	33	27	651	79
217	Jan 19-07	61	39	408	120
220	Jan 22-07	76	52	471	499
222	Jan 24-07	79	61	451	371
224	Jan 26-07	150	98	478	427
227	Jan 29-07	150	63	526	283
229	Jan 31-07	135	50	401	196
231	Feb 02-07	76	41	430	96
235	Feb 06-07	54	20	567	55

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236	Feb 07-07	74	54	445	61
238	Feb 09-07	761	742	1472	1280
241	Feb 12-07	757	521	1490	1490
243	Feb 14-07	704	587	1492	1250
245	Feb 16-07	757	423	1496	1256
248	Feb 19-07	692	260	1472	1252
250	Feb 21-07	688	271	1482	1284
252	Feb 23-07	568	491	1533	1228
255	Feb 26-07	711	157	1422	1252
257	Feb 28-07	609	454	1145	1090
259	Mar 02-07	536	292	1385	1339
262	Mar 05-07	517	491	1247	1302
263	Mar 06-07	571	395	1791	1773
266	Mar 09-07	558	650	1840	1550
269	Mar 12-07	620	432	1840	1480
271	Mar 14-07	588	316	1780	1610
273	Mar 16-07	518	288	1620	1510
276	Mar 19-07	602	316	1760	1300
278	Mar 21-07	666	324	1480	1230
280	Mar 23-07	624	330	1430	1220
283	Mar 26-07	596	334	1110	1040
285	Mar 28-07	588	290	1250	1120
287	Mar 30-07	558	340	1270	1140
290	Apr 02-07	614	320	1190	1110
292	Apr 04-07	654	332	1190	1080
294	Apr 06-07	682	340	1320	1120
297	Apr 09-07	740	384	1320	1060
299	Apr 11-07	730	310	1410	930
301	Apr 13-07	744	302	1410	1210
304	Apr 16-07	734	310	1420	860
306	Apr 18-07	732	292	1340	730
308	Apr 20-07	744	632	1640	930
311	Apr 23-07	740	272	1310	960
313	Apr 25-07	724	252	1240	1030
315	Apr 27-07	714	270	1430	900
318	Apr 30-07	762	254	1210	740
320	May 02-07	764	280	1280	1410
322	May 04-07	758	328	1520	1170
325	May 07-07	738	310	1420	980
327	May 09-07	1790	1715	2010	1800
329	May 11-07	2935	2849	2382	1294
332	May 14-07	1254	667	2365	1248
334	May 16-07	2511	422	2040	1613
336	May 18-07	2516	676	2388	1465
339	May 21-07	1261	1128	2245	1487
341	May 23-07	1222	1144	2018	1935
343	May 25-07	1458	1402	2129	2018
346	May 28-07	1341	457	2105	1842
348	May 30-07	1627	583	2277	2038
350	June 01-07		322	2314	1848

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**Appendix B Effluent Suspended Solids Data [mg/L]**

<b>Day</b>	<b>Date</b>	<b>thermophilic SBR1</b>	<b>mesophilic SBR2</b>	<b>thermophilic SBR3/MABR</b>	<b>mesophilic SBR4/MABR</b>
3	19 June 2006	62.5	88.8	136	100.6
6	22 June 2006	73.8	73.2	77	49
7	23 June 2006	66.8	100.4	78.8	63.6
10	26 June 2006	66.4	56.6	78.6	66.4
13	June 29-06	83.8	73	92.2	74.2
17	July 03-06	95.4	71.4	93.2	61.4
20	July 06-06	52	49	63	62.8
24	July 10-06	206	44.2	387.4	56.2
27	July 13-06	264.2	75	335	81
31	July 17-06	261.2	75.6	226.8	60.2
34	July 20-06	196.8	50.4	243.6	46.2
38	July 24-06	221.8	41	257.6	54.8
41	July 27-06	266.6	68.8	246	52.8
45	July 31-06	251	50.8	229.4	64.2
48	Aug 03-06	261.4	102	167.8	50.2
52	Aug 07-06	223.6	205.8	179.6	36.2
55	Aug 10-06	245.4	55	138	44.8
59	Aug 14-06	236.6	34.8	155.8	53.2
62	Aug 17-06	257.4	40	151.2	52
66	Aug 21-06	173.2	36	142.8	40.4
69	Aug 24-06	120.4	33.6	187.4	33.8
73	Aug 28-06	108.6	48.4	125.8	43
76	Aug 31-06	89.2	34.4	84.2	47.2
80	Sep 04-06	230	30	242	40
83	Sep 07-07	142	32	158	36
87	Sep 11-06	98	20	134	44
90	Sep 14-06	128	38	190	70
94	Sep 18-06	712	46	356	66
96	Sep 20-06	434	48	228	60
98	sep 22-06	258	76	112	84
101	Sep 25-06	360	30	272	58
103	Sep 27-06	440	36	252	36
105	Sep 29-06	602	14	152	32
108	Oct 02-06	548	32	118	32
110	Oct 04-06	402	20	130	42
112	Oct 06-06	496	34	132	36
115	Oct 09-06	504	44	110	252
117	Oct 11-06	420	40	114	388
119	Oct 13-06	456	30	146	398
122	Oct 16-06	304	32	126	190
124	Oct 18-06	240	34	158	56
126	Oct 20-06	228	56	82	76
129	Oct 23-06	370	68	226	52
131	Oct 25-06	188	32	200	38
133	Oct 27-06	422	38	212	30
136	Oct 30-06	360	56	226	30

