Anaerobic membrane bioreactor for the treatment of low strength wastewater

by

Jae Ho Ho

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Co-majors: Civil Engineering; Biorenewable Resources and Technology

Program of Study Committee:
Shihwu Sung, Major Professor
Robert C. Brown
Say-Kee Ong
Hans van Leeuwen
Samir K. Khanal

Iowa State University

Ames, Iowa

2007

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ABSTRACT

This research investigated the fundamentals of anaerobic membrane bioreactor (AMBR) operated at low trans-membrane pressure (TMP) and cross-flow velocity (CFV) using poly-tetrafluoroethylene (PTFE) membrane for the treatment of low strength wastewater.

Specific methanogenic activity (SMA) test was used to examine the methanogenic activity profiles of suspended and attached sludge in AMBR treating synthetic municipal wastewater at 25 and 15°C. It was hypothesized that accumulated biomass on the membrane surface could act as a secondary membrane as well as a biofilm which removed chemical oxygen demand (COD) biologically. The results showed that attached sludge on the membrane surface had lower activity than suspended sludge. Attached sludge on the membrane surface contained less extractable extracellular polymeric substance (EPS), especially protein content, than the suspended sludge, which could be related to the decreased methanogenic activity. Membrane in AMBR system is likely not only to retain all biomass in the reactor, but also complement decreased biological removal efficiency by rejecting soluble organics.

AMBR was operated at COD loading rates of 1-2 $kg/m^3 \cdot d$ for 280 days. Permeate TCOD concentration was always less than 40 mg/L, and no noticeable volatile fatty acids (VFAs) were detected regardless of hydraulic retention time (HRT) variations, while soluble COD was accumulated in the reactor at lower HRT. The particle size reduction was relatively less than other studies reported even after long operation time due to the low operation CFV. Approximately 30% of COD was not recovered as methane irrespective of applied HRTs, due to the COD loss by dissolved methane, sulfate reduction. The observed

methane yield was 0.21 to 0.22 CH_4/g $COD_{removed}$ regardless of the applied HRTs due to the COD loss by dissolved methane and sulfate reduction.

The filtration characteristics of anaerobic sludge suspension containing different solid contents were investigated. The initial rapid flux decline was in good agreement with standard blocking filtration law, while the latter gentle flux decline was attributable to the cake filtration law, which represented a Class II type dynamic membrane. The highest pseudo-steady state flux and lowest normalized flux reduction were observed at TS concentration of 13-17 g/L, Particles are likely to act as agglomerated particles by a bridging effect through particle-particle interactions at concentrated TS levels. However, the lower particle concentration does not necessarily yield the higher flux due to the internal fouling by dispersed particles. Moreover, the higher particle concentration also caused a gradual deterioration in flux due to the severe cake fouling. The increased CFV influenced the pseudo-state flux more significantly at low or high TS concentration. Anaerobic sludge suspension which had been filtered previously at CFV of 0.1-0.7 m/s had a lower flux than fresh anaerobic sludge suspension at the same CFV, because the higher shear force increased the concentration of soluble microbial product (SMP) and decreased the mean particle size in anaerobic sludge suspension. The extractable EPS content in anaerobic sludge, however, was not changed regardless of applied CFV.

CHAPTER 1. GENERAL INTRODUCTION

Introduction

The anaerobic treatment of low strength wastewaters, such as domestic sewage, has started to attract much attention, which at present is largely treated by aerobic processes. Two major factors are of concern with the activated sludge process, high sludge production and high operating cost associated with aeration. Anaerobic treatment offers many inherent benefits compared to aerobic treatment such as low energy consumption, low sludge production, and useful methane production. However, high biomass inventory and long hydraulic and solids retention times (SRT) are needed to achieve efficient treatment, particularly for low strength wastewater due to low biomass yield. In addition, the effluent quality of anaerobic system is poorer than the aerobic one. These limitations have prevented a wide application of anaerobic technology for treating such wastewater. Therefore, different strategies have been developed to achieve long SRT in the reactor such as anaerobic contact process, anaerobic filter, upflow anaerobic sludge blanket (UASB) reactor, expanded granular sludge bed (EGSB), anaerobic fluidized bed reactor and anaerobic sequencing batch reactor. Such reactor configurations maintain significantly longer SRT irrespective of hydraulic retention time (HRT). The UASB and EGSB processes have been widely adopted among all these reactor configurations due to their superior performance. However, those systems require meticulous process control to achieve and maintain sludge granulation.

Anaerobic membrane bioreactor (AMBR) has gained more interest to cope with treatment challenges. AMBR could essentially retain all the biomass in the reactor without the danger of wash-out irrespective of HRT. However, AMBR has not been widely used due to several critical limitations such as expensive membrane material and operational cost, high fouling potential and filtration characteristics of anaerobic broth. Currently, most membrane bioreactor research is focused on aerobic membrane bioreactor (MBR) which has several unique advantages in terms of operational issues. Air scouring can effectively retard membrane fouling by particle or biomass accumulation at the membrane surface and aerobic sludge tends to agglomerate and form large floc which contributes less pore clogging. Thus, there are two major challenges: flux or fouling control and cost effectiveness of AMBR.

As a solution, cost effective membranes and membrane systems were investigated. Non-woven fabric filter made of polypropylene has a relatively large pore size and is mostly used for pore clogging filtration due to the low cost, especially for low suspension and for cake filtration. Actual filtration occurs in the fouling layer, either inside of fabric or on the cake layer formed on the top of the fabric. In this case, the secondary membrane, which is formed after particle clogging and deposition is more important in terms of flux stabilization and permeate quality. This research developed a cost-effective AMBR system and investigated the fundamentals of the AMBR for the treatment of low strength wastewater including module configuration, membrane fouling, microbial activity dynamics, and reactor performance at ambient temperature.

Background

Anaerobic digestion

Although anaerobic digestion is a mature technology, it is still an ideal and attractive treatment for waste or wastewater. Application of aerobic treatment is restricted by organic loading rate due to the low oxygen transfer rate and associated with high sludge production.

Thus, anaerobic digestion has been employed at most municipal sludge treatment facilities and high strength wastewater treatment plants because it allows high loading rates and produces a valuable energy source, methane, which can be used to generate heat or electricity. However, it has been believed that anaerobic treatment is only beneficial to treat high strength wastewater due to its poor effluent quality and solid-liquid separation. Eckenfelder *et al*. (1988) found that anaerobic treatment would be economic at high strength wastewater which contains more than 1,000 mg BOD/L. However, warm climate would make it more economic in terms of maintenance of operation temperature. Jewell (1985) insisted that development of a suitable anaerobic sewage technology would be an epoch-making progress in wastewater treatment. Thus, there has been a lot of effort to develop efficient anaerobic processes to treat low strength wastewater. Several processes have been developed to alleviate these problems, which include anaerobic contact process, anaerobic filter, anaerobic fluidized bed, upflow anaerobic sludge blanket, and expanded granular sludge bed (Rittmann and McCarty, 2001). These processes involve some unique technology such as sludge granulation, packed bed, and an internal or external solid-liquid separator to retain enough biomass in the reactor and enhance solid-liquid separation. UASB and EGSB have been given much attention for sewage treatment. Lettinga (1995) asserted that EGSB would be a sustainable alternative for a high rate anaerobic process under psychrophilic conditions due to its very high substrate affinity. There are several full scale anaerobic treatment plants in tropical countries like India, Colombia, and Brazil. However, COD and BOD removal efficiency is not as good as lab scale results (Seghezzo *et al*., 1998). Thus, in most cases, anaerobic treatment is followed by another polishing step such as a trickling filter or stabilization pond. Membrane coupled anaerobic digestion has been limited to treatment of high strength wastewater such as wine distillation wastewater, because membrane processes are too expensive to treat non profit making wastewater. Several researchers have tried to develop a cost effective membrane using low cost material such as non-woven filters. Muhammad *et al*. (1996) tested 20-40 μm polyester woven fiber for secondary effluent and settled sewage. The results showed that the flux was 10 L/m^2/hr at 280 mg/L of settled sewage for couple of hours and 30 L/m^2/hr for secondary effluent. Pillay *et al*. (1994) investigated woven fiber coupled to an anaerobic digester. They tried limestone pre-coating on the surface to enhance flux and got 50 L/m^2/hr at 2 m/s of CFV, 200 kPa of TMP, and 1.8 % of MLSS concentration. It ran successfully for a relatively long period without cleaning. Nomura *et al*. (1997) used PTFE as skin layer on the ceramic membrane. They found that PTFE membrane showed superior performance due to the hydrophobic nature.

Membrane fouling

Membrane is a material through which some substance can pass selectively, resulting in a separation process (Judd and Jefferson, 2003). Membrane has been considered the most effective separation technology and has extended its application from medical equipment to wastewater treatment. Since the early 1990s, there has been a rapid growth of the membrane market and a corresponding decrease in membrane cost (Judd and Jefferson, 2003). Although membrane bioreactors (MBRs) have become more popular for the treatment of municipal or industrial wastewater, membrane fouling is still a major obstacle to wide spread use of MBRs. AMBR is more susceptible to fouling than aerobic, which is the main reason why AMBR has not been widely applied in wastewater treatment. The fouling phenomena are very complex and very different in each case. There are many variables which affect membrane fouling such as concentration, pH, temperature, trans-membrane pressure, and cross flow velocity. Membrane fouling results from physicochemical interactions between membrane material and particles or solutes in the liquid. The main reactions are adsorption and precipitation. Membrane fouling is classified to organic and inorganic fouling according to what the fouling material is. In general, organic fouling results from particle adsorption or deposition on or into the membrane and inorganic membrane fouling is caused by the precipitation of inorganic materials such as struvite and calcium carbonate. Membrane fouling is also divided into reversible and irreversible fouling according to flux recovery after cleaning. Reversible fouling is easily removed by suitable physical cleaning methods depending on the strength of adhesion. However, irreversible fouling is only removed by chemical cleaning. Thus, there are two strategies to minimize membrane fouling. One is operation cleaning by regular or irregular short term back flushing with or without chemicals. The other is recovery cleaning by long term cleaning with chemicals. There are many chemicals for membrane cleaning. Sodium hypoclorite and citric acids are widely used for organic and inorganic fouling control, respectively.

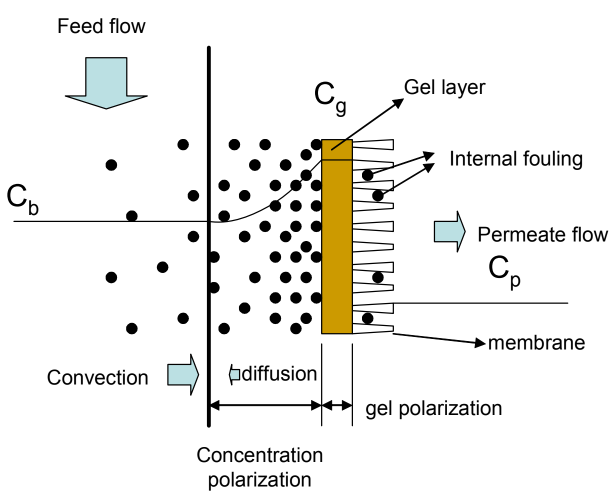


Figure 1. Fouling in crossflow membrane

Flux and Resistance

Flux decline is inevitable phenomena and the most important parameter in membrane process. Flux decline is strongly related to the membrane fouling which results in reduction of active filtration area by membrane pore blocking and particle deposition. A cake filtration equation which is derived from Darcy's law has been widely used to describe membrane flux. Flux increases in proportion to the applied trans-membrane pressure and reciprocal proportion to liquid's viscosity and total fouling resistance.

$$J = \frac{\Delta P}{\mu \cdot R_t}$$

Where J : flux ($L \cdot T^{-1}$, m/sec)

ΔP: trans-membrane pressure ($M \cdot L^{-1} \cdot T^{-2}$, N/m^2)

μ: dynamic viscosity ($M \cdot L^{-1} \cdot T^{-1}$, $N \cdot sec/m^2$)

R_t: total membrane resistance (L^{-1}, m^{-1})

Total resistance can be determined by resistance-in-series model (Choo and Lee, 1998).

$R_t = R_m + R_g + R_i$

Where R_m: intrinsic membrane resistance

R_g: cake resistance

R_i: internal fouling resistance

Reference

Choo, K.H., and Lee, C.H. (1998) Hydrodynamic behavior of anaerobic biosolids during crossflow filtration in the membrane anaerobic bioreactor. *Wat. Res*. 32, 3387-3397.

Eckenfelder, W.W., Patoczka, J.B., and Pulliam, G.W. (1988) Anaerobic versus aerobic treatment in the USA. *IWAPRC*, 105-114.

Jewell, W.J. (1985) The development of anaerobic wastewater treatment. *Proc. Seminar/Workshop on Anaerobic Treatment of Sewage*, Amherst, USA, 17-54.

Judd, S., and Jefferson, B. (2003) Membranes for industrial wastewater recovery and reuse. Elsevier Science Ltd., UK.

Lettinga, G. (1995) Anaerobic digestion and wastewater treatment systems. *Antonie van Leeuwenhoek*, 67, 3-28.

Muhammad, H., Al-Malack, and Anderson, G.K. (1997) Use of crossflow microfiltration in wastewater treatment. *Wat. Res*., 31, 3064-3071.

Nomura, T., Fujii, T., and Suzuki, M. (1997) Application of the ceramic membrane with hydrophobic skin layer to separation of activated sludge. *Wat. Sci. Tech*., 35, 137-144.

Pillay, V.L., Townsend, B., and Buckley, C.A. (1994) Improving the performance of anaerobic digesters at wastewater treatment works: The coupled cross-flow microfiltration/digester process. *Wat. Sci. Tech*., 30, 329-337.

Rittmann, B.E. and McCarty, P.L. (2001) Environmental Biotechnology: Principles and Applications. McGraw-Hill Book Co. Inc., New York, USA.

Seghezzo, L., Zeeman, G., van Lier, J.B., Hamelers, H.V.M., and Lettinga, G. (1998) A review: The anaerobic treatment of sewage in UASB and EGSB reactors. *Bioresource Tech*., 65, 175-190.

CHAPTER 2. PERFORMANCE EVALUATION OF ANAEROBIC MEMBRANE BIOREACTORS TREATING LOW STRENGTH WASTEWATER

A paper to be submitted to the Journal of Membrane Science

Jaeho Ho, Samir Kumar Khanal, Shihwu Sung*

Abstract

Anaerobic reactors coupled with non-woven filters with different pore sizes were investigated to determine their applicability for treating low strength synthetic wastewater. This study primarily focused on developing an anaerobic membrane bioreactor (AMBR) system that could be operated at low transmembrane pressure (TMP) and cross flow velocity (CFV) using cost effective membrane materials such as non-woven filter. Two different module configurations namely, outside-to-in and inside-to-out flow filtration modules, were compared with respect to both membrane and bioreactor performances. Even though outside-to-in module facilitated easier cleaning of membrane surface, inside-to-out flow module was better in terms of TMP and CFV control. It is hypothesized that the formation of thin cake layer on the porous medium (e.g., non-woven filter) acted as a dynamic membrane. Thus, the capturing of thin sludge cake on the non-woven fabric matrix formed a secondary membrane system equivalent to a commercial membrane. The rough nature of non-woven filter surface, however, caused pore clogging, resulting severe decline in flux. The permeate quality improved as the cake became dense with filtration time. Poly-tetrafluoroethylene (PTFE) laminated non-woven filter enhanced the filtration performance by both improving the flux and minimizing the propensity of cake fouling. An anaerobic reactor coupled with PTFE laminated membrane was operated continuously during the experiment at CFV of 0.1 to 0.2 m/sec and TMP of 6.9 to 20 kPa. Although about a month of acclimation period was required to reach a steady state, the effluent chemical oxygen demand, volatile fatty acids and suspended solids concentrations were below 30, 20 and 10 mg/L, respectively, during continuous 90-day operation with intermittent back washing at every 4 to 10 days.

Keywords: Anaerobic membrane bioreactor (AMBR), fouling, low strength wastewater, non-woven filter, poly-tetrafluoroethylene (PTFE)

Introduction

The development of submersible membrane bioreactor (MBR) system using coarse bubble aeration and material improvement significantly reduced the operational cost, and MBRs are now becoming increasingly popular for wastewater treatment [1,2]. There are a number of full scale MBR systems currently in operation worldwide [3]. Although MBR systems are increasingly employed for municipal and industrial wastewater treatments, anaerobic membrane bioreactors (AMBRs) also have the potential to treat such wastewater due to several inherent merits, including less sludge production, potential for bioenergy generation (for high strength wastewater), and saving in aeration energy cost. The application of AMBR for low strength wastewater treatment, such as municipal wastewater, has been limited due to several issues. Firstly, AMBR should adopt a membrane in an external circuit for easy maintenance, although submersible membrane modules commonly adopted for MBR are more compact and consume less energy than external membrane module; secondly, low strength wastewater does not produce enough biogas to heat the digester; and thirdly, AMBR is more susceptible to fouling than the aerobic MBR [4]. Membrane fouling is considered to be one of the major impediments to the successful development of AMBR. Fouling depends on several factors, including types of membrane, biomass characteristics and concentrations, and membrane operating conditions [5]. The cake resistance is regarded as a primary component of total resistance in an MBR system [6]. Although cake accumulation on the membrane surface can be ameliorated by controlling the cross flow velocity (CFV), particle deposition is inevitable even at high CFVs. In addition, high CFV may also cause loss in microbial activity due to shear stress. Therefore, shear stress control to mitigate membrane fouling and to maintain microbial activity is key issue to the successful operation of an AMBR system.

Cost of membrane is another major factor governing the operating cost of an AMBR system [7]. The use of low cost membrane will abate the capital and operating costs of AMBR. Non-woven filter is a low cost membrane with a relatively large pore size and is mostly used for pore clogging filtration [8]. It is a random, entangled and multi-layer assembly of fibers. Actual filtration occurs in the fouling layer, either inside of fabric or on the cake layer formed on the top of the fabric. A secondary membrane formed following particle clogging and deposition is more important to obtain stable flux stabilization and better permeate quality. The characteristics of non-woven filter can be modified by lamination usually with a poly-tetrafluoroethylene (PTFE) film [9]. Recently, several researchers tried to develop cost effective membranes using low cost materials such as woven or non-woven filters for both MBR and AMBR [7, 10-14]. Pillay *et al*. [11] used flexible woven fiber precoated with limestone suspension to decouple the solids retention time (SRT) and the hydraulic retention time (HRT) in order to improve the performance of anaerobic digesters. Hernandez *et al*. [12] investigated a granular sludge inoculated AMBR using immersed filtration cartridges employed with coarse polypropylene and fiber glass. Several studies used non-woven filter as an alternative membrane material for MBR studies without any surface modification [7,13,14]. These studies suggested that woven or non-woven filter with a relatively large pore size could be used for MBR studies. However, surface modification would be required, particularly in a AMBR due to the more dispersed growth of anaerobic sludge compared to flocculated sludge in an activated sludge process. Based on these premises, the goals of this research were to develop a cost effective AMBR system using relatively large pore size non-woven filter for treating low strength wastewater at room temperature and to examine the fouling mechanism in a non-woven filter.

Materials and Methods

Anaerobic membrane bioreactor (AMBR) set-up

Two completely stirred anaerobic reactors (Bioflow 2000 fermentor, New Brunswick Scientific, NJ, USA) of 4 L working volume were used. Outside-to-in and inside-to-out flow separation modules of non-woven filter were coupled to each anaerobic reactor as shown in Figure 1 (a) and (b) to examine the effect of membrane configuration on AMBR performance. Cross flow was applied over the surface of the filter to avoid excess cake deposition in both filter modules. Air-powered double-diaphragm pump (Sandpiper II, Warren Rupp Inc, OH, USA) and peristaltic pump (MasterFlex I/P variable-speed drive, Cole-Parmer Instrument Co., IL, USA) were used as a recirculation pump for outside-to-in and inside-to-out modules, respectively. Following the module configuration experiments, both reactors were coupled to inside-to-out flow membranes to evaluate the effects of filter materials on AMBR performance. The filter employed in the outside-to-in flow configuration was made-up of polypropylene with pore size of 25 µm and filtration surface area of 0.05 m^2. Non-woven filter made of polypropylene with pore size of 25 and 12 µm and thin film PTFE laminated non-woven filter with pore size of 10 µm were used in inside-to-out flow modules. Four single modules with total filtration area of 0.06 m^2 were connected in series. Back flushing and mechanical cleaning were carried out to restore the flux. No chemical cleaning was attempted during the entire experiment. The characteristics of the membranes are given in Table 1. The anaerobic reactors were equipped with pH and oxidation-reduction potential (ORP) monitoring units (pH2100, Mettler Toledo, Germany), and level sensor to control permeate rate. The AMBRs were maintained at 25±1°C using heating and cooling loops.

AMBR start-up and operation

The seed sludge was obtained from secondary anaerobic digester of a local municipal wastewater treatment plant. The total solids (TS) concentration of the anaerobic sludge ranged from 30 to 36 g/L after sieving to remove debris. The seed sludge was diluted with tap water to achieve a TS level of 10,000 mg/L in the reactor. The influent was continuously fed into the reactors by peristaltic pump (MasterFlex, Cole-Parmer Instrument Co., IL, USA). During the start-up, the HRT was maintained at 48 h and then decreased to 24 h for the module configuration and membrane material tests. The HRT was controlled at 18 h during the AMBR performance evaluation experiment. No sludge was withdrawn during the entire experiment except for measurement of solid concentration.

Synthetic wastewater

Low to medium strength synthetic wastewater was prepared to represent a typical municipal wastewater. The characteristics of the prepared wastewater were modified from that of Syntho, which was developed to represent a pre-settled domestic wastewater [15]. The characteristics of synthetic wastewater are presented in Table 2. The synthetic wastewater used in this research did not have particulate matters, but contain soluble and colloidal matters. The major component of chemical oxygen demand (COD) was non-fat dry milk (NFDM). The properties of NFDM and required trace elements can be found elsewhere [16]. Synthetic wastewater was prepared every alternate day and stored at a 4°C storage room to minimize biodegradation.

Chemical analyses

Total volatile fatty acids (VFA), COD, suspended solids (SS), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were determined as per Standard Methods [17]. A wet-test gas meter (Schlumberger Industries, Dordrecht, The Netherlands) was used to measure the biogas production rate. Gas composition was analyzed using Gas Chromatography (Series 350, GOW-MAC Co., NJ, USA). The microscopic observation of the filter surface was carried out using a scanning electron microscope (SEM, Hitachi S2460-N, Hitachi, Japan).

Flux and cake resistance

A filtration equation, which is based on Darcy's law, has been widely used to describe the membrane flux. Flux increases in direct proportion to the applied TMP and inversely proportion to the liquid viscosity and total fouling resistance. Total resistance was calculated by using the following equation.

$$J = \frac{\Delta P}{\mu \cdot R_t}$$

where, J is the flux ($L \cdot T^{-1}$, m/sec); ΔP is the TMP ($M \cdot L^{-1} \cdot T^{-2}$, N/m^2); μ is the dynamic viscosity ($M \cdot L^{-1} \cdot T^{-1}$, $N \cdot sec/m^2$); R_t is the total membrane resistance (L^{-1}, m^{-1}). Permeate flow rate was manually measured using a graduated cylinder and a stop watch. The sludge cake density was measured in g TS per unit filter surface area. The cake resistance of anaerobic sludge at different sludge densities and TMPs was determined. Known amount of fresh anaerobic sludge cake (e.g., 3.9, 7.7, 11.6, and 15.4 g/m^2) was obtained on GF/C filter (Watman, Germany) with pore size of 1.2 μm, and then different pressures of 20.7, 34.5, 48.3, and 62.1 kPa were applied.

Results and Discussion

Cake resistance on porous medium

The pure water flux of sludge cake accumulated on the glass fiber filter was measured to quantify sludge cake resistance. The pure water flux test on anaerobic sludge cake showed that the flux increased with TMP under a given sludge cake density (Figure 2a). A physical limitation of sludge cake density to maintain a uniform layer and sustain the TMP of 20.7 kPa was determined to be 3.85 g/m^2. The sludge cake was loosely held at 3.85 g/m^2 of sludge cake density due to poor development of cake layer. Therefore, it was not possible to apply pressure higher than 20.7 kPa. The highest and the lowest pure water fluxes were 70 $L/m^2/h$ at TMP of 62.1 kPa and cake densities of 3.85 g/m^2, and 3 $L/m^2/h$ at TMP of 20.7 kPa and cake density of 15.4 g/m^2, respectively. The sludge cake on porous medium still showed a good flux potential at low sludge cake density, that is 44 and 28 L/m^2/hr at TMP of 20.7 kPa and cake density of 3.85 g/m^2 and 7.7 g/m^2, respectively. Thus, sludge cake layer, which acts as secondary membrane, with cake captured either inside or on the surface of non-woven filter could substitute for the membrane in a commercial membrane system. Figure 2 (b) shows the anaerobic sludge resistance at different sludge densities and TMPs. The cake resistance remained nearly constant at 3.3×10^{12} and 8.0×10^{12} m^{-1} in spite of TMP variation at sludge cake density of 7.7 and 11.55 g/m^2, respectively. On which sludge densities, the flux was directly proportional to the applied TMP. The resistance, however, decreased with increase in TMP at higher sludge cake of 15.4 g/m^2, which suggested that high TMP is required at denser cake.

Module configurations

Two lab-scale CSTRs coupled with different types of external separation modules using non-woven filter, outside-to-in and inside-to-out filtration, were operated. The results showed that inside-to-out flow configuration had a better performance in terms of low CFV and TMP as presented in Figure 3. The outside-to-in flow module operated at TMP of 85 kPa and CFV of 0.8 m/s, resulted a flux of 2.5 L/m^2/h after 6 days of continuous operation, while out-to-inside flow module needed a lower TMP (~ 24 kPa) and CFV (~ 0.1 m/s) to obtain a flux of 4.5 L/m^2/h. Although the CFV was relatively high, pore clogging occurred rapidly by finer sludge particles. Therefore, the TMP of outside-to-in flow module was gradually increased right after the start. From operational standpoint, the outside-to-in configuration module is preferable due to easy clean-up. The inside-to-out flow module, however, is desirable due to better flux even at lower TMP and CFV.

Due to pore clogging and severe cake fouling, the back flushing with permeate was not effective to restore the flux in an outside-to-in module. Thus, mechanical cleaning using brush was tried on Day 13, which led to regain in flux to its original level (Figure 3a). Consequently, mechanical cleaning was carried out at every 2 to 3-day interval to maintain flux higher than 3.5 $L/m^2/h$. After 30 days of operation, cake fouling on the non-woven filter surface was measured. The amount of cake on the non-woven filter surface of the outside-to-in flow module was approximately 55 g TS/m^2. The major components of cake in the fouled membrane surface appeared to be extracellular polymeric substances (EPS) and microbial mass, which served as a secondary membrane. This conclusion was drawn based on VS/TS ratio of the cake, which was in the range of 0.81 to 0.84, instead of 0.60 in the anaerobic reactor mixed liquor. On the other hand, inside-to-out flow module was continuously operated for nearly 35 days without back flushing. The TMP varied from 6.9 to 34 kPa and CFV was fixed at 0.1 m/s to maintain the flux of 3.5 $L/m^2/h$. Low CFV was applied to develop thin cake layer on the membrane surface.

It is important to point out that shear stress on the membrane surface associated with CFV is important to control fouling. However, higher shear stress may also cause loss in microbial activity [18]. Table 3 summarizes the results of AMBRs operation for these two configurations. Both configurations were able to remove nearly all COD and SS from mixed liquor. The COD and SS concentrations in the inside-to-out flow module were 26.9 ± 9.1 and 7.8 ± 3.1 mg/L, respectively; while for the outside-to-in flow module, the respective concentrations were 32.7 ± 9.7 and 14.8 ± 6.4 mg/L, respectively. High CFV and TMP associated with the outside-to-in flow module resulted slightly higher permeate COD and SS concentrations compared to the inside-to-out flow module.

Dynamic membrane can be divided into Classes 1, 2 and 3 [19], based on particle and pore sizes. According to this classification, the secondary membrane developed in this research falls into Class 2, which occurs when the pore size of membrane is larger than the particle size. Short initial pore filling is followed by thin cake deposition. Therefore, it is essential to operate AMBR at low CFV and TMP, especially during the start-up period due to the relatively large pore size. Specific cake resistance of AMBR was determined by simple cake filtration equation which is derived from Darcy's filtration equation.

$$\frac{t}{V} = \frac{\alpha \mu c}{2A^2 \Delta P} V + \frac{\mu R}{A \Delta P}$$

where t is the filtration time (s); V is the cumulative volume of permeate (L^3, m^3); α is the specific cake resistance ($L \cdot M^{-1}$, $m \cdot kg^{-1}$); μ is the dynamic viscosity ($M \cdot L^{-1} \cdot T^{-1}$, Pa·sec); c is the concentration of solids in the suspension ($M \cdot L^{-3}$, $kg \cdot m^{-3}$); A is the membrane surface (L^2, m^2); ΔP is the TMP ($M \cdot L^{-1} \cdot T^{-2}$, Pa); and R is the membrane resistance (L^{-1}, m^{-1}).

The specific cake resistance (α) was determined by plotting t/V against V (data not shown here). The alpha values of the inside-to-out and outside-to-in modules were 2×10^{13} and 7.6×10^{13} $m \cdot kg^{-1}$, respectively. The alpha value of the outside-to-in module was slightly higher than that of the inside-to-out flow module due to high TMP, which resulted in the formation of the dense cake layer. These values are higher than that of aerobic sludge but lower than the anaerobic sludge compared to other research as shown in Table 4. Lower porosity of anaerobic sludge cake, resulting from smaller sludge particles in comparison to aerobic sludge, might have led to higher cake resistance. This result suggests that the operation of AMBR under low TMP with a thin sludge cake layer as a secondary membrane could result in relatively lower sludge cake resistance. The rough nature of non-woven filter surface, however, caused more biomass deposition on the surface (Figure 4). Even after the mechanical cleaning, the inner part of the non-woven fabric was still clogged. Thus, surface modification is essential to reduce bio-fouling and to enhance the filtration performance.

Comparison of PTFE membrane and non-woven filter

The PTFE laminated non-woven filter was compared with non-woven filters. Permeate quality was investigated at TMP of 3.4 kPa and CFV of 0.1 m/s. As shown in Figure 5 (a), permeate SS concentration was related to the pore size. Initial permeate SS concentrations were 150, 40 and 20 mg/L for 25 and 12 μm pore size non-woven filter, and 10 μm pore size PTFE laminated non-woven filter, respectively. After one day of operation, however, the permeate SS reached nearly the same level due to the formation of a secondary membrane. This suggests that non-woven filter, which has a larger pore size than the sludge particles, could be used as a separation medium following the development of a secondary membrane. In field application, it requires a meticulous control strategy to develop a secondary membrane.

Although non-woven filter with large pore sizes such as 25 to 100 μm has been used in MBRs [7,13,14], such large pore size filter can not be employed in AMBR due to the smaller size of anaerobic sludge. Figure 5 (b) shows the flux decline profiles of the non-woven filters and the PTFE laminated non-woven filter for a short-term test. One PTFE laminated non-woven filter was pre-wetted using methanol to overcome the hydrophobic characteristics and the other one was not pretreated with methanol to investigate the effect on hydrophobicity on membrane flux. The hydrophobic characteristic caused a lower flux in the beginning, but it increased gradually and eventually overcome after 5 hours of operation. Large pore size did not necessarily yield a higher flux. As shown in Figure 5 (b), non-woven filter with 12 μm of pore size showed higher flux than 25 μm. The PTFE laminated non-woven filter showed less tendency of biomass deposition on the surface compared to the non-woven filter. The biomass depositions on the non-woven filter with and without PTFE lamination after 90 hours of filtration were 4.6 and 11 g/m^2, respectively.

The surface texture of both materials was investigated through SEM. Figure 6 shows SEM images of a non-woven filter and a PTFE laminated non-woven filter. As apparent from the figure, the nature of non-woven filter surface appears to be the governing factor affecting cake deposition. The rough surface without PTFE lamination was easier to retain biomass. The flux decline profile of both membranes showed a similar trend. However, after mechanical cleaning, PTFE had a higher flux than non-woven filter due to a reduced cake fouling layer. Even though the equivalent pore sizes of both filters were nearly the same, the pore pathways were somewhat different. The actual pore size of non-woven filter would be larger than the measured nominal pore size due to the tortuous passage of non-woven filter by several fiber layers. Even after mechanical brushing, the entangled fabric of non-woven filter was clogged as shown in Figure 4 (c). Figure 7 shows the permeability profile for a long-term flux test. The permeability of PTFE laminated non-woven filter reached 0.4 to 0.5 L/m^2/h/kPa. On the other hand, non-woven filter had a permeability of 0.2 to 0.4 L/m^2/h for 12 μm pore size filter and 0.15 to 0.2 L/m^2/h for 25 μm filter. The performance of the PTFE laminated non-woven filter was superior to the non-woven filter with better flux and less occurrence of cake fouling.

AMBR performance

AMBR coupled with PTFE laminated non-woven filter was operated at HRT of 18 and temperature of 25°C. Influent COD was kept constant at 500 mg/L in Run 1, while the feed COD was increased to 1,000 mg/L in Run 2. The flux and TMP variations during the operation are shown in Figure 8(a). Once the flux declined below 5 $L/m^2/h$, back flushing using permeate was carried out to restore the flux. Backwashing was carried out using permeate at every 4 to 10 days depending on the flux decline and TMP increase. Total volume of permeate used for backwashing was about 500 ml which was less than 10% of total daily filtration volume. The flux was immediately restored after the back flushing and remained fairly constant at 5 $L/m^2/h$ after one day of operation. Initial CFV after back flushing was 0.1 m/s for one day afterwards it increased to 0.2 m/s. It was, however, possible to achieve a constant flux of 5 $L/m^2/h$ at TMP of 6.9 kPa for more than 50 days in a continuous AMBR operation. After 53 days, a gradual increase in TMP was needed to maintain a constant flux. One point interested as shown in Figure 8(b) is that both permeability and total resistance gradually improved until 50 days. Influent COD may be the possible cause because the permeability decreased as the influent COD increased. Seed sludge contained about 250 mg/L of soluble COD, while the effluent COD was around 30 mg/L at a steady state operation. The permeability improved as the effluent COD became stable. Although, the effluent COD reached lower than 30 mg/L even at higher influent COD of 1,000 mg/L, the permeability declined gradually. Several researchers reported that soluble substance in reactor was associated with flux decline [24, 25]. Wisniewski and Grasmick [25] found that half of the total resistance resulted from the soluble compounds in the reactor. Thus, it may be inferred that increased organic loading rate would result in permeability decline due to the increased SS, colloidal and dissolved matters in the reactor. Further research is needed to evaluate an optimal operating HRT with respect to both reactor and membrane performances.

Table 5 presents the results of AMBR operation at HRT of 18 h and temperature of 25°C. Influent alkalinity was slightly higher than the alkalinity stated in the recipe of synthetic municipal wastewater, because the wastewater was prepared using tap water which contained additional alkalinity. Although the permeate COD and VFA in Run 2 were slightly higher than Run 1, COD and VFA concentrations were less than 30 and 20 mg/L, respectively, at a steady performance of operation. Effluent SS concentration was always lower than 10 mg/L. Maintenance of complete anaerobic condition was not possible in the lab-scale AMBR, because the permeate side was exposed to the atmosphere, which allowed air to contact with the retentate stream. This might be a reason why the nitrogen content in the gas phase was higher than expected. Methane content was 56.3 and 76.4 % at Runs 1 and 2, respectively. Average methane yield ranged from 0.13 to 0.27 m^3 CH_4/kg $COD_{removed}$, which was lower than the theoretical value. One possible reason could be consumption of part of organic carbon for sulfate reduction; since the influent contained 70 to 90 mg/L of sulfate. No sludge was withdrawn during the experiment except for measurement of solid concentration. Initial MLSS and MLVSS concentrations were 9,650 and 5,900 mg/L, respectively. After 90 days of operation, the MLSS and MLVSS concentrations reached 15,900 and 10,600 mg/L, respectively. The synthetic wastewater used in this research did not contain particulate matters. It was obvious that the increase in MLSS concentration was resulted from the microbial growth. Table 6 summarizes the performance of the AMBR with PTFE laminated non-woven filter under this study and other similar studies reported in literature. The observed total resistance was lower than other AMBR studies [27, 28]. Choo and Lee [28] reported significant decrease in MLVSS concentration due to high shear stress from recirculation pump. The authors also found that significant amount of biomass was accumulated within the membrane system. The AMBR used in this research was operated at lower TMP and CFV compared to other studies, which could somewhat compensate for the low flux.

Conclusions

The results obtained in this research demonstrated that inside-to-out flow configuration module with PTFE laminated non-woven filter could be an alternative for microfiltration membrane. Non-woven filter with large pore size did not yield high flux due to severe pore clogging. PTFE lamination on the non-woven filter surface, however, enhanced the filtration performance by improving flux and minimizing the propensity of cake fouling. Completely stirred anaerobic reactor coupled with PTFE laminated non-woven filter was operated successfully to treat synthetic municipal wastewater at an HRT of 18 h and temperature of 25°C without sludge withdrawal. The effluent COD, VFA, and SS concentrations were below 30, 20 and 10 mg/L, respectively, during 90 days of operation with intermittent back washing. Low CFV and TMP were applied to reduce operation cost as well as to minimize shear stress. Therefore, thin anaerobic sludge cake accumulated on the PTFE laminated non-woven filter acted as a dynamic membrane. These secondary membranes improved permeate quality, even though the membrane pore size was larger than sludge particle size. Class 2 type of secondary membrane cake captured inside of the non-woven fabric matrix and accumulated on the PTFE membrane surface could substitute for the membrane and cake in the commercial membrane system.