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138	Nov 01-06	276	94	268	38
140	Nov 03-06	144	134	238	28
143	Nov 06-06	222	158	220	42
145	Nov 08-06	124	214	348	38
147	Nov 10-06	278	212	268	86
150	Nov 13-06	256	44	152	34
152	Nov 15-06	250	74	154	48
154	Nov 17-06	264	118	118	20
157	Nov 20-06	294	260	68	30
159	Nov 22-06	432	262	86	64
161	Nov 24-06	180	68	40	64
164	Nov 27-06	308	87	86	14
166	Nov 29-06	318	92	88	38
168	Dec 01-06	286	104	74	46
171	Dec 04-06	596	410	64	48
173	Dec 06-06	884	370	68	38
178	Dec 11-06	138	332	74	42
180	Dec 13-06	176	346	74	28
182	Dec 15-06	200	408	70	40
185	Dec 18-06	222	270	76	44
187	Dec 20-06	258	210	92	38
189	Dec 22-06	214	276	86	60
192	Dec 25-06	254	100	88	44
194	Dec 27-06	340	236	92	38
196	Dec 29-06	210	90	78	26
199	Jan 01-07	202	58	80	34
201	Jan 03-07	320	68	90	38
203	Jan 05-07	240	74	116	36
206	Jan 08-07	260	98	90	48
208	Jan 10-07	210	106	102	82
210	Jan 12-07	214	78	72	46
213	Jan 15-07	230	50	72	14
215	Jan 17-07	500	48	72	54
217	Jan 19-07	278	40	68	64
220	Jan 22-07	76	32	38	36
222	Jan 24-07	128	34	56	28
224	Jan 26-07	562	72	70	56
227	Jan 29-07	282	26	80	60
229	Jan 31-07	258	30	40	30
231	Feb 02-07	468	46	76	36
235	Feb 06-07	408	28	128	34
236	Feb 07-07	506	36	146	32
238	Feb 09-07	182	126	150	82
241	Feb 12-07	122	212	144	94
243	Feb 14-07	172	194	132	132
245	Feb 16-07	160	260	138	94
248	Feb 19-07	118	72	128	80
250	Feb 21-07	146	118	174	92
252	Feb 23-07	156	150	140	82
255	Feb 26-07	118	216	98	78

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257	Feb 28-07	116	140	212	76
259	Mar 02-07	140	104	226	84
262	Mar 05-07	96	148	342	90
264	Mar 07-07	174	150	640	118
266	Mar 09-07	184	202	530	112
269	Mar 12-07	134	150	166	142
271	Mar 14-07	132	62	160	112
273	Mar 16-07	126	110	228	238
276	Mar 19-07	196	170	158	160
278	Mar 21-07	244	58	456	84
280	Mar 23-07	132	56	640	112
283	Mar 26-07	136	76	220	102
285	Mar 28-07	118	100	196	126
287	Mar 30-07	276	98	264	312
290	Apr 02-07	284	86	214	202
292	Apr 04-07	146	46	94	64
294	Apr 06-07	208	68	108	80
297	Apr 09-07	60	44	162	110
299	Apr 11-07	146	34	240	88
301	Apr 13-07	264	40	184	374
304	Apr 16-07	632	54	210	146
306	Apr 18-07	632	54	210	146
308	Apr 20-07	524	182	346	196
311	Apr 23-07	606	48	300	120
313	Apr 25-07	496	50	440	362
315	Apr 27-07	480	96	394	306
318	Apr 30-07	532	58	302	236
320	May 02-07	498	28	340	552
322	May 04-07	330	140	464	266
325	May 07-07	392	78	472	258
327	May 09-07	272	354	360	162
329	May 11-07	328	276	240	178
332	May 14-07	336	244	228	202
334	May 16-07	446	266	258	176
336	May 18-07	402	194	262	236
339	May 21-07	316	230	222	208
341	May 23-07	556	394	266	184
343	May 25-07	376	280	202	210
346	May 28-07	462	166	246	198
348	May 30-07			156	100

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**Appendix C Sludge Volume Index Data [mL/g MLSS]**

Day	Date	thermophilic SBR1	mesophilic SBR2	thermophilic SBR3	mesophilic SBR4
4	20 June 2006	263	361	379	359
7	23 June 2006	268	268	259	180
11	27 June 2006	197	242	275	167
14	June 30-06	235	246	244	258
18	July 04-06	256	182	255	139
21	July 07-06	227	111	175	129
25	July 11-06	272	118	385	140
28	July 14-06	320	86	297	181
32	July 18-06	73	53	216	137
35	July 21-06	84	56	219	135
39	July 25-06	73	36	172	101
42	July 28-06	54	32	133	89
46	Aug 01-06	47	50	127	102
49	Aug 04-06	52	29	179	74
53	Aug 08-06	47	36	183	64
56	Aug 11-06	62	27	181	51
60	Aug 15-06	110	36	149	65
63	Aug 18-06	207	43	157	76
67	Aug 22-06	199	44	202	46
70	Aug 25-06	209	47	267	50
74	Aug 29-06	181	55	260	62
77	Spt 01-06	123	62	214	50
81	Sep 05-06	187	75	234	115
84	Sep 08-06	175	111	251	134
88	Sep 12-06	204	174	278	143
91	Sep 15-06	173	153	278	139
95	Sep 19-06	396	170	130	84
98	Sep 22-06	452	116	389	55
101	Sep 25-06	842	139	707	107
103	Sep 27-06	1045	130	821	122
105	Sep 29-06	1221	158	615	155
108	Oct 2-06	1128	105	710	132
110	Oct 04-06	1185	122	655	113
112	Oct 06-06	1054	90	328	82
115	Oct 09-06	1289	84	784	94
117	Oct 11-06	1333	114	352	112
119	Oct 13-06	1031	146	400	130
122	Oct 16-06	1276	125	222	123
124	Oct 18-06	893	131	340	81
126	Oct 20-06	530	143	271	100
129	Oct 23-06	727	122	393	179
131	Oct 25-06	1042	135	440	110
133	Oct 27-06	925	118	746	124
136	Oct 30-06	1099	117	768	198

Day	Date	thermophilic SBR1	mesophilic SBR2	Day	Date	thermophilic SBR1	mesophilic SBR2
138	Nov 01-06	253	105	238	Feb 09-07	117	16
140	Nov 03-06	375	100	241	Feb 12-07	86	32
143	Nov 06-06	318	61	243	Feb 14-07	48	35
145	Nov 08-06	209	35	245	Feb 16-07	82	56
147	Nov 10-06	260	41	248	Feb 19-07	36	31
150	Nov 13-06	277	144	250	Feb 21-07	61	19
152	Nov 15-06	284	254	252	Feb 23-07	62	23
154	Nov 17-06	1124	332	255	Feb 26-07	16	35
157	Nov 20-06	318	161	257	Feb 28-07	50	36
159	Nov 22-06	424	83	259	Mar 02-07	55	42
161	Nov 24-06	793	246	262	Mar 05-07	53	300
164	Nov 27-06	818	390	264	Mar 07-07	70	142
166	Nov 29-06	333	149	266	Mar 09-07	214	185
168	Dec 01-06	251	120	269	Mar 12-07	157	71
171	Dec 04-06	189	57	271	Mar 14-07	48	63
173	Dec 06-06	237	32	273	Mar 16-07	68	43
175	Dec 08-06	214	67	276	Mar 19-07	44	26
178	Dec 11-06	495	97	278	Mar 21-07	57	32
180	Dec 13-06	325	63	280	Mar 23-07	61	25
182	Dec 15-06	212	29	283	Mar 26-07	60	35
185	Dec 18-06	950	42	285	Mar 28-07	61	37
187	Dec 20-06	410	38	287	Mar 30-07	52	31
189	Dec 22-06	720	53	290	Apr 02-07	29	33
192	Dec 25-06	1042	142	292	Apr 04-07	50	31
194	Dec 27-06	971	110	294	Apr 06-07	35	38
196	Dec 29-06	377	51	297	Apr 09-07	73	81
199	Jan 01-07	204	64	300	Apr 12-07	56	57
201	Jan 03-07	628	112	304	Apr 16-07	10	34
203	Jan 05-07	574	57	306	Apr 18-07	43	40
206	Jan 08-07	459	101	308	Apr 20-07	26	42
208	Jan 10-07	490	71	311	Apr 23-07	17	40
210	Jan 12-07	261	75	313	Apr 25-07	20	43
213	Jan 15-07	322	78	315	Apr 27-07	33	22
215	Jan 17-07	442	85	318	Apr 30-07	10	20
217	Jan 19-07	407	78	320	May 02-07	24	16
220	Jan 22-07	252	84	322	May 04-07	21	37
222	Jan 24-07	200	108	325	May 07-07	3	31
224	Jan 26-07	1087	154	327	May 09-07	31	48
227	Jan 29-07	980	223	329	May 11-07	34	42
229	Jan 31-07	1333	172	332	May 14-07	20	54
231	Feb 02-07	709	190	334	May 16-07	18	38
234	Feb 05-07	1695	112	336	May 18-07	16	42
236	Feb 07-07	161	114	339	May 21-07	17	44
				341	May 23-07	20	52
				343	May 25-07	28	47
				346	May 28-07	40	47
				348	May 30-07	41	56
				350	June 01-07	36	77

**Appendix D Mixed Liquor Suspended Solids Data [mg/L]**

Day	Date	thermophilic SBR1	mesophilic SBR2	thermophilic SBR3/MABR	mesophilic SBR4/MABR
4	20 June 2006	1750	1799	1717	1952
7	23 June 2006	1791	2013	1895	2050
11	27 June 2006	1877	2104	1745	2210
14	June 30-06	1487	2137	1555	2129
18	July 04-06	1287	1702	1215	1723
21	July 07-06	1408	1978	1546	1937
25	July 11-06	1653	2036	1558	2360
28	July 14-06	1625	2431	1786	2812
32	July 18-06	1791	2621	1763	2772
35	July 21-06	1786	2138	1623	2885
39	July 25-06	1787	2193	2154	3055
42	July 28-06	2021	1867	2099	3046
46	Aug 01-06	1713	2214	2203	2053
49	Aug 04-06	1547	2041	1729	2294
53	Aug 08-06	1713	1952	1805	2021
56	Aug 11-06	1620	1829	2153	2769
60	Aug 15-06	1271	1395	2012	2623
63	Aug 18-06	1352	1380	2295	2516
67	Aug 22-06	2256	2249	2622	2379
70	Aug 25-06	1671	2149	1984	2220
74	Aug 29-06	1768	2070	1958	1601
77	Spt 01-06	2430	2090	2480	3200
81	Sep 05-06	2350	3850	2480	4700
84	Sep 08-06	2400	4320	2110	4940
88	Sep 12-06	2110	4380	1690	5180
91	Sep 15-06	2250	4310	1800	4810
95	Sep 19-06	1390	3880	2690	3570
98	Sep 22-06	1660	3220	1930	3110
101	Sep 25-06	1140	3300	1330	3260
103	Sep 27-06	880	2470	1170	2050
105	Sep 29-06	770	3300	1560	3040
108	Oct 02-06	860	2570	1380	2430
110	Oct 04-06	810	1800	1450	2210
112	Oct 06-06	930	1770	1370	1820
115	Oct 09-06	760	1670	1250	1920
117	Oct 11-06	750	1750	1590	1690
119	Oct 13-06	970	1440	1500	1540
122	Oct 16-06	760	2080	1850	2040
124	Oct 18-06	1120	1910	1620	990
126	Oct 20-06	1810	2310	2070	2010
129	Oct 23-06	1320	2220	1780	2570
131	Oct 25-06	960	1710	1250	1450
133	Oct 27-06	1060	1870	1300	1860
136	Oct 30-06	910	2130	1250	2020
138	Nov 01-06	990	2290		
140	Nov 03-06	1200	2100		