References

[1] K. Yamamoto, M. Hiasa, T. Mahmood, and T. Matsuo, Direct solid-liquid separation using hollow fiber membrane in an activated sludge aeration tank, *Wat. Sci. Technol*., 21 (1989) 43-54.

[2] S. Judd, and B. Jefferson, Membranes for industrial wastewater recovery and reuse. Elsevier Science Ltd., UK., 2003.

[3] R. S. Trussell, S. Adham and R. R. Trussell, Process limits of municipal wastewater treatment with the submerged membrane bioreactor, *J. Environ. Engr*., 131 (2005) 410-416.

[4] K-H. Choo, I-J. kang, S-H. Yoon, H. Park, J-H. Kim, S. Adiya and C-H. Lee, Approachs to membrane fouling control in anaerobic membrane bioreactors, *Wat. Sci. Technol*., 41 (2000) 363-371.

[5] I.-S. Chang, P. L. Clech, B. Jefferson, and S. Judd, Membrane fouling in membrane bioreactors for wastewater treatment. *J. Environ.Engr*., 128 (2002), 1018-1029.

[6] Choo, K.H. and Lee, C.H. (1996) Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor. *Wat. Res*., 30, 1771-1780.

[7] I.-S. Chang, M. Gander, B. Jefferson and S. J. Judd, Low-cost membranes for use in asubmerged MBR, *Trans IChemE*, 79 (2001), 183-188.

[8] N. P. Cheremisinoff, Liquid Filtration, Butterworth-Heinemann, Massachusetts, USA, 1998.

[9] A. Rushton, A. S. Ward, and R. G. Holdich, Solid-liquid filtration and separation technology, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1996.

[10] H. Muhammad, Al-Malack, and G. K. Anderson, Use of crossflow microfiltration in wastewater treatment. *Wat. Res*., 31 (1997), 3064-3071.

[11] V. L. Pillay, B. Townsend, and C. A. Buckley, Improving the performance of anaerobic digesters at wastewater treatment works: The coupled cross-flow microfiltration/digester process. *Wat. Sci. Tech*., 30 (1994), 329-337.

[12] A. E. Hernandez, L. C. Belalcazar, M. S. Rodriguez and E. Giraldo, Retention of granular sludge at high hydraulic loading rates in an anaerobic membrane bioreactor with immersed, *Wat. Sci. Tech*., 45 (2002), 169-174.

[13] G. T. Seo, B. H. Moon, T. S. Lee, T. J. Lim, and I. S. Kim, Non-woven fabric filter separation activated sludge reactor for domestic wastewater reclamation. *Wat. Sci. Tech*., 47 (2003), 133-138.

[14] M. R. Alavi Moghaddam, Y. Guan, H. Satoh and T. Mino, Performance and microbial dynamics in the coarse pore filtration activated sludge process at different SRTs, *Wat. Sci. Tech*., 47 (2003), 73-80.

[15] I. Nopens, C. Capalozza, and P. A. Vanrolleghem, Technical Report: Stability analysis of a systematic municipal wastewater. Dept. Applied Mathematics, Biometrics and Process Control, Universiteit Gent, Gent, Belgium, 2001.

[16] R. R. Dague, G. C. Banik, and T. G. Ellis, Anaerobic sequencing batch reactor treatment of dilute wastewater at psychrophilic temperatures. *Wat. Environ. Res*., 70 (1998), 155-160.

[17] American Public Health Association/American Water Works Association/Water Environmental Federation, Standard Methods for the Examination of Water and Wastewater, 20th edn,, Washington DC, USA, 1998.

[18] M. Brockmann and C. F. Seyfried, Sludge activity and cross-flow microfiltration - A non-beneficial relationship, *Wat. Sci. Tech*., 34 (1996), 205-213.

[19] J. Murkes, C. G. Carsson, Crossflow Filtration. John Wiley & Sons, UK, 1998.

[20] K. H. Choo, and C. H. Lee, Hydrodynamic behavior of anaerobic biosolids during crossflow filtration in the membrane anaerobic bioreactor. *Wat. Res*. 32 (1998), 3387-3397.

[21] H. park, K. H. Choo and C. H. Lee, Flux enhancement with powdered activated carbon addition in the membrane anaerobic bioreactor, *Sep. Sci. Technol*., 34 (1999), 2781-2792.

[22] J. Lee, W. Y. Ahn and C. K., Lee, Comparison of the filtration characteristics between attached and suspended growth microorganisms in submerged membrane bioreactor, *Wat. Res*., 35 (2001), 2435-2445.

[23] J.S. Kim, C. H. Lee and H. D. Chun, Comparison of ultrafiltration characteristics between activated sludge and BAC sludge, *Wat. Res*., 32 (1998), 3443-3451.

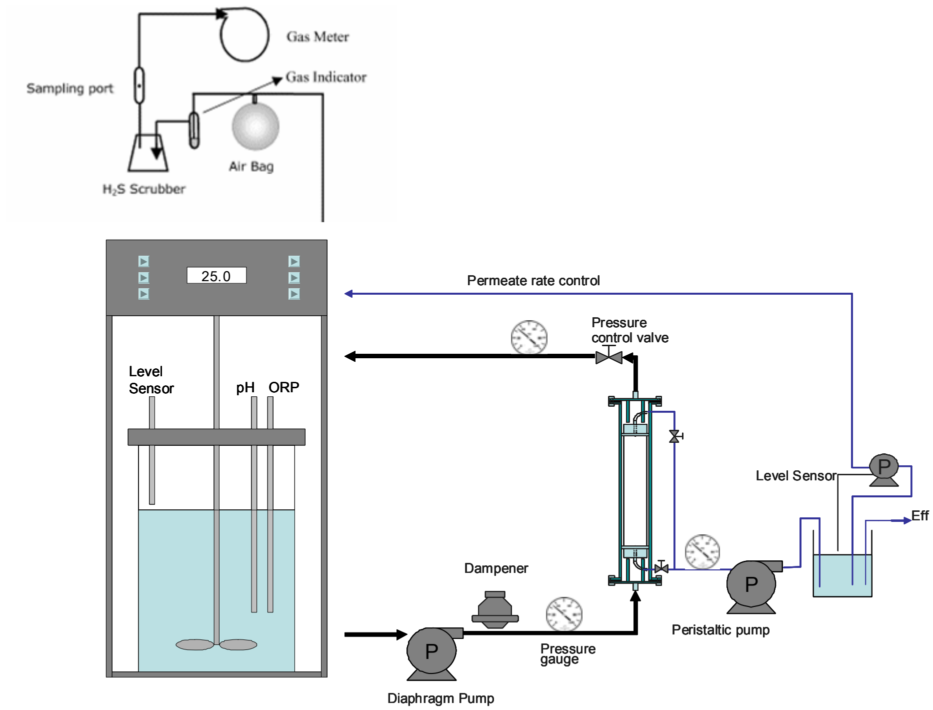
[24] H. Harada, K. Momonoi, S. Yamazaki and S. Takizawa, Application of anaerobic UF membrane reactor for treatment of a wastewater containing high strength particulate organics, *Wat. Sci. Tech*., 30 (1994), 307-319.

[25] C. Wisniewski, and A. Grasmick, Floc size distribution in a membrane bioreactor and consequences for membrane fouling, *Colloids and Surfaces A*, 138 (1998) 403-411.

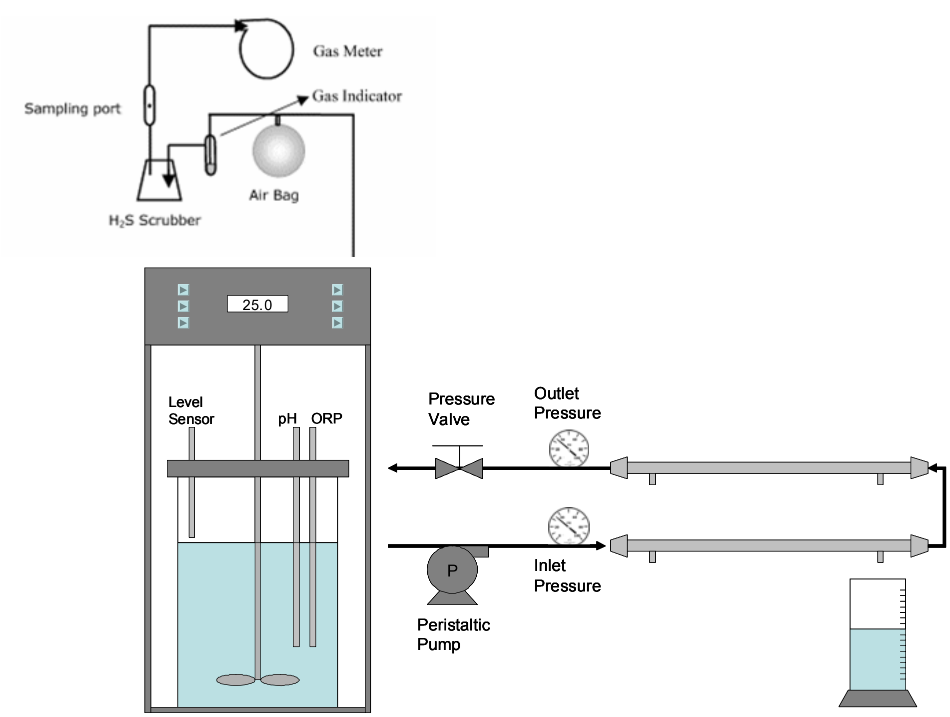
[26] S. Elmaleh, and L. Abdelmoumni, Cross-flow filtration of an anaerobic methanogenic suspension. *J. Mem. Sci*., 131 (1997), 261-274.

[27] J. Zhang, S. Padmasiri, M. Fitch, L. Raskin, and E. Morgenroth, Membrane fouling in anaerobic membrane bioreactor (AMBR) treating swine manure. Proceeding on WEFTEC 04; 77th annual technical exhibition and conference, New Orleans, Louisiana USA, 2004.

[28] K.-H. Choo, and C.-H. Lee, Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor, *Wat. Res.*, 30 (1996), 1771-1780.

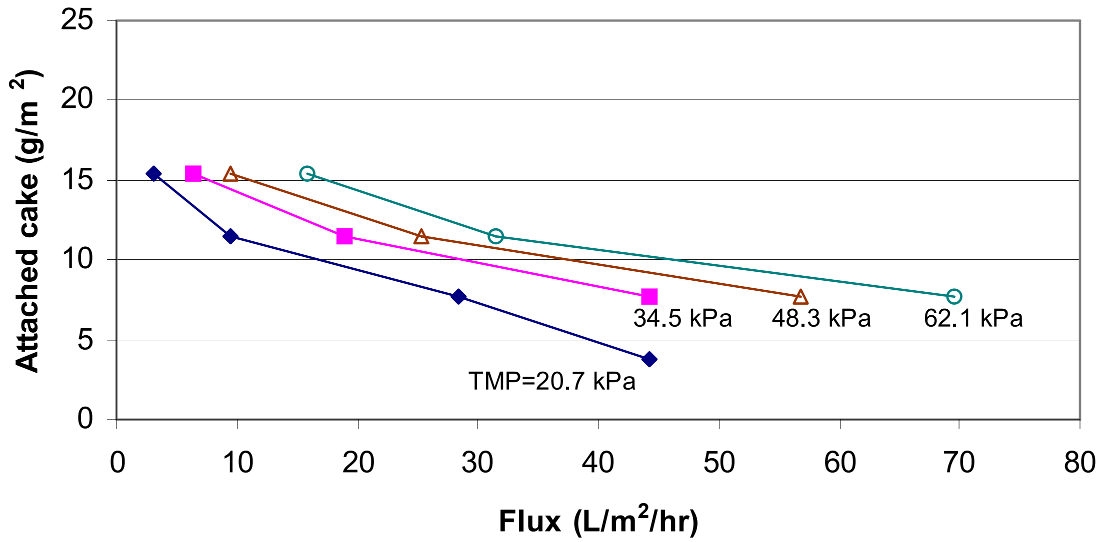


(a) AMBR coupled with outside-to-in flow separation module

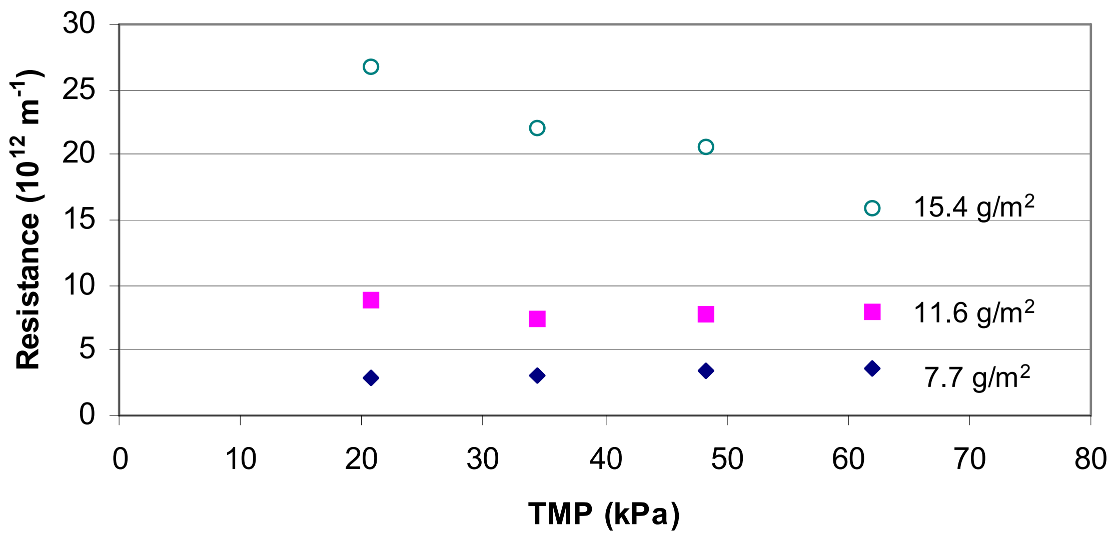


(b) AMBR coupled with inside-to-out flow separation module

Figure 2-1 Experimental set-up of AMBRs

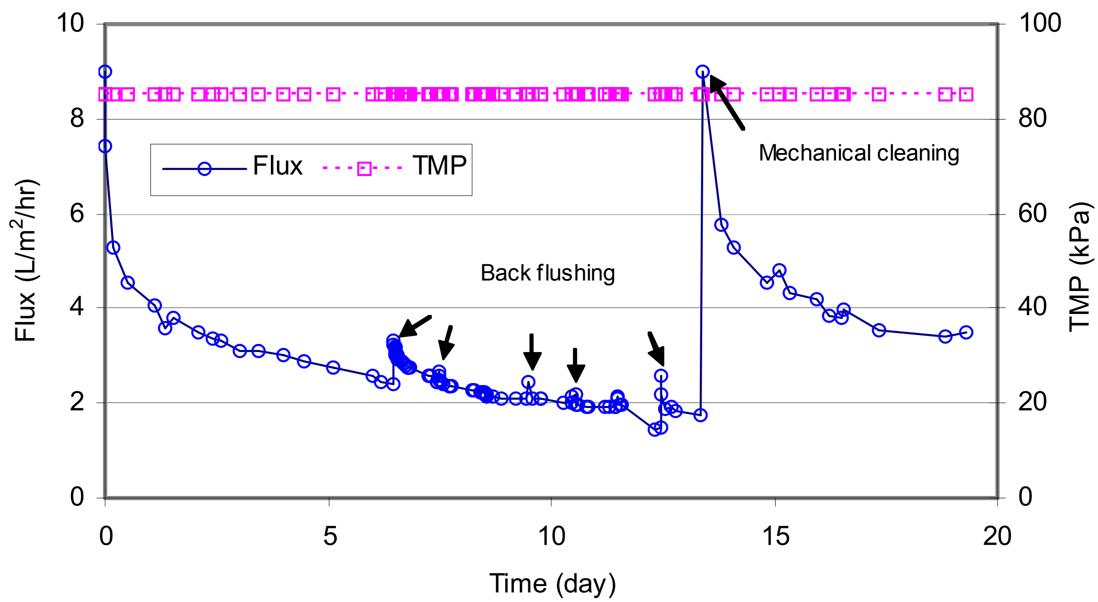


(a) Flux

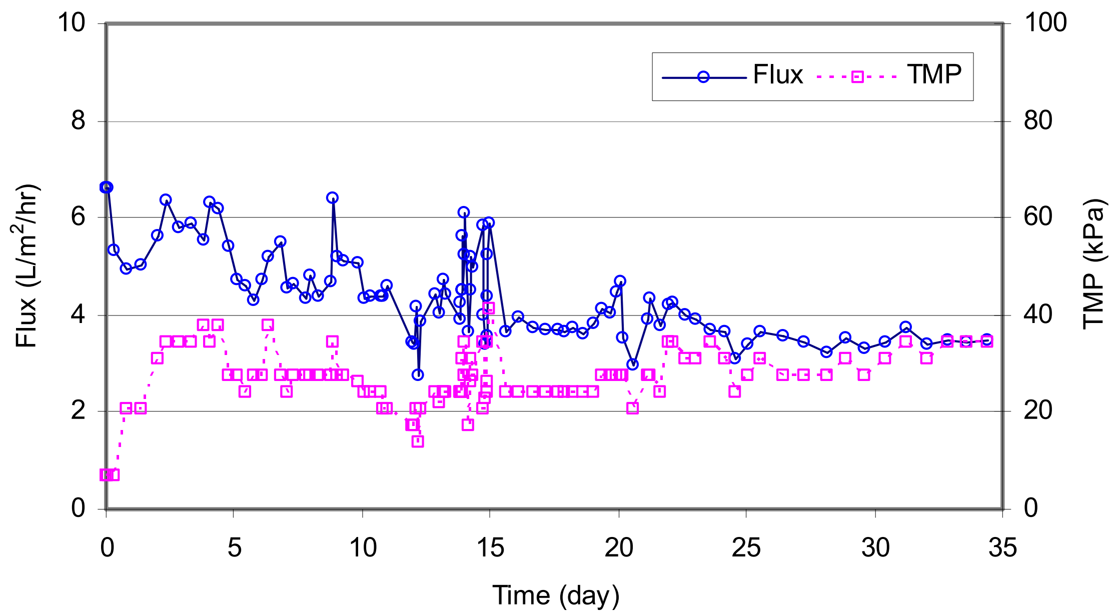


(b) Cake resistance

Figure 2-2 Flux and cake resistance at different cake density and TMP

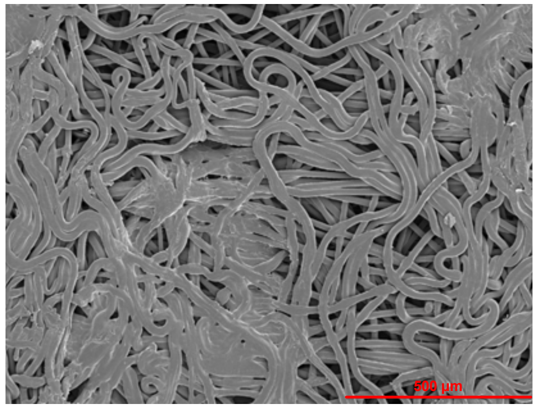


(a) Outside-to-in flow module

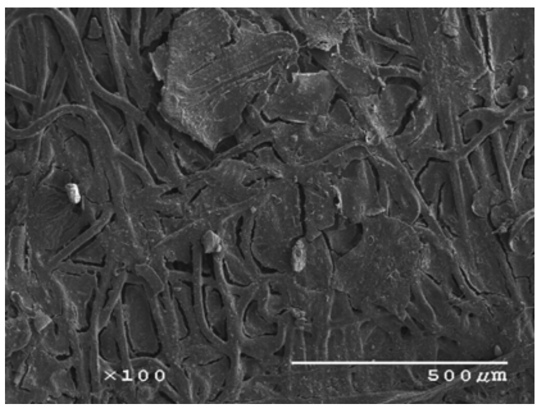


(b) Inside-to-out flow module

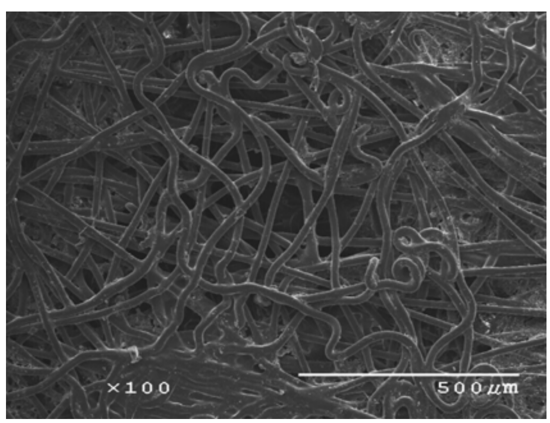
Figure 2-3 Flux declines of non-woven filters



(a) Before use

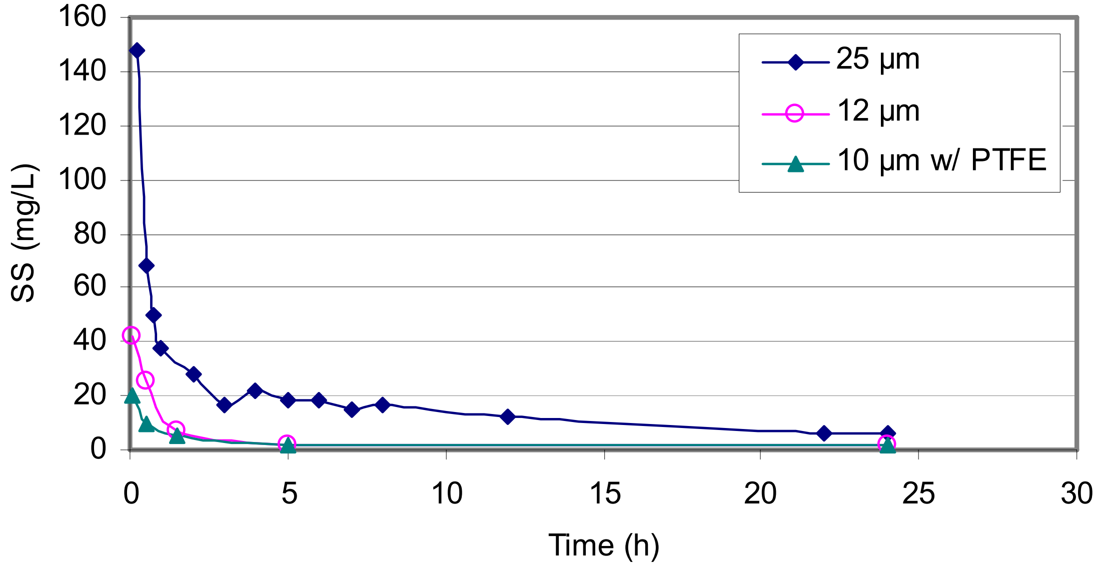


(b) Cake fouled surface

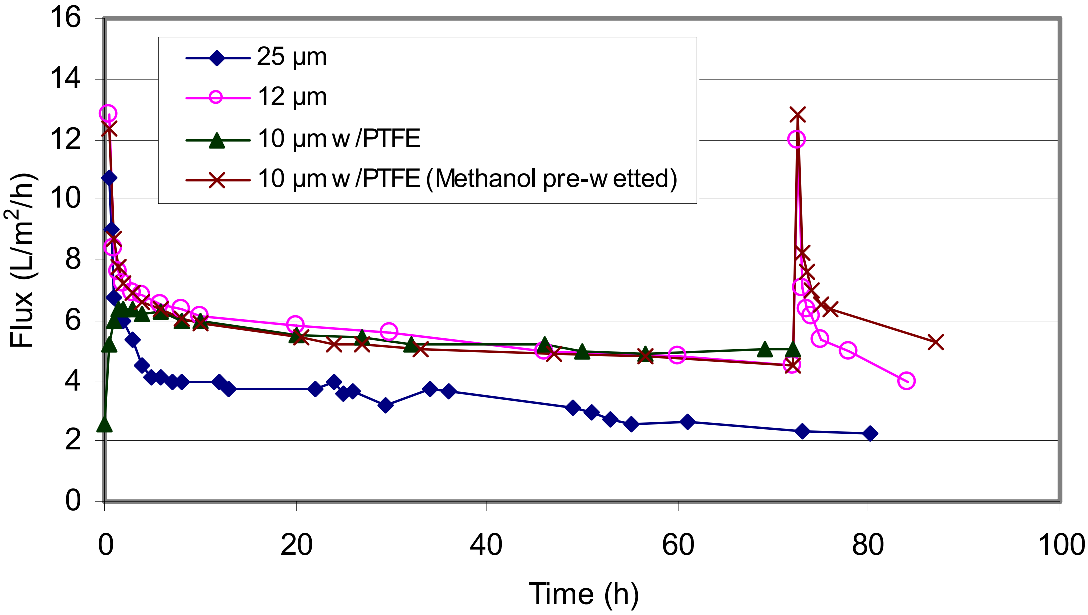


(c) After mechanical cleaning

Figure 2-4 Scanning electron micrographs of non-woven filter with 25 μm pore size

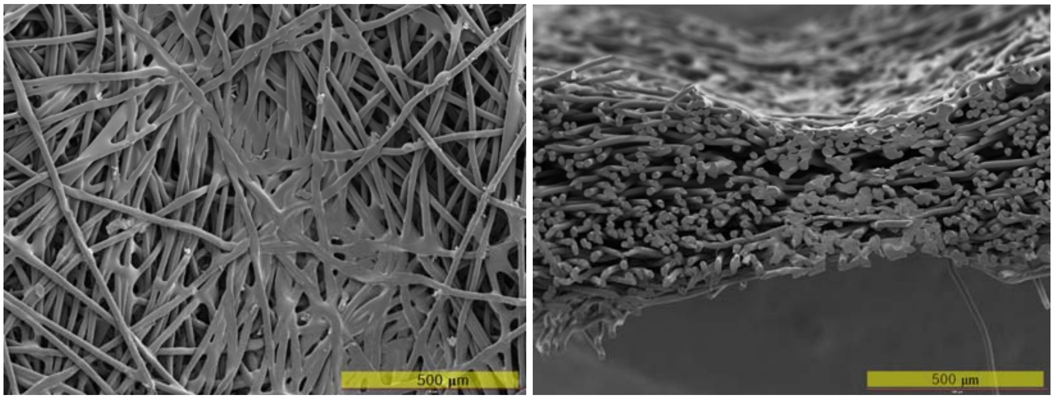


(a) Permeate SS concentration

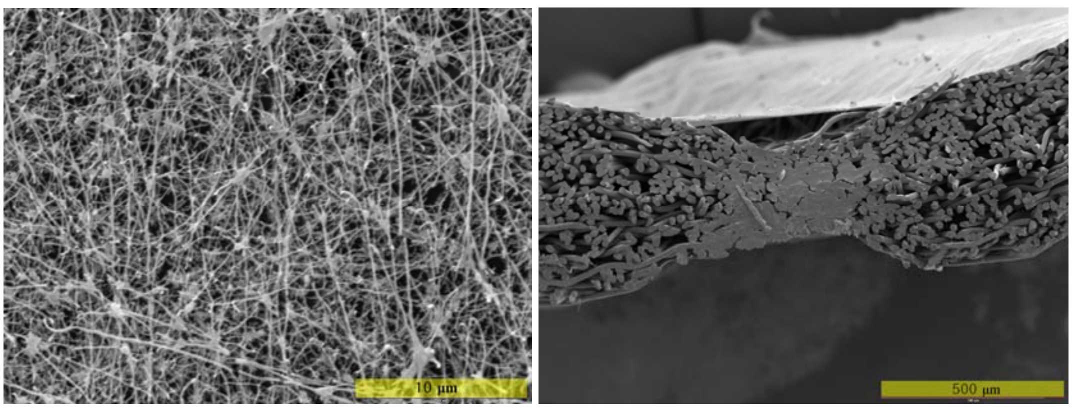


(b) Flux variations of PTFE and non-woven filter with different pore size

Figure 2-5 Performance of non-woven filter and PTFE laminated non-woven filter



(a) 12 μm non-woven filter



(b) 10 μm with PTFE

Figure 2-6 Scanning electron micrographs of non-woven filter and PTFE laminated non-woven filter

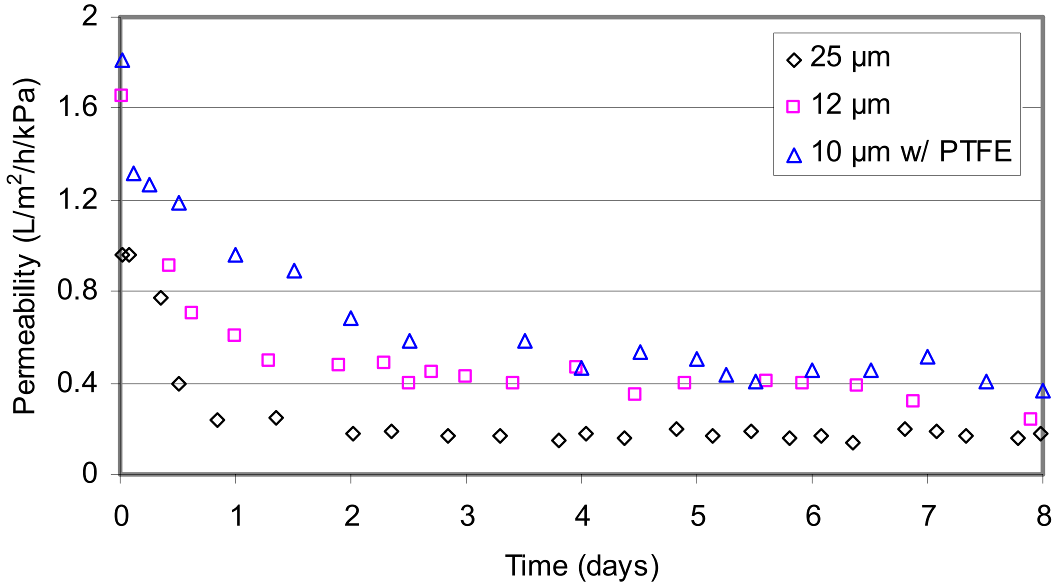
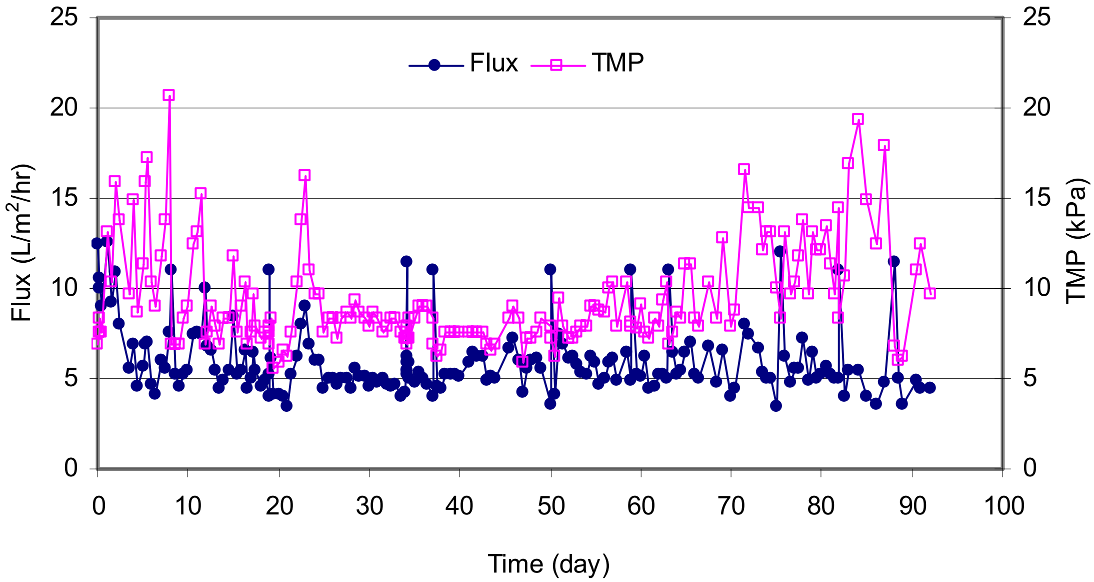
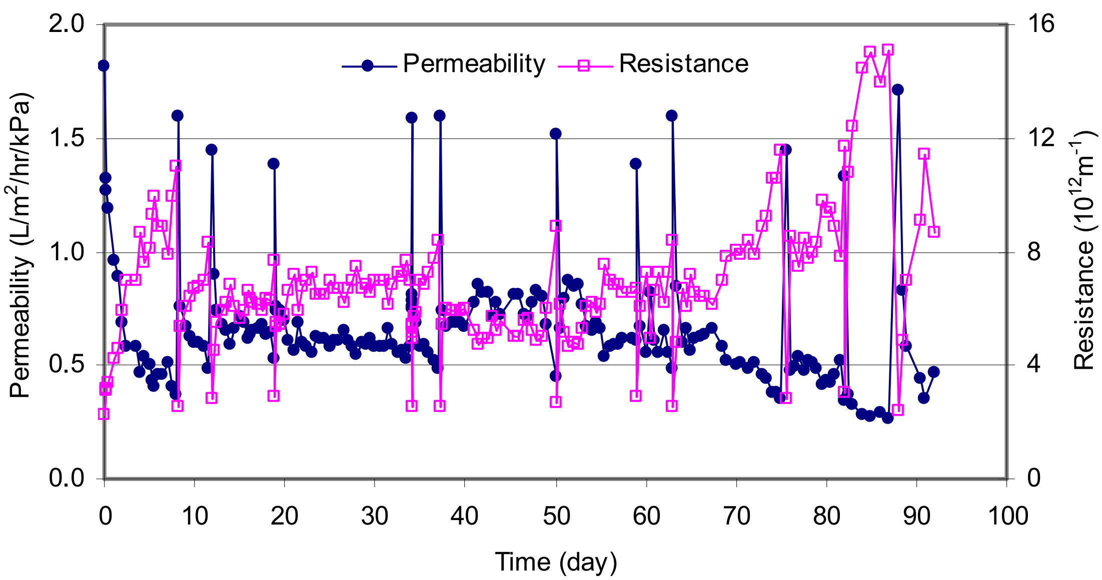


Figure 2-7 Long term permeability profiles of non-woven filter and PTFE laminated non-woven filter



(a) Flux and TMP variations



(b) Permeability and total resistance

Figure 2-8 Long term performance of PTFE laminated non-woven filter

Table 2-1 Non-woven filter and PTFE laminated non-woven filter characteristics

	Non-woven filter		PTFE membrane
Type	Tubular	Tubular	Tubular
Material	Poly propylene	Poly propylene	PTFE laminated on non-woven support
Length (mm)	300	600	600
Diameter (mm)	50	8	8
Pore size* (μm)	25	25 and 12	10
Surface area (m^2)	0.05	0.015	0.015
Weight (g/m^2)	200	200 (25μm) 270 (12μm)	270

* Equivalent pore size

Table 2-2 Characteristics of synthetic municipal wastewater

	COD = 500mg/L				COD = 1,000mg/L			
	COD	N	P	Alkalinity	COD	N	P	alkalinity
NFDM	250				540			
Starch	130				260			
Acetate	80				160			
Yeast	40				40			
NH_4Cl		20				20		
Urea		20				20		
KH_2PO_4			10				10	
$KHCO_3$				300				600
Total	500	40	10	300	1000	40	10	600

Unit: mg/L

Table 2-3 Module comparison

	Outside-to-in module	Inside-to-out module
Permeability ($l/m^2/hr/kPa$)	0.02	0.1
CFV (m/sec)	0.8	0.1
Permeate TCOD (mg/l)	32.7 ± 9.7*	26.9 ± 9.1*
Permeate SS (mg/l)	14.8 ± 6.4*	7.8 ± 3.1*

Sample size n = 12

Table 2-4 Specific cake resistance (α) comparison

Membrane	Sludge	MLSS (mg/l)	Feed	α ($m \cdot kg^{-1}$)	Reference
UF, 20 kDa	Anaerobic		Alcohol distillery wastewater	$3.9 \sim 6.4 \times 10^{15}$	[20]
MF, 0.1 μm	Anaerobic		Synthetic wastewater	15.4×10^{15}	[21]
MF, 0.1 μm	Anaerobic + PAC		Synthetic wastewater	9.8×10^{15}	[21]
MF, 0.1 μm	Aerobic		Synthetic wastewater	$10^{11} \sim 4 \times 10^{13}$	[22]
UF, 20 kDa	Aerobic	3,000	Synthetic wastewater	7.14×10^{13}	[23]
MF, 25 μm	Anaerobic	12,000	Synthetic municipal wastewater	$2 \sim 7.6 \times 10^{13}$	This study

Table 2-5 Summary of AMBR operation

	Run 1	Run 2
Operation time (days)	53	37
ORL (kg $COD/m^3 \cdot d$)	0.67	1.33
Influent		
COD (mg/L)	500	1,000
pH	8.2 ± 0.2	8.3 ± 0.3
Alkalinity (mg/L as $CaCO_3$)	391 ± 30.5	731 ± 32.4
Effluent		
COD (mg/L)	22.5 ± 6.9	30.3 ± 14.3
VFA (mg/L)	11.0 ± 2.8	14.8 ± 5
SS (mg/L)	6.0 ± 1.7	7.6 ± 2.3
pH	7.9 ± 0.1	7.6 ± 0.0
Alkalinity (mg/L as $CaCO_3$)	548 ± 22.5	890 ± 40.4
Biogas		
CH_4 content (%)	56.3 ± 1.6	76.4 ± 1.8
CH_4 yield (L CH_4/g COD)	-	0.19 ± 0.04