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143	Nov 06-06	1730	1970		
145	Nov 08-06	1910	1710		
147	Nov 10-06	1730	1230	370	340
150	Nov 13-06	1880	1950	320	360
152	Nov 15-06	1480	2440	420	280
154	Nov 17-06	890	2650	90	110
157	Nov 20-06	1100	2490	70	140
159	Nov 22-06	1320	1800	250	290
161	Nov 24-06	1210	1710	120	60
164	Nov 27-06	1210	2050	210	160
166	Nov 29-06	1260	1540	200	200
168	Dec 01-06	1830	1840	150	170
171	Dec 04-06	2380	2300	190	150
173	Dec 06-06	2190	2490	80	340
175	Dec 08-06	1400	1190	150	290
178	Dec 11-06	970	1450	190	210
180	Dec 13-06	1600	860	190	260
182	Dec 15-06	1700	1750	240	310
185	Dec 18-06	1010	1190	310	30
187	Dec 20-06	1170	1600	90	240
189	Dec 22-06	1250	2270	290	270
192	Dec 25-06	960	2330	130	320
194	Dec 27-06	1030	1820	60	80
196	Dec 29-06	1380	2340	20	10
199	Jan 01-07	1520	2190	400	350
201	Jan 03-07	1560	2510	260	180
203	Jan 05-07	1220	2610	250	180
206	Jan 08-07	1220	1690	110	120
208	Jan 10-07	1430	1980	210	380
210	Jan 12-07	1530	2140	320	170
213	Jan 15-07	1460	2450	360	400
215	Jan 17-07	1470	2230	230	270
217	Jan 19-07	1230	2550	570	700
220	Jan 22-07	1390	2370	230	740
222	Jan 24-07	1800	1950	150	530
224	Jan 26-07	920	1950	140	430
227	Jan 29-07	1020	2020	210	350
229	Jan 31-07	750	2320	110	240
231	Feb 02-07	1410	2100	100	60
234	Feb 05-07	1590	1970	220	60
236	Feb 07-07	1860	1850	490	120
238	Feb 09-07	1540	3220	540	350
241	Feb 12-07	1740	1560	640	640
243	Feb 14-07	2920	2880	490	580
245	Feb 16-07	2670	3060	440	760
248	Feb 19-07	1660	2920	620	600
250	Feb 21-07	4090	2620	730	680
252	Feb 23-07	4510	2170	470	290
255	Feb 26-07	4280	2280	370	770
257	Feb 28-07	2810	3340	560	380

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259	Mar 02-07	1890	2360	500	280
262	Mar 05-07	1500	2670	590	160
264	Mar 07-07	4580	3530		440
266	Mar 09-07	2520	2050	560	670
269	Mar 12-07	3430	5330	660	270
271	Mar 14-07	3550	6400	610	400
273	Mar 16-07	3240	2560	340	340
276	Mar 19-07	5680	5710	430	430
278	Mar 21-07	4210	2510	750	230
280	Mar 23-07	4560	2810	410	250
283	Mar 26-07	3520	2850	200	500
285	Mar 28-07	3920	2450	780	490
287	Mar 30-07	3820	2540	380	600
290	Apr 02-07	1400	1530	500	580
292	Apr 04-07	1990	1910	370	620
294	Apr 06-07	3110	2110	370	460
297	Apr 09-07	1240	1110	290	570
300	Apr 12-07	1070	1580	520	580
304	Apr 16-07	3890	2900	420	850
306	Apr 18-07	2570	2620	550	190
308	Apr 20-07	3420	7140	390	380
311	Apr 23-07	2950	4950	610	390
313	Apr 25-07	1490	3640	480	460
315	Apr 27-07	1200	5670	600	830
318	Apr 30-07	3090	2510	900	710
320	May 02-07	1230	2570	530	700
322	May 04-07	1410	810	1460	610
325	May 07-07	630	1310	1410	430
327	May 09-07	980	5050	640	440
329	May 11-07	890	2380		440
332	May 14-07	1010	1670	720	390
334	May 16-07	1130	2380	1130	460
336	May 18-07	1850	3120	990	470
339	May 21-07	1780	2730	490	380
341	May 23-07	3030	4270	1120	560
343	May 25-07	2530	3860	510	450
346	May 28-07	3790	3200	680	510
348	May 30-07			780	500

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**Appendix E Mixed Liquor Suspended Solids Average Particle Diameter (d<sub>4,3</sub>) Data [μm]**

Day	Date	thermophilic SBR1	mesophilic SBR2	thermophilic SBR3/MABR	mesophilic SBR4/MABR
5	June 21-06	149.0	119.8	117.2	104.6
8	June 23-06	104.0	94.6	74.6	95.9
10	June 26-06	163.9	136.2	137.4	138.2
14	June 30-06	159.4	145	168.9	160.4
18	July 04-06	185.6	185.5	243.6	231.3
21	July 07-06	224.4	205.1	214.1	214.1
25	July 11-06	214.2	234.8	194.4	247.8
28	July 14-06	215.2	207.3	212.9	218.8
32	July 18-06	196.8	161.5	219.3	236.1
39	July 25-06	178.1	168.0	248.3	230.3
42	July 28-06	162.7	181.5	244.8	280.9
46	Aug 01-06	173.5	209.2	250.8	267.2
49	Aug 04-06	147.5	229.3	216.4	341.5
53	Aug 08-06	175.9	182.1	226.4	236.4
60	Aug 15-06	162.9	291.4	206.9	242.2
67	Aug 22-06	176.1	242.4	201.9	218.9
73	Aug 29-06	158.5	267.9	162.2	257.6
81	Sep 05-06	153.1	263.5	174.2	241.0
88	Sep 12-06	129.6	162.8	131.5	169.2
97	Sep 21-06	169.4	153.3	166.4	134.8
101	Sep 25-06	162.5	155.7	82.4	157.8
103	Sep 27-06	162.3	131.8	112.6	161.6
108	Oct 02-06	110.9	125.3	87.4	135.8
110	Oct 04-06	118.1	141.8	79.0	120.3
116	Oct 10-06	158.9	160.8	69.1	112.5
117	Oct 11-06	168.2	163.2	95.8	119.9
122	Oct 16-06	257.4	165.9	82.8	145.7
129	Oct 23-06	145.1	145	83.7	225.3
131	Oct 25-06	127.4	176.7	95.4	161.4
136	Oct 30-06	144.6	149.8	119.4	123.4
140	Nov 03-06	135.8	146.6		
145	Nov 08-06	120.5	160.4		
147	Nov 10-06	116.5	167.0		
150	Nov 13-06	141.9	158.2		
152	Nov 15-06	140.5	215.8		
157	Nov 20-06	185.5	122.1		
159	Nov 22-06	138.6	105.7		
164	Nov 27-06	157.7	152.4		

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168	Dec 01-06	141.5	126.8		
173	Dec 06-06	80.7	108.4		
180	Dec 13-06	95.8	166.8		
185	Dec 18-06	111.4	181.5		
187	Dec 20-06	114.1	169.5	171.2	191.7
203	Jan 05-07	147.8	94.3	252.5	142.1
208	Jan 10-07	161.1	98.8		117.4
210	Jan 12-07	143.3	103.6		154.2
215	Jan 17-07	160.5	101.6		130.9
217	Jan 19-07	167.1	101.4	207.7	167.6
222	Jan 24-07	150.9	106.5	109.1	140.8
224	Jan 26-07	206.4	116.1	164.1	144.7
229	Jan 31-07	180.7	131.2	304.4	271.5
231	Feb 02-07	308.9	142.2	232.9	126.5
234	Feb 05-07	211.1	144.6	255.3	193.7
238	Feb 09-07	208.3	185.6	130.9	168.8
241	Feb 12-07	175.7	177.9	231.5	165.9
245	Feb 16-07	242.7	92.9	123.4	205.7
248	Feb 19-07	272.2	109.0	85.3	218.4
250	Feb 21-07	216.5	77.1	73.1	153.7
257	Feb 28-07	168.7	83.9	126.1	216.4
259	Mar 02-07	141.0	60.4	112.6	201.1
264	Mar 07-07	123.8	72.3	96.8	214.6
266	Mar 09-07	144.8	92.8	74.9	199.2
271	Mar 14-07	140.9	104.8	128.7	303.8
273	Mar 16-07	104.3	94.3	85.4	158.1
278	Mar 21-07	65.1	59.8	179.7	181.4
280	Mar 23-07	83.5	56.6	75.5	98.1
285	Mar 28-07	72.4	47.9	99.1	210.2
287	Mar 30-07	98.1	54.1	114.4	143.4
294	Apr 06-07	67.5	46.1	92.2	146.0
300	Apr 12-07	57.1	42.7	98.1	118.2
308	Apr 20-07	71.1	83.9	186.1	93.1
315	Apr 27-07	44.2	52.9	57.0	57.6
320	May 02-07	33.4	48.0	52.8	67.1
327	May 09-07	33.0	89.0	93.6	170.3
336	May 18-07	74.2	134.9	91.5	41.8
343	May 25-07	40.8	77.7	95.3	101.3

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**Appendix F Effluent Suspended Solids Average Particle Diameter (d4,3) Data [ $\mu\text{m}$ ]**