Table 2-6 Comparison of anaerobic CSTR coupled external membrane module

Reference	This study	[24]	[26]	[27]	[28]
Types of wastewaters	Synthetic	Synthetic	Synthetic	Swine waste	Distillery wastewater
Types of membrane/module	Tubular/MF	Flate plate/UF	Tubular/MF	Tubular/UF	Flate plate/UF
Membrane materials	PTFE	Polysulfonate	Ceramic	PES	Fluoropolymer
Operation day	90	190	300	135	200
Pore size	10μm	3000kDa	0.14μm	20kDa	20kDa
TMP, bar	0.067–0.2	0.5	0.5 – 1.0	0.3-0.7	1 – 2
CFV, m/s	0.1–0.2	0.8	3.0	1.5–1.9	0.24 – 0.95
Cross flow, l/min	0.3–0.6	NA*	5	10-12.7	NA*
Temperature, ^{o}C	25	35	35	37	55
pH	6.8 – 7.0	7.0	8.5	7.5	7.5-8.5
MLSS(MLVSS), g/l	10–16 (6–10.5)	3.9 – 18.5 (2.6–16.5)	0.13	NA*	8 – 0.5 (3–0.33)
HRT, days	0.75	2 – 5	0.4 - 13.8	6	10-15
Influent COD, g/l	0.5–1.0	5	5.34	NA*	22.6
COD removal , %	95	98	95	96	94
Flux, l/m^2-h	5	80–20	120	5	70–1
Backflushing, day	4-10	7-10	NA*	None	NA*
Total Resistance (10^{12}m^{-1})	15	NA*	NA*	33	209
Methane yield, l CH_4/g COD	0.19	NA*	0.26	NA*	NA*

*NA: not applicable

CHAPTER 3. RHEOLOGICAL PROPERTIES OF ANAEROBIC SLUDGE IN ANAEROBIC MEMBRANE BIOREACTOR

A paper submitted to IWA special conference, Facing Sludge Diversities: Challenges, Risks and Opportunities, Mar. 28-30, 2007, Antalya, Turkey

Jaeho Ho, Aysenur Ugurlu, and Shihwu Sung

Abstract

Rheological properties of sludge in wastewater treatment plants are important parameters in terms of sludge handling and treatment. Maintenance of high sludge inventory in AMBR would require significant energy to control fouling and permeate rate due to the elevated viscosity. The rheological properties of anaerobic sludge and the effects of sludge concentration on the hydrodynamics in AMBR were investigated. The result showed that TS concentration significantly affected rheological properties as well as flux decline in AMBR. TS concentration of 5 g/L or less characterizes the transition from Newtonian to non-Newtonian behavior. Both Casson and power-law equations were fit for rheological modeling of anaerobic sludge with TS concentration of 10g/L or above. The minimum CFV to produce turbulent flow (Reynolds number ~ 2,100) increased almost linearly to 0.5-0.8 m/s at TS concentration of 10-20 g/L. The highest flux was observed at TS concentration of 15-25 g/L. After that the severe cake fouling caused a gradual deterioration in flux.

Keywords: Rheology, non-Newtonian, anaerobic sludge, anaerobic membrane bioreactor, Reynolds number

Introduction

In recent years, the anaerobic treatment of low and medium strength wastewaters such as sewage and some industrial processing wastewaters have attracted much attention, which at present is largely treated by aerobic processes. Three major factors are of concern with aerobic treatment system especially the activated sludge process such as high sludge production, high cost associated with aeration and potential filamentous growth and foaming. Anaerobic treatment processes, on the other hand yield significantly less sludge, require no aeration and no issue of sludge bulking. From these perspectives, anaerobic treatment of such wastewaters appears to be economically more attractive. However, extremely low sludge yield of anaerobic microorganisms requires longer sludge retention time (SRT) to prevent the wash-out of slow growing microorganisms. Moreover, final effluent quality is poorer than that of aerobic treatment. Application of membrane technology in wastewater treatment processes has drawn considerable attention recently. Membrane is a material through which some substance can pass selectively, resulting in a separation process (Judd and Jefferson, 2003). Membrane has been considered the most effective separation technology and has extended its application from medical equipment to wastewater treatment. Since the early 1990s, there has been a rapid growth of the membrane market and a corresponding decrease in membrane cost (Judd and Jefferson, 2003). Most membranes related to water or wastewater treatment are microfiltration and ultrafiltration. Generally, the range of pore size for micro and ultrafiltration membranes is 0.1 to 10 μm and 1 to 100 nm, respectively. Anaerobic membrane bioreactors (AMBR) could essentially retain all of the biomass in the reactor without any fear of sludge wash-out irrespective of short hydraulic retention time (HRT). AMBR also produces superior effluent quality in term of suspended solids, chemical oxygen demand and pathogen count and there is a possibility of reuse and recycling of the treated effluent. However, membrane technology is costly and complicated process in order to maintain a hydraulic flux, especially in high solid content system. The membrane fouling associated with anaerobic digestion depends on various operation parameters, including types of membrane, biomass characteristics and concentrations, and membrane operating conditions (Chang *et al*., 2002). The cake resistance is regarded as a primary component of total resistance in an MBR system (Choo *et al*., 1996).

Determination of the rheological properties of sludge in wastewater treatment plants is important in terms of sludge handling and treatment, because sludge behaves in non-Newtonian fluid (Forster, 2002; Sanin, 2002; Dentel, 1997). There are several factors affecting sludge rheology; particle size, particle size distribution, particle shape, and concentration (Ferguson *et al*., 1991). Among these factors, only sludge concentration could be controllable in practice. Rheological properties of sludge are also important in MBR or AMBR. The sludge viscosity is related to the hydrodynamics of membrane scouring to control membrane fouling as well as oxygen transfer in MBR. Rheological properties of activated sludge in MBR have been reported (Hasar *et al*., 2004; Rosenberger *et al*., 2002; Xing, *et al*., 2001). However, the rheological properties in AMBR have not been studied. Maintenance of high sludge inventory in AMBR could be beneficial for reactor performance, but, on the other hand, it will require significant energy to control fouling and permeate rate. The purpose of this study was to investigate the rheological properties of anaerobic sludge in AMBR, and the effects of sludge concentration on the membrane performance.

Materials and Methods

Flux test

Tubular poly-tetrafluoroethylene (PTFE) microfiltration membrane with pore size of 1μm and total filtration surface area of $0.015m^2$ (supplied by KNH Co. Ltd., Taiwan) was used in this study. Flux and fouling tests were carried out using the flux test module as shown in Figure 1. Fresh anaerobic sludge stored in refrigerator was placed in warm water bath to adjust temperature to 25°C before conducting flux test. The anaerobic sludge was continuously stirred at 150 rpm and circulated through membrane module by peristaltic pump with variable-speed modular drive (I/P modular pump, Cole-Parmer, IL). The flux test was performed at various TS concentrations ranging from 5 to 30 g/L, and fixed CFV of 0.1 m/s, TMP of 0.9 psi, and temperature of 25°C. Membrane was cleaned using hypochlorite after every set of flux test. Permeate flow rate was manually measured using a graduated cylinder and a stop watch.

Rheological characterization

Anaerobic sludge was obtained from the secondary anaerobic digester of local water pollution control facilities. The collected total solid (TS) concentration of the anaerobic sludge was approximately 30 g/L after sieving to remove big particles. The sludge was diluted with tap water to achieve TS levels of 30, 25, 20, 15, 10, and 5 g/L. A rotational type viscometer (Haake GmbH) was used to determine sludge rheology. The rheological data were modeled using Casson, Power-law, and Newtonian equation.

Results and Discussion

Rheological properties of anaerobic sludge

The rheological properties of anaerobic sludge were found to be related to TS concentration and shear rates. The viscosity decreased with increasing shear rate, which characterizes shear-thinning or pseudoplastic behavior. The rheological properties of aerobic or anaerobic sludge have been reported to be either pseudoplastic (Moeller and Torres, 1997; Sanin, 2002) or yield pseudoplastic (Slatter, 1997; Forster, 2002; Mikkelsen, 2001), which is likely to depend on the sludge concentration and applied shear rate. With increasing TS concentration and decreasing shear rates, the particle-to-particle interaction formed a network, which resulted an increase in aqueous viscosity. Casson (yield pseudoplastic), power-law (pseudoplastic), and Newtonian model presented in Eq. (1), (2), and (3), respectively, were applied to the actual rheological data obtained in this study.

$$\tau = \sqrt{\tau_n^{0.5} + (\gamma \cdot n_\rho)^{0.5}} \qquad (1)$$

$$\tau = k \cdot \gamma^n \qquad (2)$$

$$\tau = \mu \cdot \gamma \qquad (3)$$

where τ is the shear stress, τ_n is the Casson yield, γ is the shear rate, n_ρ is the Casson viscosity, k is the consistency index, n is the flow behavior index, and η is the apparent viscosity.

Table 1 shows rheological properties of anaerobic sludge using Casson, power-law, and Newtonian model. It should be noted that the rheological properties at TS concentration of 5 g/L deviated from data trend for Casson and power-law model. However, Newtonian equation was fit. It should follow Newtonian flow behavior as the TS concentration approach zero, assuming that the liquid phase is Newtonian. Therefore, TS concentration of

5 g/L characterizes the transition from Newtonian to non-Newtonian behavior. Both Casson and power-law equations were fit for rheological modeling of anaerobic sludge with TS concentration of 10 g/L or above.

The lines in Figure 2 (a) and (b) were drawn using power-law equation as shown in Eq. (2). Power-law relation has represented the rheological properties for a variety of non-Newtonian fluid (Dodge and Metzner, 1959), so that the associated fluid index, n and k, has been widely adopted for a theoretical analysis of non-Newtonian flow. With increase of TS concentration, rheological characteristics of sludge became more non-Newtonian as shown in Figure 2. Rheological study showed that the apparent viscosity of anaerobic sludge ranged from 1.3 to 10 mPa·s at TS concentration ranging from 5 to 30 g/L. The corresponding shear rate was 500 s^{-1}. However, the viscosity increased to 1.9 to 50 mPa·sec at shear rate of 30 s^{-1}. Therefore, it is clear that the apparent viscosity increases exponentially with an increase of particle concentration. Mikkelsen (2001) also reported an exponential increase of apparent viscosity at solid contents ranging from 1 to 10g/L.

Effect of TS concentration on hydrodynamics

Reynolds number is often used to determine the type of flow, either laminar or turbulent, in Newtonian fluid (Ferguson and Kemblowski, 1991). The turbulent flow on the membrane surface is essential to control fouling and flux in AMBR system. The critical Reynolds number is approximately 2,100, which may slightly vary in non-Newtonian fluid. Many equations have been proposed in the literature for the turbulent flow of non-Newtonian fluids (Liu, 2003). The non-Newtonian Reynolds number of anaerobic sludge was calculated using Eq. (5) for laminar flow (Re ≤ 2,100) and Eq. (6) for turbulent flow (Re ≥ 2,100), which allow to use the same Moody diagram for Newtonian fluids (Liu, 2003; Tanner, 2000).

$$\mathrm{Re}_n = \frac{\rho \cdot v \cdot d}{\mu} \tag{4}$$

$$\mathrm{Re}_l = \frac{v^{2-n} \cdot d^n \cdot \rho}{k \cdot [(3n+1)/4n]^n \cdot 8^{n-1}} \tag{5}$$

$$\mathrm{Re}_t = \frac{6[(1+3n)/n]^{1-n} v^{2-n} \cdot d^n \cdot \rho}{2^n \cdot [(1+2n)/n] \cdot k} \tag{6}$$

where Re_n is the Reynolds number for Newtonian fluid, Re_l is the Reynolds number for laminar flow of non-Newtonian fluid, Re_t is the Reynolds number for turbulent flow of non-Newtonian fluid, ρ is the density of the fluid, v is the mean velocity of the flow, d is the inner diameter, μ is the dynamic viscosity.

The coefficients n and k were estimated by regression of obtained data in Figure 2. Figure 3 showed that the required CFV to produce tangential flows corresponding to Reynolds number of 200, 1,000, 2,100, 3,000, and 4,000. It was assumed that the sludge with TS concentration of 5g/L or less is in the region of Newtonian. There was a slight difference between the critical Reynolds number calculated from Eq. (5) and (6). The required CFV to produce turbulent flow (Reynolds number ~ 2,100) increased almost linearly to 0.5-0.8 m/s at TS concentration of 10-20 g/L. The minimum CFV for turbulent flow on the membrane surface in an AMBR operated at a similar TS concentration is likely to be less than 1 m/s. At higher TS concentration of 25-35 g/L, the CFV increased rather sharply to 1.0-2.0 m/s. The result is comparable to that of activated sludge in MBR. Rosenberger *et al*. (2002) found that the minimum velocity to achieve Reynolds number of

5,000 in a tubular membrane module ranged from 2.2 – 2.9 m/s at MLSS concentration of 10 - 20 g/L. The required CFV to produce turbulent flow with a Reynolds number of 4,000 is found to be 1.0 - 1.5 m/s at the same TS concentration in this study. The sludges originated from different sources and treated by different methods showed distinct rheological properties (Moeller and Torres, 1997; Pevere *et al*., 2005). Therefore, it would be essential to study the rheological properties of sludge for the determination of membrane operation parameters.

It was proposed that the Reynolds number for transition from laminar to turbulent flow of non-Newtonian fluids could be estimated by following Ryan and Johnson equation (Liu, 2003)

$$Re_{t-l} = \frac{6464 \cdot n}{(1+3n)^2 \cdot (\frac{1}{2+n})^{\frac{2+n}{1+n}}} \tag{7}$$

The critical Reynolds number increased with increases of TS concentration up to 2,400 at TS concentration of 30 g/L. The required CFV also increased accordingly. This adjustment resulted in an increase of required CFV approximately 7 to 9 % compared to that calculated from Eq. (6).

Figure 6 shows flux decline in membrane filtration of anaerobic sludge. The flux tests at TMP of 6.2 kPa and CFV of 0.1 m/s with different solid contents showed that MLSS concentration affected the initial and pseudo-steady state flux. Initial flux decreased abruptly to 23 L/m^2/h with increase in MLSS concentration to 15 g/L. However, the flux improved to 26-32 L/m^2/h at TS concentration of 20 g/L or above. The highest pseudo-steady state flux was observed at TS concentration of 15-25 g/L. After that the severe cake fouling caused a gradual deterioration in flux. Therefore, the lower particle concentration does not necessarily yield the higher flux. One possible reason is the adsorption of dispersed particles in diluted solution on membrane pore which causes internal fouling. However, with increasing TS concentration, the particle-to-particle interaction formed a network, which built up cake layer. Normalized flux decline profile is presented in Figure 6 (b). The highest and lowest pseudo-steady state flux was observed at TS concentration of 15 and 30 g/L, respectively. The normalized flux at 15 and 30 g TS/L was 0.4 and 0.15, respectively, after 6 h filtration. This result suggests that there is an optimal TS concentration range at a given hydrodynamic condition, which was 15 g/L at CFV of 0.1 m/s in this study. Further study will elucidate the effect of TS concentration on membrane performance under different hydrodynamic conditions.

Conclusions

The rheological properties of anaerobic sludge and the effects of sludge concentration on the hydrodynamics in AMBR were investigated. The result showed that both yield pseudoplastic and pseudoplastic model were fit for anaerobic sludge with TS concentration of 10 g/L or above. The rheological characteristics of anaerobic sludge became more non-Newtonian as sludge concentration increased. The apparent viscosity of anaerobic sludge ranged from 1.3 to 10 mPa·s at TS concentration ranging from 5 to 30 g/L and at the corresponding shear rate of 500 s^{-1}. The required CFV for turbulent flow increased significantly at a higher TS concentration due to the pseudo-plastic behavior of anaerobic sludge. The minimum CFV to produce turbulent flow (Reynolds number ~ 2,100) increased almost linearly to 0.5-0.8 m/s at TS concentration of 10-20 g/L. The highest pseudo-steady state flux was observed at TS concentration of 15 g/L. Network effect of concentrated anaerobic sludge improved the flux at MLSS concentration of 15-20 g/L. However, the lower particle concentration does not necessarily yield the higher flux due to the internal fouling by dispersed particles. Moreover, the higher particle concentration also caused a gradual deterioration in flux due to the severe cake fouling.

References

Chang, I.-S., Clech, P. L., Jefferson, B., Judd, S., 2002. Membrane fouling in membrane bioreactors for wastewater treatment. *J. Environ.Engr*. **128**, 1018-1029.

Choo, K. H. and Lee, C. H. (1996) Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor. *Wat. Res*., **30**, 1771-1780.

Dentel, S. (1997) Evaluation and role of Rheological properties in sludge management, *Wat. Sci. Tech*, **11**, 1-8.

Dodge, D. W., Metzner, A. B. (1959) Turbulent flow of non-Newtonian system, *A.I.Ch.E. Journal*, **5**, 189-203.

Ferguson, J., Kemblowski, Z. (1991) *Applied Fluid Rheology*. Elservier Science Publishers Ltd., England.

Forster, C.F. (2002) The rheological and physico-chemical characteristics of sewage sludge. *Enzyme and Microbial Tech*., **30**, 340-345.

Hasar, H., Kinaci, C., Ünlű, A., Toĝrul, H., Ipek, U. (2004) Rheological properties of activated sludge in a sMBR. *Biochemical Engineering Journal*, **20**, 1-6.

Liu, H. (2003) *Pipeline Engineering*, Lewis Publishers, NY.

Mikkelsen, L. H. (2001) The shear sensitivity of activated sludge Relations to filterability, rheology and surface chemistry, *Colloids and Surfaces A*, **182**, 1-14.

Moeller, G., Torres, L. G. (1997) Rheological characterization of primary and secondary sludges treated by both aerobic and anaerobic digestion, *Bioresource Technilogy*, **61**, 207-211.

Pevere, A., Guibaud, G., van Hullebusch, E., Lens, P., Baudu, M. (2005) Effect of inoculum and sludge concentration on viscosity of anaerobic granular sludges, *Wat. Sci. Tech*., **52**, 509-514.

Rosenberger, S., Kubin, K., Kraume, M. (2002) Rheology of activated sludge in membrane bioreactors. *Eng. Life Sci*., **2**, 269-275.

Sanin, F.D. (2002) Effect of solution physical chemistry on the rheological properties of activated sludge. *Water SA*, **28**, 207-211.

Slatter, P.T. (1997) The rheological characterisation of sludges. *Wat. Sci. Tech*., **36**, 9-18.

Tanner, R. I. (2000) *Engineering Rheology*, Oxford University Press Inc., NY.

Xing, C.-H., Qian, Y., Wen, X.-H., Wu, W.-Z., Sun, D. (2001) Physical and biological characteristics of a tangential-flow MBR for municipal wastewater treatment, *Journal of Membrane Science*, **191**, 31-42.