Day	Date	thermophilic SBR1	mesophilic SBR2	thermophilic SBR3/MABR	mesophilic SBR4/MABR
3	June 21-07	167.5	112	60.8	51.3
7	June 23-07	66.5	69.2	53	73
10	June 26-07	142.1	107.3	110.5	114.1
14	June 30-07	138.5	130.2	137.7	131.6
28	July 14-06	138.4	86.2	89	170.7
35	July 21-06	186.3	168.6	234.5	211.6
38	July 24-06	99.8	95	58.1	76.7
41	July 27-06	47.3	160.1	35.2	116.3
45	July 31-06	242.2	70.2	110.5	239.7
48	Aug 03-06	10.4	63.3	169.9	258.8
52	Aug 07-06	74.6	206.7	134.2	
59	Aug 14-06	26.9		112	
73	Aug 28-06	127.7		105.6	
80	Sep 04-06	91.4		67.6	
87	Sep 11-06	116.7	113.9	112.4	52.5
98	sep 22-06	105.8	159.4	102.9	34.6
101	Sep 25-06	91	125.6	62.7	115.9
108	Oct 02-06	99.8	125.5	77.7	144.2
117	Oct 11-06	123.5	164.7	91.5	101.3
122	Oct 16-06	182.8	138.7	70.5	247.7
124	Oct 18-06	125.3	160.5	86.9	123.3
129	Oct 23-06	126.3	149.1	86.7	233
136	Oct 30-06	139.6	141.8	102.2	89.7
145	Nov 08-06	115.1	153.8	11.4	180.6
150	Nov 13-06	136.9	226.1	54.8	114.4
157	Nov 20-06	80.9	100.3	159.3	259.5
164	Nov 27-06	120.2	132.4	151.8	22.9
171	Dec 04-06	72.8	54.4	145.6	125.4
189	Dec 22-06	139.2	140.3	113.1	174.9
203	Jan 05-07	96.7	114.6	167.1	77.5
208	Jan 10-07	99.4	59.1		
210	Jan 12-07	110.9	85.8	4.4	8.1
217	Jan 19-07	142.6	80.5	67.1	143.6
224	Jan 26-07	165.3	111.7	2.6	7.6
231	Feb 02-07	290.8	149.2	244.8	191.2
235	Feb 06-07	262.7	162.1	257.1	175.8
241	Feb 12-07	290.5	57.3	36	40.6
248	Feb 19-07	183.7	40.1	158.9	2.4
259	Mar 02-07	127.5	49.1	43.9	14.9
266	Mar 09-07	137	27.9	11.2	20.6
273	Mar 16-07	16.2	79.6	84.2	65.5
280	Mar 23-07	42.8	45.5	19.9	82.1
287	Mar 30-07	35.8	42.6	51.9	90
294	Apr 06-07	54.7	40.3	5.7	78.1



301	Apr 13-07	10.6	52.5	1.4	23.7
308	Apr 20-07	3.9	10.3	9.1	88.2
315	Apr 27-07	5.3	49.1	1.2	7.1
320	May 02-07	4.9	35.4	3.4	137
327	May 09-07	15.3	15.1	7.4	8.8
336	May 18-07	12.3	42.6	93.8	88.2
343	May 25-07	72.6	77.1	125	112.5

### Appendix G ESS Zeta Potential Data [mV]

Day	Date	thermophilic SBR1	mesophilic SBR2	thermophilic SBR3/MABR	mesophilic SBR4/MABR
5	June 21-06	-8.35	-12.73	-11.2	-11.84
7	June 23-06	-5.67	-12.28	-9.74	-8.35
11	June 27-06	-14.55	-8.47	-9.57	-7.37
13	June 29-06	-9.57	-6.96	-9.67	-8.89
17	July 03-06	-8.38	-7.67	-7.76	-7.83
20	July 06-06	-13.12	-10.74	-13.09	-9.03
24	July 10-06	-11.54	-12.68	-9.6	-12.52
27	July 13-06	-10.55	-9.69	-10.52	-9.63
31	July 17-06	-7.36	-8.8	-9.27	-11.14
34	July 20-06	-10.2	-8.7	-11.31	-12.54
38	July 24-06	-8.79	-8.91	-12.6	-13.44
41	July 27-06	-10.01	-12.38	-14.41	-17.15
45	Aug 31-06	-8.93	-10.81	-14	-12.14
48	Aug 03-06	-9.42	-14.37	-15.32	-14.56
59	Aug 14-06	-10.26	-12.46	-13.45	-12.75
66	Aug 21-06	-12.32	-16.15	-12.5	-13.43
73	Aug 28-06	-11.6	-11.34	-11.96	-9.96
80	Sept 04-06	-9.24	-9.56	-13.78	-11.65
87	Sept 11-06	-12.72	-14.16	-11.48	-12.97
96	Sept 20-06	-13.29	-8.49	-10.37	-6.61
101	Sept 25-06	-11.32	-8.34	-13.07	-6.53
108	Oct 02 -06	-9.43	-10.96	-14.1	-8.52
111	Oct 10-06	-9.43	-10.99	-14.08	-8.45
122	Oct 16-06	-9.44	-6.41	-9.29	-11.66
129	Oct 23-06	-11.38	-9.95	-13.66	-11.26
136	Oct 30-06	-12.01	-11.33	-10.24	-9.74
145	Nov 08-06	-9.3	-11.95	-9.8	-12.75
150	Nov 13-06	-9.49	-11.83	-9.23	-11.38
157	Nov 20-06	-10.56	-14.72	-9.33	-11.95
164	Nov 27-06	-4.29	-6.32	-5.22	-7.49
172	Dec 05-06	-7.87		-11.83	-13.25
180	Dec 13-06	-9.66		-11.74	-11.48
185	Dec 18-06	-7.61	-8.41	-5.59	-7.61

189	Dec 22-06	-6.47	-7.86	-5.8	-6.63
207	Jan 07-07	-8.79	-12.49	-11.74	-11.64
210	Jan 12-07	-7.74	-14.26	-13.39	-13.83
217	Jan 19-07	-8.56	-12.63	-11.93	-14.43
224	Jan 26-07	-15.16	-14.2	-5.7	-10.57
231	Feb 02-07	-9.45	-9.21	-11.94	-10.71
234	Feb 05-07	-8.41	-15.15	-11.54	-7.69
241	Feb 12-07	-13.54	-15.75	-24.14	-16.04
248	Feb 19-07	-15.45	-11.77	-14.58	-14.23
259	Mar 02-07	-9.6	-10.35	-10.39	-11.3
266	Mar 09-07	-12.45	-12.6	-10.98	-13.7
273	Mar 16-07	-8.22	-13.9	-10.75	-9.2
280	Mar 23-07	-12.56	-11.98	-8.9	-11.26
287	Mar 30-07	-12.51	-12.47	-11.69	-14.38
294	Apr 06-07	-21.62	-14.69	-23.63	-28.12
301	Apr 13-07	-23.59	-16.81	-21.98	-33.74
308	Apr 20-07	-18.29	-20.61	-21.41	-21.17
315	Apr 27-07	-23.55	-18.4	-25.85	-26.26
320	May 02-07	-19.59	-11.43	-9.97	-15.38
327	May 09-07	-17.32	-22.56	-19.41	-20.81
336	May 18-07	-21.93	-25.44	-25.01	-28.54
343	May 25-07	-26.6	-24.87	-21.42	-25.12

### Appendix H Dissolved Oxygen (DO) Concentration Data [mg/L]

#### 1. DO concentration during Jan 07-07 operational cycle (Synthetic wastewater HRT=12 Hours)

minutes	Date	thermophilic SBR	mesophilic SBR	thermophilic MABR	mesophilic MABR
0	Jan 07-07-c1	2.3	6.8	0.4	1.8
90	Jan 07-07-c2	2.4	4.1	0.2	0.6
180	Jan 07-07-c3	1.6	6.8	0.2	0.4
270	Jan 07-07-c4	2.4	5.6	0.2	1.1
360	Jan 07-07-c5	1.9	5.5	0.2	0.3
450	Jan 07-07-c6	2.3	5.6	0.2	0.3
540	Jan 07-07-c7	2.2	5.7	0.2	0.3
650	Jan 07-07-c8	2.3	6.1	0.2	5.1

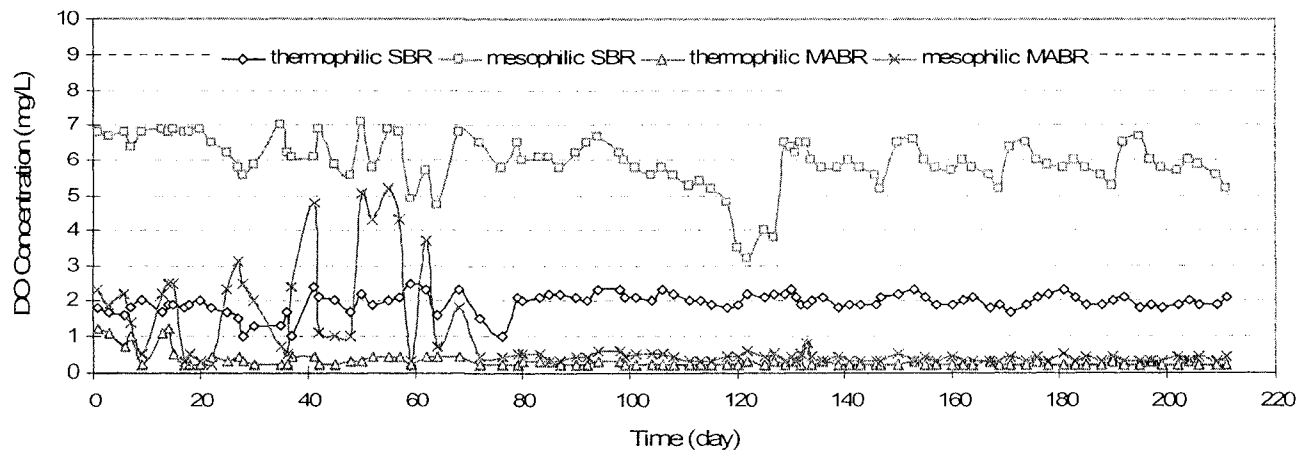
## 2. DO concentration during Jan 18-07 operational cycle (Synthetic wastewater HRT=12 Hours)

minutes	Date	thermophilic SBR	mesophilic SBR	thermophilic MABR	mesophilic MABR
0	Jan -18-c1	2.4	3.2	0.6	0.5
90	Jan -18-c2	1.3	6.1	0.3	4.5
180	Jan -18-c3	1.4	5.8	0.3	0.4
270	Jan -18-c4	1.6	6.4	0.2	0.3
360	Jan -18-c5	1.7	6.2	0.2	0.4
450	Jan -18-c6	2.5	6.1	0.2	0.2
540	Jan -18-c7	2.4	6.4	0.2	0.3
650	Jan -18-c8	2.3	6.7	0.2	0.4

## 3. DO concentration during March 06-07 operational cycle (Real wastewater HRT=12 Hours)

minutes	Date	thermophilic SBR	mesophilic SBR	thermophilic MABR	mesophilic MABR
0	Mar -06-c1	3.0	6.8	0.5	0.6
90	Mar -06-c2	2.5	5.4	0.2	0.3
180	Mar -06-c3	1.7	5.4	0.2	0.3
270	Mar -06-c4	2.2	5.5	0.2	0.3
360	Mar -06-c5	2.4	5.6	0.2	0.3
450	Mar -06-c6	2.6	6.5	0.2	0.3
540	Mar -06-c7	3.2	6.5	0.2	0.3
650	Mar -06-c8	3.1	6.5	0.2	0.3