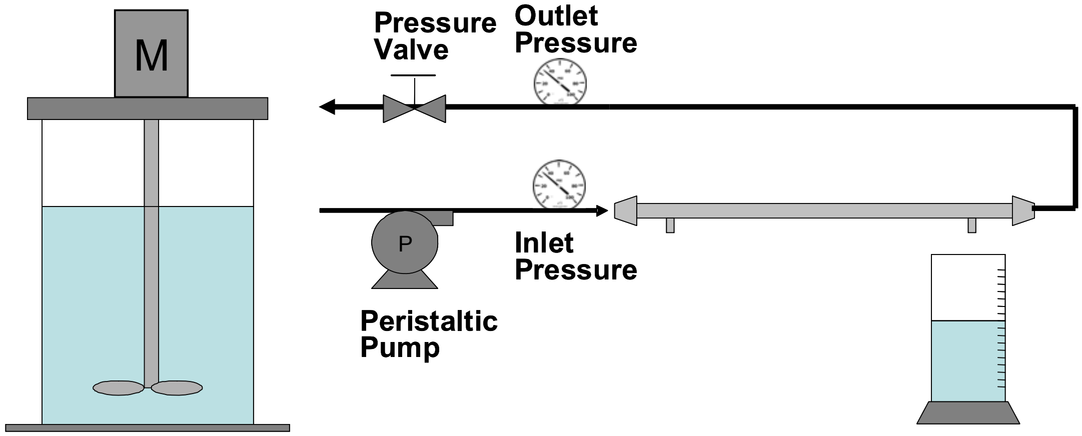
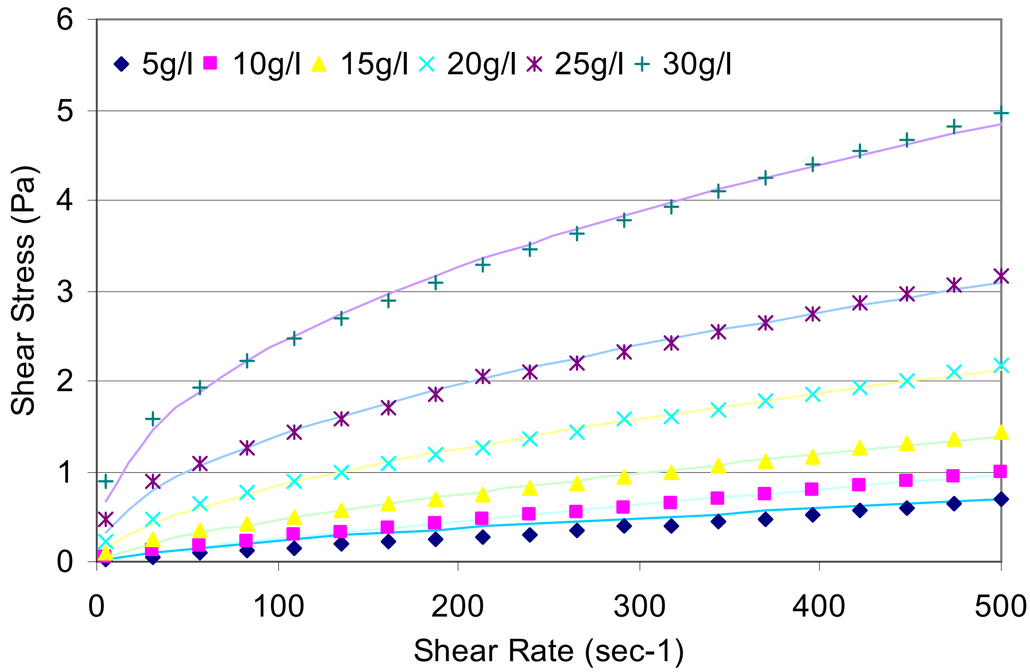
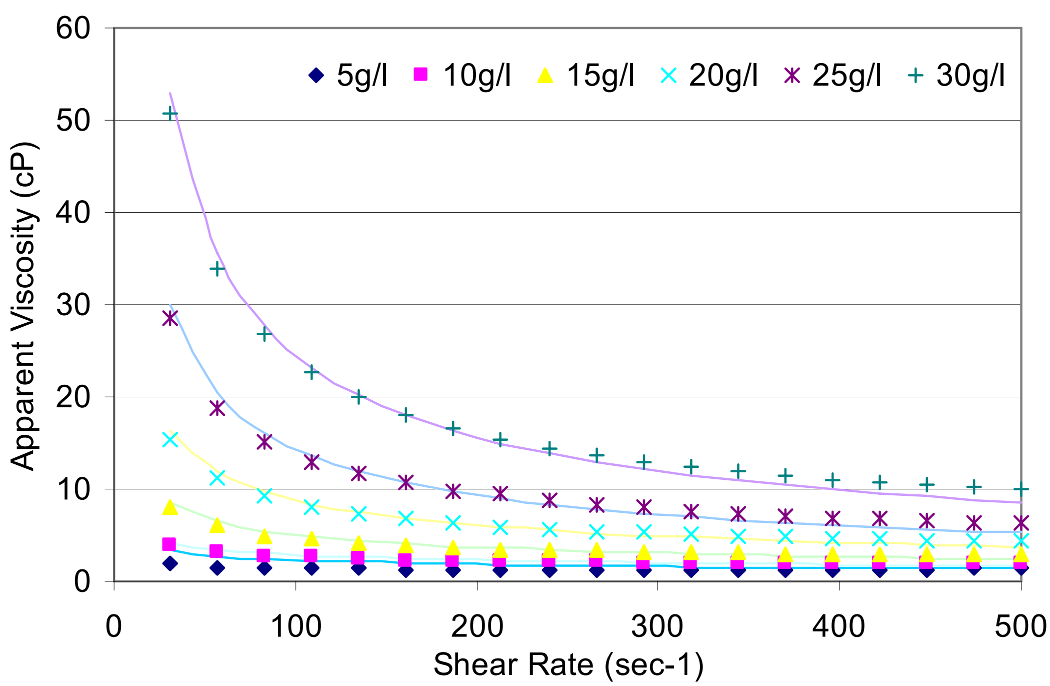


Figure 3-1 Flux test module



(a) Shear rate – Shear Stress



(b) Shear Rate – Apparent Viscosity

Figure 3-2 Rheogram of anaerobic sludge

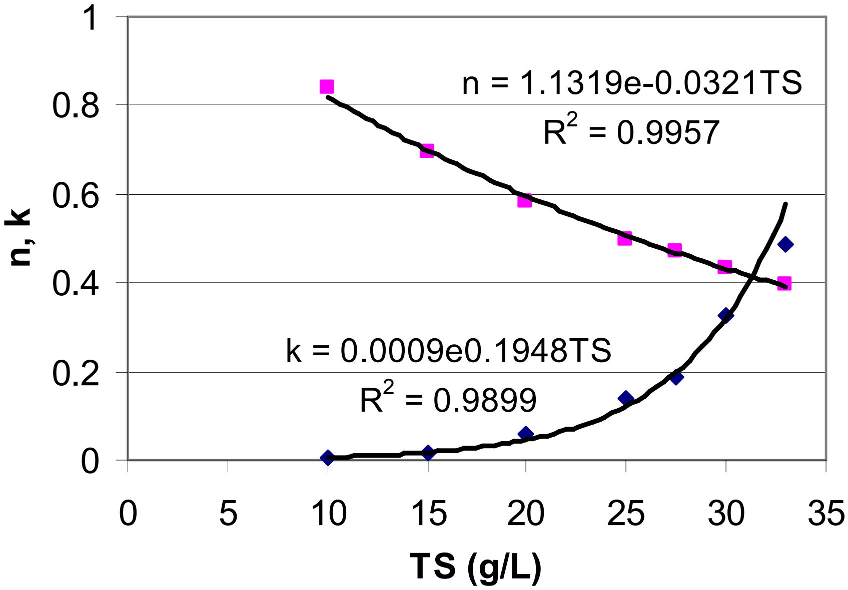


Figure 3-3 Coefficients of n and k estimation

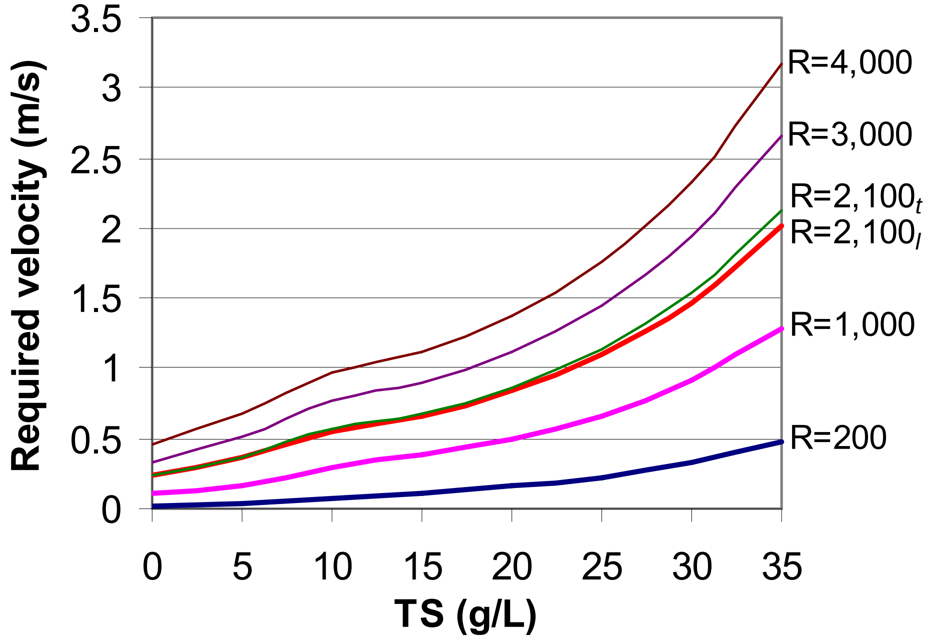


Figure 3-4 Required CFV for turbulent flow

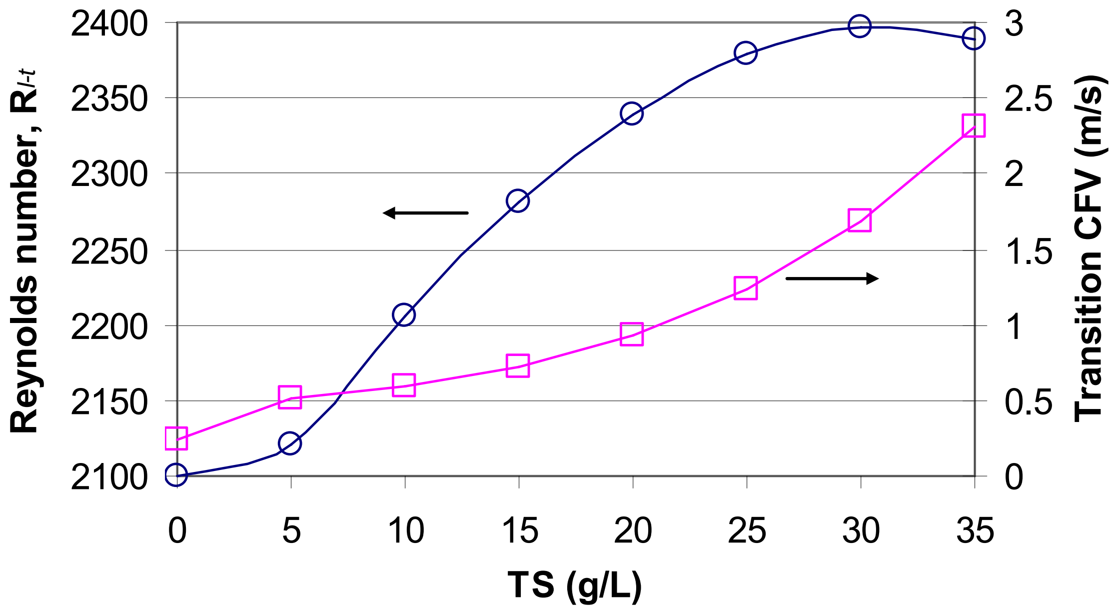
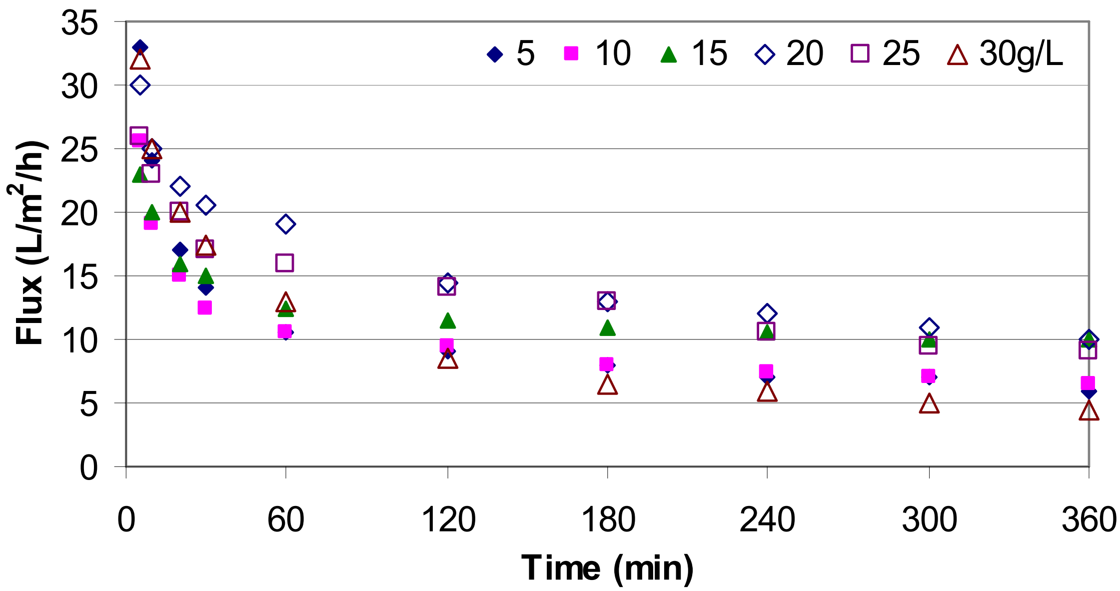
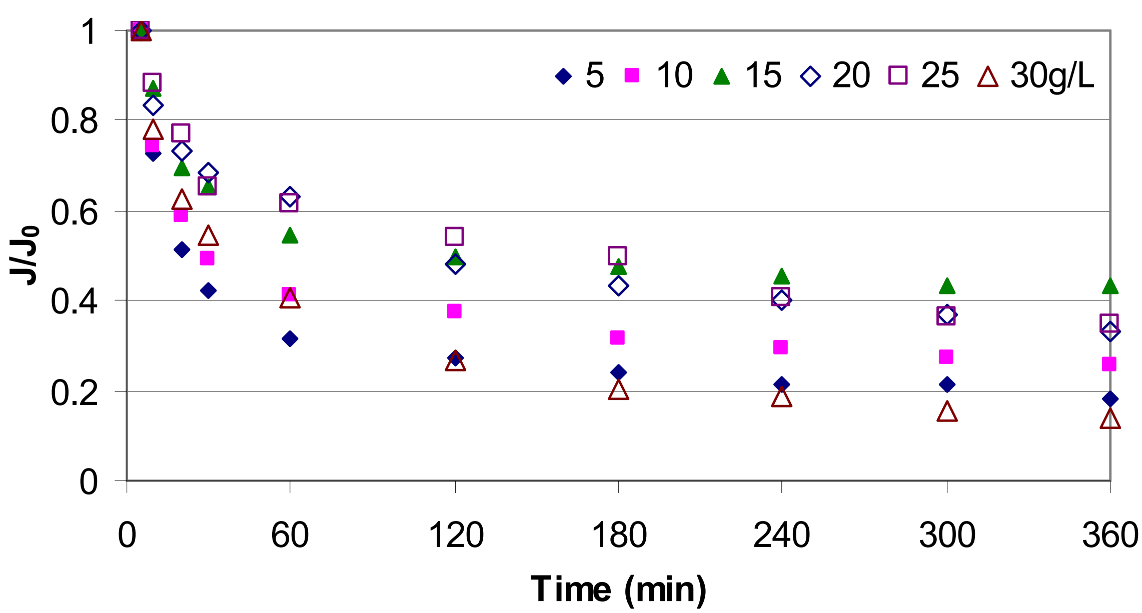


Figure 3-5 Critical Reynolds number and corresponding CFV



(a) Flux decline



(b) Normalized flux decline

Figure 3-6 Flux profiles on different TS concentration.

Table 3-1 Rheological properties of anaerobic sludge

TS (g/L)	Casson model			Power law model			Newtonian model	
	τ_n	n_ρ	r^2	k	n	r^2	μ	r^2
5	0.0001	0.001284	0.9977	0.01076	0.6675	0.9977	0.001362	0.9977
10	0.0137	0.001514	0.9993	0.00525	0.8396	0.9982	0.002038	0.9911
15	0.0685	0.001727	0.9996	0.01862	0.6943	0.9981	0.003079	0.9622
20	0.1999	0.002126	0.9989	0.05734	0.5814	0.9986	0.004894	0.9054
25	0.4420	0.002506	0.9987	0.14150	0.4958	0.9970	0.007322	0.8124
30	0.9034	0.003335	0.9976	0.32550	0.4345	0.9975	0.011790	0.6870

CHAPTER 4. SLUDGE CHARACTERISTICS AND METHANOGENIC ACTIVITIES IN ANAEROBIC MEMBRANE BIOREACTOR TREATING SYNTHETIC MUNICIPAL WASTEWATER

A paper to be submitted to Water Research

Jaeho Ho, Shihwu Sung*

Abstract

Specific methanogenic activity (SMA) test was used to investigate the methnogenic activity profiles of suspended and attached sludge in AMBRs treating synthetic municipal wastewater at 25 and 15°C. It was hypothesized that accumulated biomass on the membrane surface could act as a secondary membrane as well as a biofilm which removes COD biologically. The SMA test for suspended sludge in the reactor and attached sludge on the membrane surface was carried out on days 1, 15, 30, 45, 60, and 75 during a 110-day operation. The results showed that attached sludge on the membrane surface has lower activity than suspended sludge. The microbial activity of suspended sludge continuously increased, while that of attached sludge gradually decreased in this study. Although many different types of microorganisms on the membrane surface, including short and long rods, filaments, and cocci, were observed by SEM photographs, the methanogenic activity of attached sludge was far lower than that of suspended sludge. Attached sludge on the membrane surface contained less extractable EPS, especially lower protein content, than suspended sludge, which could be related to the decreased methanogenic activity. Although

the environmental conditions on the membrane surface may not be favorable for attached-growth microorganism due to the shear force by cross flow, the membrane in AMBR systems is likely not only to retain all biomass in the reactor, but also complement decreased biological removal efficiency at low temperature by rejecting soluble organics.