## 4. The graph of DO concentration versus operational time after the membrane was put in SBR



## 5. DO concentration [mg/L] after the membrane was put in SBR

Date	Day (since using the membrane)	thermophilic SBR	mesophilic SBR	thermophilic MABR	mesophilic MABR
Nov 01-06	1	1.8	6.8	1.2	2.3
Nov 03-06	3	1.7	6.7	1.1	1.9
Nov 06-06	6	1.6	6.8	0.7	2.2
Nov 07-06	7	1.8	6.4	1.0	1.4
Nov 09-06	9	2.0	6.8	0.2	0.5
Nov 13-06	13	1.7	6.9	1.1	2.2
Nov 14-06	14	1.9	6.8	1.2	2.5
Nov 15-06	15	1.9	6.9	0.5	2.5
Nov 17-06	17	1.8	6.8	0.2	0.3
Nov 18-06	18	1.9	6.8	0.2	0.5
Nov 20-06	20	2.0	6.9	0.2	0.3
Nov 22-06	22	1.8	6.5	0.4	0.2
Nov 25-06	25	1.7	6.2	0.3	2.3
Nov 27-06	27	1.5	5.8	0.4	3.1
Nov 28-06	28	1.0	5.6	0.3	2.5
Nov 30-06	30	1.3	5.9	0.2	2
Dec 05-06	35	1.3	7.0	0.2	0.7
Dec 06-06	36	1.7	6.2	0.2	0.5
Dec 07-06	37	1.0	6.1	0.4	2.4
Dec 11-06	41	2.4	6.1	0.4	4.8
Dec 12-06	42	2.1	6.9	0.2	1.1
Dec 15-06	45	2.0	5.9	0.2	1
Dec 18-06	48	1.7	5.6	0.3	1
Dec 20-06	50	2.2	7.1	0.3	5.1
Dec 22-06	52	1.9	5.8	0.4	4.3
Dec 25-06	55	2.0	6.9	0.4	5.2
Dec 27-06	57	2.1	6.8	0.4	4.3
Dec 29-06	59	2.5	4.9	0.2	0.3
Jan 01-07	62	2.3	5.7	0.4	3.7
Jan 03-07	64	1.6	4.7	0.4	0.7
Jan 07-07	68	2.3	6.8	0.4	1.8
Jan 11-07	72	1.5	6.5	0.2	0.4
Jan 15-07	76	1.0	5.8	0.2	0.4
Jan 18-07	79	2.1	6.5	0.2	0.5
Jan 19-07	80	2.0	6.0	0.3	0.5
Jan 22-07	83	2.1	6.1	0.3	0.5
Jan 24-07	85	2.2	6.1	0.3	0.3
Jan 26-07	87	2.2	5.8	0.2	0.3
Jan 29-07	90	2.1	6.2	0.2	0.4

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Jan 31-07	92	2.0	6.5	0.2	0.4
Feb 02-07	94	2.3	6.7	0.3	0.6
Feb 06-07	98	2.3	6.2	0.3	0.6
Feb 07-07	99	2.1	6.0	0.2	0.4
Feb 09-07	101	2.1	5.8	0.2	0.5
Feb 12-07	104	2.0	5.6	0.2	0.5
Feb 14-07	106	2.3	5.8	0.2	0.5
Feb 16-07	108	2.2	5.6	0.2	0.4
Feb 19-07	111	2.0	5.3	0.2	0.3
Feb 21-07	113	2.0	5.4	0.2	0.3
Feb 23-07	115	1.9	5.2	0.2	0.3
Feb 26-07	118	1.8	4.8	0.2	0.4
Feb 28-07	120	1.9	3.5	0.2	0.4
Mar 02-07	122	2.2	3.2	0.3	0.6
Mar 05-07	125	2.1	4.0	0.2	0.4
Mar 07-07	127	2.2	3.8	0.3	0.5
Mar 09-07	129	2.2	6.5	0.2	0.3
Mar 10-07	130	2.3	6.4	0.3	0.4
Mar 11-07	131	2.1	6.2	0.3	0.3
Mar 12-07	132	1.9	6.5	0.2	0.5
Mar 13-07	133	1.9	6.5	0.8	0.8
Mar 14-07	134	2.0	6.0	0.2	0.4
Mar 16-07	136	2.1	5.8	0.3	0.3
Mar 19-07	139	1.8	5.8	0.2	0.4
Mar 21-07	141	1.9	6.0	0.2	0.3
Mar 23-07	143	1.9	5.8	0.2	0.3
Mar 26-07	146	1.9	5.6	0.2	0.3
Mar 27-07	147	2.1	5.2	0.2	0.3
Mar 30-07	150	2.2	6.5	0.2	0.5
Apr 02-07	153	2.3	6.6	0.3	0.3
Apr 04-07	155	2.1	6.0	0.2	0.4
Apr 06-07	157	1.9	5.8	0.2	0.3
Apr 09-07	160	1.9	5.7	0.2	0.4
Apr 11-07	162	2.0	6.0	0.2	0.3
Apr 13-07	164	2.1	5.8	0.2	0.3
Apr 16-07	167	1.8	5.6	0.3	0.3
Apr 18-07	169	1.9	5.2	0.2	0.3
Apr 20-07	171	1.7	6.4	0.2	0.4
Apr 23-07	174	1.9	6.5	0.2	0.3
Apr 25-07	176	2.1	6.0	0.3	0.4
Apr 27-07	178	2.2	5.9	0.2	0.3
Apr 30-07	181	2.3	5.8	0.2	0.5
May 02-07	183	2.1	6.0	0.2	0.3
May 04-07	185	1.9	5.8	0.2	0.4
May 07-07	188	1.9	5.6	0.2	0.3

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May 09-07	190	2.0	5.3	0.3	0.4
May 11-07	192	2.1	6.5	0.2	0.3
May 14-07	195	1.8	6.7	0.2	0.3
May 16-07	197	1.9	6.0	0.3	0.3
May 18-07	199	1.8	5.8	0.2	0.3
May 21-07	202	1.9	5.7	0.2	0.4
May 23-07	204	2.0	6	0.3	0.3
May 25-07	206	1.9	5.9	0.2	0.4
May 28-07	209	1.9	5.6	0.2	0.3
May 30-07	211	2.1	5.2	0.2	0.4

\* About 2700 microscopical pictures, which are not included in this appendix, were observed and taken with a light microscope (Olympus, BH2-RFCA) and recorded in a computer to investigate the morphology of activated sludge flocs.