Keywords: specific methanogenic activity (SMA), anaerobic membrane bioreactor (AMBR), extracellular polymeric substance (EPS), synthetic municipal

Introduction

Application of anaerobic processes for the treatment of low strength wastewater has drawn considerable attention recently due to its inherent benefits compared to aerobic treatment, including less energy consumption, less sludge production, and valuable methane generation, and as a result it is gaining popularity in developing countries. However, maintaining a long sludge retention time (SRT) is one of the challenges of anaerobic treatment processes due to the slow growth rate of anaerobic microorganisms. Therefore, the key to successful high-rate anaerobic technology is to decouple hydraulic retention time (HRT) and SRT in order not only to maintain high sludge concentration in the system but also to decrease reactor size. Attached growth or biofilm processes have been considered as an alternative due to excellent biomass retention and accumulation in the system (Rittmann *et al*., 2001). Most of high rate anaerobic processes, such as up-flow anaerobic sludge blanket (UASB), expanded granular sludge blanket (EGSB), and anaerobic filter adopt an attached growth system. UASB and EGSB have had wide applications for the treatment of industrial and municipal wastewater. Under unfavorable environmental conditions, however, granules disintegrated, which led to irreversible reactor failure (Connaughton *et al*., 2006). Anaerobic membrane bioreactors (AMBR) also retain all of the biomass in the reactor more effectively without any fear of sludge wash-out irrespective of short HRT. In addition, AMBR could produce superior effluent quality in terms of suspended solids, chemical oxygen demand and pathogen count, and there is the possibility of reuse and recycling of the treated effluent for non-potable purpose. Previous studies elucidated the potential of AMBR for the treatment of low strength wastewater at ambient temperature (Ho *et al*., 2006). It was found that a considerable amount of biomass accumulated on the membrane surface over the operation time. Cake layer on the membrane surface as a secondary membrane could play a role in the physical separation of permeate from mixed liquor as well as the biological degradation of organic matters. It was observed clearly that cake accumulation over time resulted in decrease of permeate suspended solids (SS) concentration (Ho *et al*., 2006). However, the role of cake as a biofilm involved in biological organic removal is not yet clear.

Extracellular polymeric substance (EPS) would play an important role not only in cake formation on the membrane surface but also in enzymatic activities to digest exogenous macromolecules. EPS is believed to be responsible for the biomass attachment on the surface in biofilm process or floc aggregation in suspended-growth systems and scavenging nutrients from the outer cell (Wuertz *et al*., 2003). There are many factors to affect EPS formation and composition, such as operational and environmental conditions, wastewater compositions, and microbial growth patterns. Many studies have elucidated the EPS composition in different wastewater treatment processes (Morgan *et al*., 1990; Schmidt *et al*., 1994). However, direct comparison of each study is not possible, because a number of methods have been proposed and used for quantitative EPS extraction, including various chemical, mechanical, and physicochemical methods (Wingender *et al*., 1999). Cation exchange resin (CER) method combined with mechanical stirring has been regarded as a suitable method to extract EPS from biofilm or biomass without significant cell lysis (Wuertz *et al*., 2003).

In addition to retaining plenty of biomass in the reactor, maintaining sufficient microbial activity and community is essential for the successful reactor operation. The long SRT and high biomass content in an anaerobic process may not always be reliable indicators of proper reactor operation, if it does not have adequate microbial activity. It has been found that membrane bioreactor (MBR) operation under prolonged SRT results in a decrease of microbial activity (Li *et al*., 2006; Han *et al*., 2005). The decreased microbial activity, however, did not affect overall reactor performance due to the higher biomass content in the reactor. From a practical point of view, therefore, reactor operation with high biomass content and low microbial activity may be favorable, because unexpected sludge wash out or activity loss will be critical in low biomass content and high microbial activity systems. Specific methanogenic activity (SMA) test has been widely used to determine the anaerobic sludge activity in various anaerobic processes (Ince *et al*., 1995; McHugh *et al*., 2004; Araki *et al*., 1994; Smino *et al*., 2007). Ince *et al*. (1993) used SMA test to control the organic loading rate during start-up of a crossflow ultrafiltration membrane anaerobic reactor. McHugh *et al*. (2004) investigated microbial community structure and population dynamics through molecular technique and SMA test during the start-up of psychrophilic anaerobic digesters. The purpose of this research is to investigate the dynamics of methanogenic activity during start-up of AMBR treating synthetic municipal wastewater at 25 and 15°C, and elucidate the role of cake layer on the membrane surface as a biofilm using SMA test.

Materials and Methods

AMBR operation

Two laboratory-scale anaerobic membrane bioreactors (Bioflow 2000 fermentor, New Brunswick Scientific, NJ, USA), AMBR 1 and AMBR 2, with 4 liters of working volume were run in parallel in 25 and 15°C, respectively. The anaerobic reactors were equipped with pH and oxidation-reduction potential (ORP) monitoring units (pH2100, Mettler Toledo, Germany), and level sensor to control permeate rate. Initially, both reactors were filled with 1 L of AMBR sludge (10 g/L) previously operated at 25 °C and 1 L of concentrated mesophilic sludge (30 g/L) obtained from a secondary anaerobic digester of a local municipal wastewater treatment plant. The seed sludge was finally diluted to approximately 10 g/L with tab water. The AMBR 1 was maintained at 25 ± 1°C using a heating and cooling loop. The AMBR 2 was operated in a walk-in refrigerator where temperature was controlled at 15 ± 1°C. Both AMBRs were coupled to tubular poly-tetrafluoroethylene (PTFE) microfiltration membrane with pore size of 1μm and total filtration surface area of $0.09m^2$ (supplied by KNH Co. Ltd., Taiwan). The membrane flux was controlled at 5 $L/m^2/h$. Back flushing using permeate was carried out to restore flux at every 4 to 6 days. The cake accumulated on the membrane surface was collected every 15 days to measure SMA. No chemical cleaning was attempted during the entire experiment.

Synthetic municipal wastewater

Synthetic municipal wastewater was prepared to represent municipal wastewater. The characteristics of the prepared wastewater were modified from that of Syntho, which was developed to represent pre-settled domestic wastewater (Nopens *et al*., 2001). The synthetic municipal wastewater was composed of non-fat dry milk (NFDM) (270mg/L), soluble starch (130mg/L), $NaCH_3COO$ (80mg/L), yeast extract (20 mg/L), NH_4Cl (76mg/L), urea (43mg/L), KH_2PO_4 (44mg/L), and $KHCO_3$ (600mg/L). Accordingly, the influent COD, TN, TP, and alkalinity were 500, 40, 10, and 300 mg/L, respectively. The properties of NFDM and required trace elements prepared for the synthetic municipal wastewater can be found elsewhere (Dague *et al*., 1998).

Analytical methods

Volatile fatty acids (VFAs) were measured by high performance liquid chromatography (HPLC, DX 500, Dionex, CA, USA) with a column for detecting organic acids (MethCarb 67H HPLC column, Varian, CA, USA). Chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS) were determined as per Standard Methods (APHA, 1998). Mixed liquor collected from the reactor were first centrifuged at 12,000 g for 10 min, and then the supernatant was further filtered through 0.22μm microfiltration cartridge to measure mixed liquor SCOD and VFAs. EPS was extracted using the CER (Dowex Marathon C, Na^+ form, Dow North America, MI, USA) extraction method (Frølund *et al*., 1996). Collected sludge was centrifuged at 2000 g for 15 min and re-suspended using nano pure water. The CER (70g CER/ g VSS) was added to a bottle with 200 ml sludge sample. The sample was stirred at 600 RPM and 4 °C for 2 h. The supernatant was centrifuged to remove CER and particles at 12,000 g for 10 min. Carbohydrate and protein were measured by anthrone and Lowry method with glucose and bovine serum albumin (BAS) as the standards, respectively, which were described by Frølund *et al*. (1996). A wet-test gas meter (Schlumberger Industries, Dordrecht, The

Netherlands) was used to measure biogas production. Gas composition was analyzed using gas chromatography (Series 350, GOW-MAC, NJ, USA). The microscopic observation of the surface of the fouled membrane was carried out using a scanning electron microscope (SEM, Hitachi S2460-N, Hitachi, Japan).

SMA test

Methanogenic activities were measured in duplicate for suspended and attached sludge at temperatures of 25 and 15 °C using 250 mL serum bottles containing acetic acids as a sole substrate. Suspended and attached sludge were collected from the AMBRs at days 1, 15, 30, 45, 60, and 75 after start-up. Attached sludge on the membrane surface was sloughed off by brushing. TSS and VSS were measured to determine the quantity of sludge added in the serum bottles prior to SMA test. Calculated amount of suspended and attached sludge to satisfy sludge content of 150 mg in the serum bottle was centrifuged at 2000G for 20 minutes. After discarding the supernatant, 10 ml of nutrient solution was added into the centrifuge tube to re-suspend the settled sludge. Nutrients stock solution was composed of $NaH_2PO_4 \cdot H2O$ (7.95 g/L), K_2HPO_4 (6.0 g/L), NH_4Cl (2.8 g/L), $MgSO_4 \cdot 7H_2O$ (1.0 g/L), yeast extracts (1.0 g/L), $CaCl_2$ (0.1 g/L), and trace elements solution (10 ml/L). The composition of trace elements stock solution is given elsewhere (Zehnder *et al.*, 1980). Each serum bottle contained 15 ml of nutrient solution, 10 ml of alkalinity solution (5 M of $NaHCO_3$), and 2.5 ml of 1M acetic acid. After adjusting pH to 7 by NaOH, the final volume was adjusted to 200 ml using deionized water. Oxygen in the liquid was purged by N_2/CO_2 80/20 % gas mixture for 2 min. The serum bottles were sealed with butyl rubber stoppers and incubated in a shaker at 180 rpm and 25 and 15°C to simulate actual operational conditions. The modified Gompertz equation was used to determine the methane production rate (Van Ginkel *et al*., 2001),

$$H(t) \ = \ H \cdot \exp\left\{-\exp\left[\frac{R \cdot e}{H}(\lambda\text{-}t)+1\right]\right\} \qquad (1)$$

where, H(t) is cumulative methane production (ml) at time t; λ is time of lag-phase (h); H is methane production potential (ml); R is methane production rate (ml/h). These parameters in Eq. (1) were estimated by the least square method using Microsoft® software (Microsoft Office Excel 2003).

Results

AMBRs performance at 25 °C and 15 °C

Two identical AMBRs coupled with PTFE membrane were operated at two different temperatures of 25 and 15°C in parallel for 112 days to evaluate methanogenic activities of suspended and attached sludge in AMBRs. During the start-up period, HRT was fixed at 12 h, and the corresponding organic loading rate was 1 kg COD/m^3 ·d. The operation flux was set to 5 L/m^2/h with TMP of 6.9 to 55.2 kPa. The pH of mixed liquor was not controlled but ranged from 6.8 to 7.1 in both reactors. The permeate pH was somewhat higher than that of mixed liquor, and ranged 7.3 to 7.9. Although pH in both reactors was not controlled, the pH levels for both reactors did not affect successful anaerobic degradation of organics. Figure 2 shows mixed liquor SCOD and permeate TCOD of AMBR 1 (a) and AMBR 2 (b). It is evident that there were concentration differences between mixed liquor SCOD and permeate

TCOD, approximately 100 and 200 mg/L for the AMBR 1 and 2, respectively, at the beginning stage. The differences were gradually decreased to about 20 mg/L after 30-day operation of AMBR 1 and about 100 mg/L after 90-day operation of AMBR 2. Regardless of the fluctuation of mixed liquor SCOD, the permeate TCOD leveled off to a stable value, especially in the AMBR 1. VFAs profiles also showed a similar trend, as shown in Figure 3. However, the concentration differences between mixed liquor VFAs and permeate VFAs were smaller than COD differences. Acetic acid was the predominant VFA in both reactors. Propionic and butyric acid were not detected in AMBR 1, while the AMBR 2 contained a small amount of propionic and butyric acid. The concentration of mixed liquor acetic acid was approximately 10 mg/L and no noticeable permeate acetic acid was detected for AMBR 1. However, mixed liquor and permeate acetic acids of AMBR 2 ranged from 10 to 35 mg/L and 0 to 25 mg/L, respectively, after 65-days of operation. Therefore, it could be expected that the cake accumulated on the membrane surface plays a role to reject mixed liquor SCOD. Soluble organics can be adsorbed either inside of the membrane pore or on the cake (Chang *et al*., 2002). A portion of adsorbed soluble organics could be further removed biologically by the attached microorganism in the cake, while the rest of it may stay there or be released to mixed liquor. Some researchers distinguished "biological removal" from "physical removal" (Baek and Pagilla, 2006; Ng *et al*., 2000). Biological removal rate was calculated by the difference between influent COD and mixed liquor SCOD divided by the influent COD, while physical removal rate was the difference between the total COD removal rate and the biological removal rate. Figure 4 shows the removal efficiency in both reactors. Total COD removal efficiency was more than 95% and 85% for AMBR 1 and 2, respectively. The COD removal of AMBR 1 was mostly carried out biologically. The physical removal rate was 20% at the early stage, and later decreased to less than 10%. However, the physical removal rate of AMBR 2 was higher than that of AMBR 1.

Variation of EPS composition

Table 1 shows the composition of extracted EPS from both reactors. Protein and carbohydrate were measured to determine the EPS content in suspended and attached sludge, because they are known to be the major constituents of EPS. Each gram of seed sludge contained 51.5 g of protein and 26.4 g of carbohydrate. Both protein and carbohydrate contents in suspended sludge decreased with time and reached relatively constant values. Each gram of suspended sludge in AMBR 1 contained more protein and carbohydrate than that in AMBR 2. Temperature change seems to affect EPS secretion from microorganism. Considerable EPS loss resulted from storage of activated sludge at a low temperature (Bura *et al*., 1998). Protein loss was greater than carbohydrate at 15 °C compared to 25 °C in this study. Therefore, the corresponding protein to carbohydrate ratio was increased from 1.9 to 8.5 in AMBR 1, while there was no significant change of protein to carbohydrate ratio in AMBR 2. Attached sludge on the membrane surface contained less extractable EPS than suspended sludge, which could be due to the shear force by cross flow over the cake surface. Both protein and carbohydrate content of attached sludge in AMBR 2 was similar to or slightly higher than that in AMBR 1.

Methanogenic activity

Table 2 shows TSS and VSS concentration of suspended and attached sludge in AMBR 1 and 2. Suspended sludge was collected every 15 days after start-up of AMBRs, while attached sludge was sampled from day 30. There was no sludge withdrawal except for the analysis and SMA test for 112 days. The sludge content of AMBR 1 started with 11.2 g/l, but it decreased to 7.5 g/L on day 45 due to an unexpected sludge washout from the reactor. Attached sludge density on the membrane surface varied from 18.7 to 42.2 g/m^2 and from 11.1 to 19.9 g/m^2 for AMBR 1 and 2, respectively. The cake density decreased with temperature drop and operation time. Table 3 shows the SMA of suspended and attached sludge in AMBR 1 and 2. The methanogenic activity was 51.8 ml CH_4/g VSS·d and eventually increased 27% and reached 65.7 ml CH_4/g VSS·d on day 75 for AMBR 1. The methanogenic activity of AMBR 2 sludge was lower than that of AMBR 1, even after 75 days of operation, which indicated either methanogenic activity at low temperature was significantly suppressed or a totally different microbial community was developed. The methanogenic activity of attached sludge was always lower than that of suspended sludge. Of interest is that the activity of suspended sludge was continuously increased, while that of attached sludge was gradually decreased. During SMA test of attached sludge, the methanogenic activity of AMBR 1 decreased from 43.9 on day 30 to 25.4 ml CH_4/g VSS·d on day 75, and from 3.1 on day 30 to 2.5 ml CH_4/g VSS·d on day 60. The effect of temperature on methanogenic activity was evaluated using the SMAs at 15, 25, and 30 °C on day 75. Temperature dependent rate coefficient can be expressed by the Arrhenius equation. Although it describes temperature dependence of chemical reaction, it can be extended to the enzyme-catalyzed reactions (Lee, 1992).

$$k = A_0 e^{-\frac{E_a}{R \cdot T}}$$

$$\theta_{T1,T2} = e^{\frac{E_a}{R \cdot T_1 \cdot T_2}}$$

where k is the temperature dependent rate coefficient, A_0 is the frequency factor, E_a is the activation energy, R is the gas constant (8.32 J/mole·K), T is the absolute temperature, and θ is the temperature correction coefficient. The activation energy can be obtained by plotting the natural logarithm of the k versus 1/T. The sludge in both AMBRs showed similar temperature dependence. The values of E_a associated with the maximum specific methanogenic activity for AMBR1 and 2 sludge were found to be 46.1 and 54.0 kJ/mole, respectively, which is comparable to other results (53.1 kJ/mole associated with maximum specific substrate removal rate) obtained from an ASBR study treating dilute wastewater at 25 to 5°C (Dague *et al*., 1998). In addition, temperature correction coefficients of both sludges were almost the same with 1.07 and 1.08, which is similar to the other study (Dague *et al*., 1998).

Morphology of sludge in AMBR

SEM pictures of suspended and attached sludge from both reactors were taken at day 30, as shown in Figure 5 (a) and (b). Suspended sludge is likely to be embedded in thick slime matrix, while attached sludge seems to be adhered individually with a clear short-rod shape, more clearly shown in a SEM picture of attached sludge at day 60, (Figure 5 (c)). The cake thickness was determined through SEM observation. It varied between 340 and 622 μm in AMBR 1 and between 35 and 74 μm in AMBR 2. Cake density was estimated using the microscopic thickness measurement and the weight of collected biomass from the membrane surface. Corresponding cake densities were 49 to 90 mg/cm^3 for AMBR 1 and 148 to 320 mg/cm^3 for AMBR 2. The cake thickness depends on operating conditions such as TMP and CFV. Although the AMBR 2 was operated at slightly higher TMP compared to the AMBR 1, the cake thickness was 10 times thinner than AMBR 1. X-ray mapping by energy-dispersive spectrometers (EDS) revealed that most of the cake in both reactors consisted of organic materials (Figure 6). However, inorganic precipitations such as Mg and Ca were observed on the cake in AMBR 2.

Discussion

The AMBR 1 operated at 25 °C achieved more than 90% COD removal during the experimental period, while the AMBR 2 at 15 °C took 2 months to reach 90 % COD removal. Inoculation of AMBR sludge previously acclimated at 25 °C led to successful COD removal right after start-up of the AMBR 1. Previous studies showed that a long acclimation time of more than 30 days was required at 25 °C using mesophilic anaerobic sludge (Ho *et al*, 2007). Adequate inoculums are essential for a shorter time for reactor start-up. Although both AMBRs achieved more than 90% COD removal in this study, the removal patterns were different. The biological removal was dominant in AMBR 1 for the entire period, while the physical removal played a significant role for the AMBR 2 performance. The physical removal on the membrane surface compensated for the decreased biological removal rate in AMBR 2.

Both protein and carbohydrate contents in suspended sludge leveled off to constant values in this study. However, suspended sludge in both reactors showed different tendencies in EPS change. A marked decrease of carbohydrate content was observed in AMBR 1, while a significant protein decrease was found in AMBR 2. It should be noted that the ratio of protein to carbohydrate in sludge having a low methanogenic activity was less than 3, while it was more than 4 in AMBR 1 suspended sludge having a relatively high methanogenic activity. Production and composition of EPS in sludge may be subjected to the variation. Moreover, abrupt change of EPS production and composition could be an indicator of microbial activity loss or community shift. EPS is considered to be actively secreted by living cells (Wingender *et al*., 1999). The protein in EPS plays a role as an enzyme to break down exogenous macromolecules and introduce low molecular nutrients into the cell (Wuertz *et al*., 2003). From this point of view, the lower EPS yield, especially protein decrease, may be related to the lower methanogenic activity of the AMBR 2. There is a controversy on EPS yield associated with sludge age. Protein content was relatively constant regardless of SRT, while carbohydrate content decreased with increases of SRT from 4 to 20 days, and the ratio of protein to carbohydrate increased with increments of SRT as a consequence (Liao *et al*., 2001). However, Ng *et al*. (2005) reported that the EPS per unit biomass increased with increases of SRT from 0.25 to 5 days. It is likely that biomass exposed prolonged SRT produces less EPS than extremely short SRT. Carbohydrate seems to be a labile component of EPS variation from changes in operating conditions.

The methanogenic activity of attached sludge showed a tendency to decrease with operation time. On day 30, the methanogenic activity of attached sludge was 81% of suspended sludge. It continuously decreased to 39% at day 75 for AMBR 1 sludge. AMBR 2 sludge also showed similar trend, but the ratio was lower than AMBR 1. It was 36% at day 30 and decreased to 22% at day 60. There are two possibilities for the decreased activity of attached sludge. Prolonged SRT may yield lower sludge production, but decrease microbial activity. Villaverde *et al*. (2000) found that heterotrophic activity of suspended biomass was 2 to 90 times higher than that of attached biomass at different heights in an aerobic biofilter system. Microbial population study showed that the number and activity of nitrification bacteria in a MBR system with complete sludge retention decreased significantly (Li *et al*., 2006). Witzig *et al*. (2002) found that despite of the high MLSS concentration, the detectable counts of microorganism by fluorescence, in situ hybridization, and the microbial activities of MBR sludge were lower than conventional activated sludge. The specific microbial activity decreases in consequence of prolonged SRT, which increases inert or endogenous phase microorganisms in the system. However, the growth yield and endogenous decay of anaerobic microorganism are considerably lower than in aerobic sludge, which means long SRT does not necessary result in decrease of the specific microbial activity in anaerobic processes. In fact, the methanogenic activity of suspended sludge increased with time in this study. The other reason could be the propensity of microorganisms to be suspended or attached. Methanogenic bacteria had a higher tendency to grow in anaerobic fluidized bed reactor than in a chemostat reactor (Araki and Harada, 1994). However, the reactors were operated with different operating conditions, which may lead to an opposite result compared with this study. The microbial activity of suspended sludge continuously increased, while that of attached sludge gradually decreased in this study. This implies that the active microorganisms are likely to be suspended growth rather than attached growth in AMBR systems, or lost activity due to the harsh environment on the membrane surface. The environmental conditions on the cake layer may not be favorable for attached growth due to the shear force by cross flow. Brockmann and Seyfried (1996) reported that specific activity of MBR sludge was significantly influenced by sludge circulation. The CFV, therefore, should be maintained as low as possible for successful AMBR operation. Table 3 shows comparison of acetoclastic SMA results reported from different research. SMA of different anaerobic sludge seems to be dependent on the operational and environmental conditions under which the sludge is acclimated. Although anaerobic granules are believed to have higher methanogenic activity than suspended, the results obtained from this study are comparable to other studies using granules at low temperatures below 30 °C. The sludge grew with the simpler substrates, such as VFAs, rather than sucrose, and sucrose rather than whey processing wastewater showed higher activity. The SMA of biofilm is generally lower than that of suspended sludge in accordance with the results from this study.

SEM photographs showed attachment of different types of microorganisms on the membrane surface, including short and long rods, filaments, and cocci. The environmental conditions may be favorable to *Methaosaeta*, which has a high substrate affinity, (Ks = 20 mg/L), but a low substrate utilization rate (2 to 4 g COD/g VSS·d) (Speece, 1996). Although many microorganisms were found to be attached on the membrane surface, the methanogenic activity of attached sludge was far lower than suspended, which indicates that it is suppressed under the harsh environmental conditions, i.e. shear stress by CFV and decreased temperature.

Conclusions

AMBRs operated at 25 and 15 °C to treat synthetic municipal wastewater achieved more than 90% COD removal. The following conclusions were drawn;

- Membrane in AMBR system is likely not only to retain all biomass in the reactor, but also complement decreased biological removal efficiency at low temperature by rejecting soluble organics.

- Attached sludge on the membrane surface contained less extractable EPS than suspended sludge, which could be due to the shear force by cross flow over the cake surface.
- The lower EPS yield, especially by protein decrease, may be related to the decreased methanogenic activity of AMBR at low temperature.
- Methanogenic activity of attached sludge was far lower than suspended, which indicates that it is suppressed under the harsh environmental conditions, i.e. shear stress by CFV and decreased temperature.
- The cake accumulated on the membrane surface is more likely to act as a physical secondary barrier through lack of biological activity.

References

Álvarez, J. A., Ruiz, I., Gómez, M., Presas, J., Soto, M., 2006. Start-up alternatives and performance of an UASB pilot plant treating diluted municipal wastewater at low temperature. *Bioresource Technology*. 97, 1640-1649.

Araki, N., and Harada, H., 1994. Population dynamics of methanogenic biofilm consortium during a start-up period of anaerobic fluidized bed reactor. *Wat. Sci. Tech*. 29, 361-368.

Baek, S.H., Pagilla, K.R., 2006. Aerobic and anaerobic membrane bioreactors for municipal wastewater treatment. *Wat. Environ. Res*. 78, 133-140.

Banik, G. C., Ellis, T. G., Dague, R. R., 1997. Structure and methanogenic activity of granules from an ASBR treating dilute wastewater at low temperatures. *Wat. Sci. Tech*. 36, 149-156.

Brockmann, M., Seyfried, C. F., 1996. Sludge activity and cross-flow microfilration- A non-beneficial relationship. *Wat. Sci., Tech*. 34, 205-213.

Bura, R., Cheung, M., Liao, B., Finlayson, J., Lee, B. C., Droppo, I. G., Leppard, G. G., Liss, S. N., 1998. Composition of extracellular polymeric substances in the activated sludge floc matrix. *Wat. Sci. Tech*.. 37, 325–333.

Chang, I.-S., Clech, P. L., Jefferson, B., Judd, S., 2002. Membrane fouling in membrane bioreactors for wastewater treatment. *J. Environ.Engr*. 128, 1018-1029.

Connaughton, S., Collins, G., O'Flaherty, V., 2006. Development of microbial community structure and activity in ahigh-rate anaerobic bioreactor at 18 °C. *Wat. Res*. 40, 1009-1017.

Dague, R. R., Banik, G. C., Ellis, T. G., 1998. Anaerobic sequencing batch reactor treatment of dilute wastewater at psychrophilic temperatures. *Wat. Environ. Res*. 70, 155-160.

Frølund, B., Palmgren, P., Keiding, K., Nielsen, P. H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin. *Wat. Res*. 30, 1749-1758.

Han, S-S., Bae, T-H., Jang, G-G., Tak, T-M., 2005. Influence of sludge retention time on membrane fouling and bioactivities in membrane bioreactor system. *Process Biochemistry*. 40, 2393-2400.

Ho, J., Khanal, S. K., Sung, S., 2007. Anaerobic membrane bioreactor for treatment of synthetic municipal wastewater at ambient temperature. *Wat. Sci. Tech*., 55, 79-86.

Ince, O., Anderson, G. K., Kasapgil, B., 1995. Control of organic loading rate using the specific methanogenic activity test during start-up of an anaerobic digestion system. *Wat. Res*. 29, 349-355.

Lee, J. M., 1992. *Biochemical Engineering*, Prentice-Hall Inc. NJ, USA.

Liao, B. Q., Allen, D. G., Droppo, I. G., Leppard, G. G., Liss, S. N., 2000. Surface properties of sludge and their role in bioflocculation and settleability. *Wat. Res*. 35, 339-350.

Li, H., Yang, M., Zhang, Y., Kamagata, Y., 2006. Nitrification performance and microbial community dynamics in a submerged membrane bioreactor with coupled sludge retention. *J Biotechnology*. 123, 60-70.

McHugh, S., Carton, M., Collins, G., O'Flaherty, V., 2004. Reactor performance and microbial community dynamics during anaerobic biological treatment of wastewaters at 16-37 C. *FEMS Microbiology Ecology*. 48, 369-378.

McHugh, S., Collins, G., Mahony, T., O'Flaherty, V., 2005. Biofilm reactor technology for low temperature anaerobic waste treatment: microbiology and process characteristics. *Wat. Sci. Tech.* 52, 107-113.

Morgan, J. W., Forster, C. F., Evison, L., 1990. A comparative study of the nature of biopolymers extracted from anaerobic and activated sludges. *Wat. Res.* 24, 743-750.

Ng, H. Y., Hermanowicz, S. W., 2005. Membrane bioreactor operation at short solids retention times: performance and biomass characteristics, *Wat. Res*. 39, 981-992.

Ng, W. J., Ong, S. L., Gomex, M. J., Hu, J. Y., Fan, X. J., 2000. Study on a sequencing batch membrane bioreactor for wastewater treatment. *Wat. Sci. Tech*. 41, 227-234.

Nopens, I., Capalozza, C., Vanrolleghem, P. A., 2001. Technical Report: Stability analysis of a systematic municipal wastewater. Dept. Applied Mathematics, Biometrics and Process Control, Universiteit Gent, Gent, Belgium.

Rittmann, B. E., McCarty, P. L., 2001. Environmental Biotechnology: Principles and Applications. McGraw-Hill Book Co., New York.

Schmidt, J. E., Ahring, A. K., 1994. Extracellular polymers in granular sludge from different upflow anaerobic sludge blaket (UASB) reactors. *Appl. Microbial Biotechnol*. 42, 457-462.

Speece, R.E. 1996. Anaerobic Biotechnology: For Industrial Wastewaters. Archae Press, Tennessee.

Sumino, H., Takahashi, M., Yamaguchi, T., Abe, K., Araki, N., Yamazaki, S., Shimozaki, S., Nagano, A., Nishio, N. 2007. Feasibility study of a pilot-scale sewage treatment system combining an up-flow anaerobic sludge blanket (UASB) and an aerated fixed bed (AFB) reactor at ambient temperature. *Bioresource Technology*. 98, 177-182.

Van Ginkel, S., Sung, S., Lay, J. J., 2001. Biohydrogen production as a function of pH and substrate concentration. *Environ. Sci. Technol*. 35, 4726-4730.

Villaverde, S., Fdz-Polanco, F., Lacalle, M. L., García, P. A., 2000. Influence of the suspended and attached biomass on the nitrification in two submerged biofilters in series system. *Wat. Sci. Tech*. 41, 169-176.

Wingender, J., Neu, T. R., Flemming, H.-C., 1999. Microbial Extracellular Polymeric Substances. Springer-Verlag Berlin Beidelberg, Germany.

Witzig, R., Manz, W., Rosenberger, S., Kruger, U., Kraume, M., and Szewzyk, U., 2002. Microbiological aspects of a bioreactor with submerged membranes for aerobic treatment of municipal wastewater. Wat. Res. 36, 394-402.

W Wuertz, S., Bishop, P., Wilderer, P., 2003. Biofilms in Wastewater Treatment. AnInterdisciplinary Approach. IWA Publishing, Cornwall, UK.

Zehnder A.J.B., Huser B.A., Brock T.D., Wuhrmann, K., 1980. Characterization of an acetate-decarboxylating, non-hydrogen-oxidizing methane bacterium. *Archives of Microbiology*. 124, 111-119.

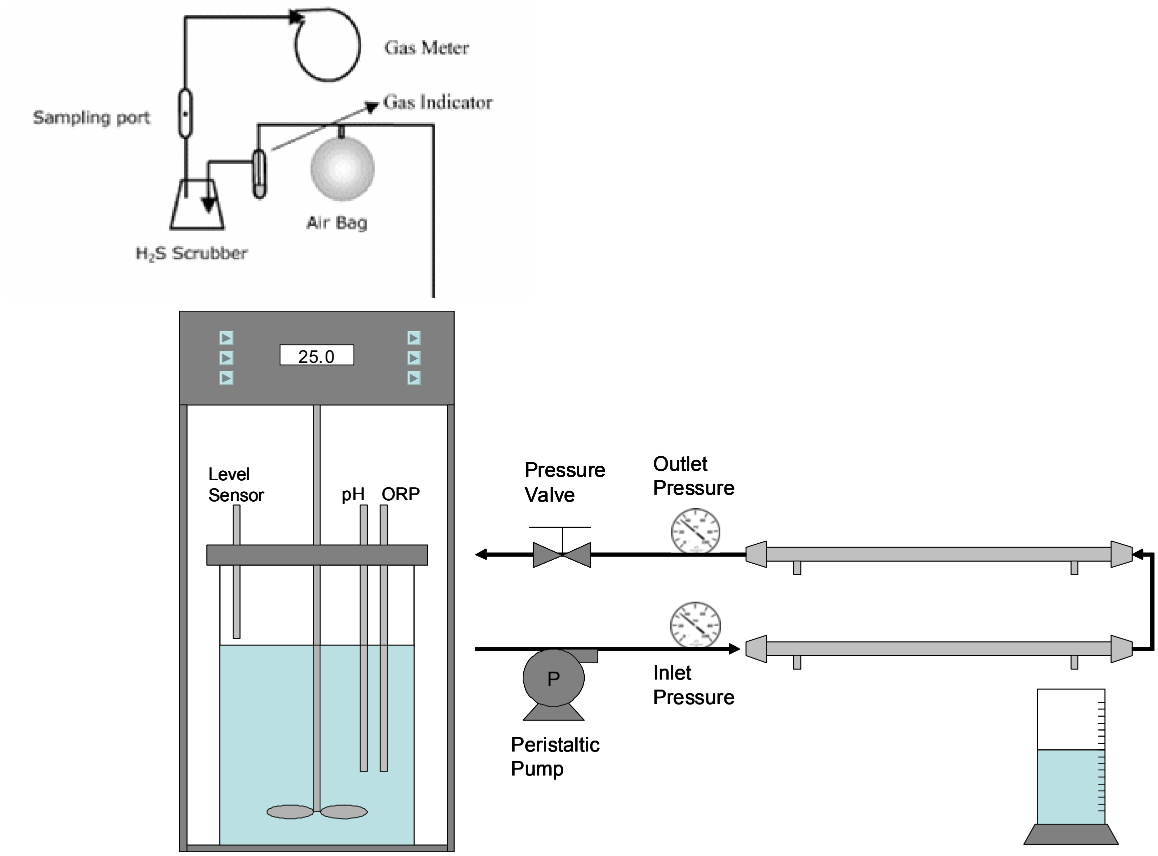
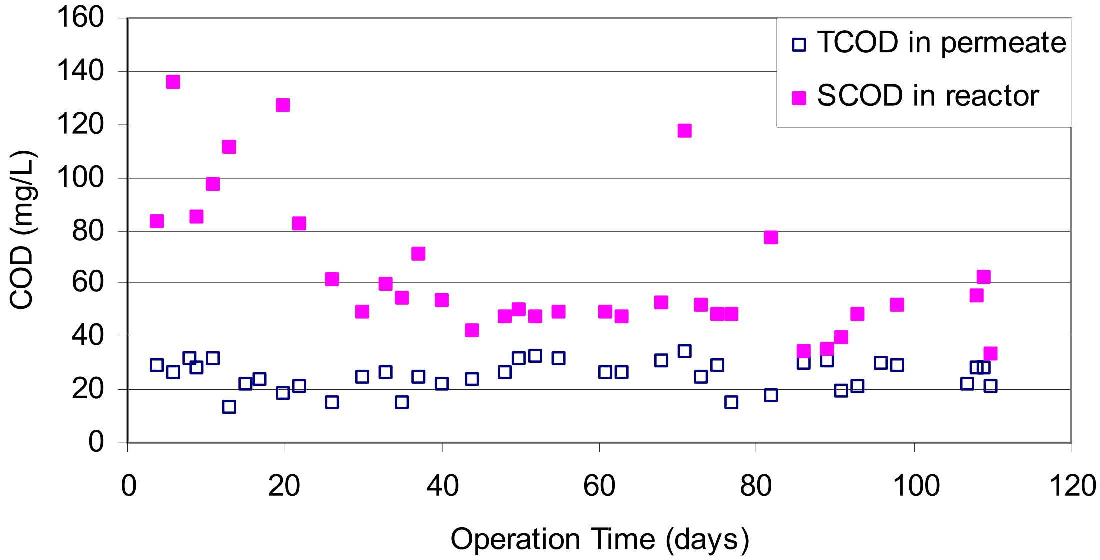
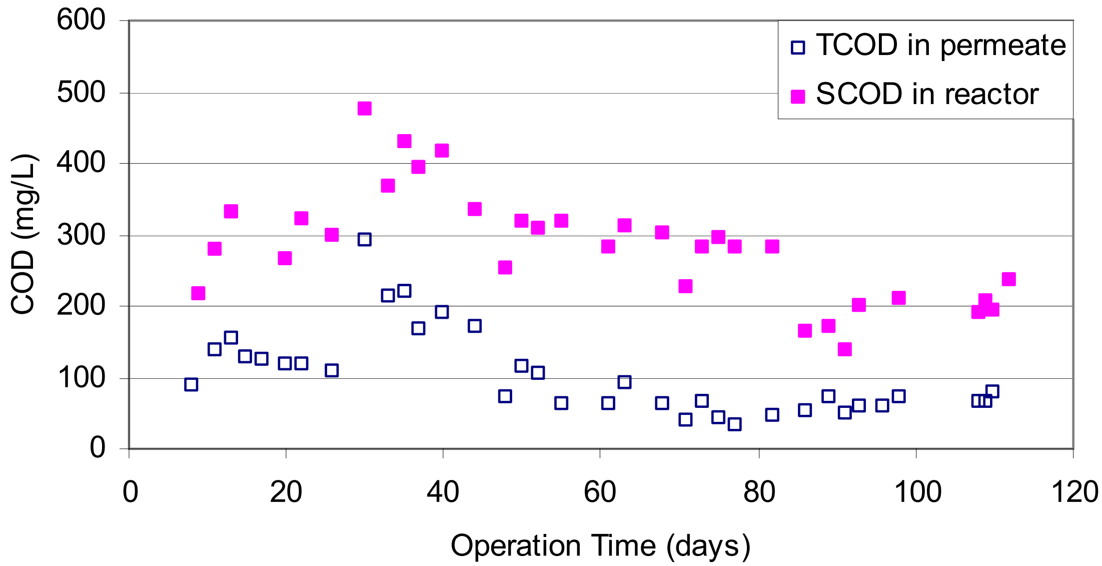


Figure 4-1 Schematic diagram of AMBR

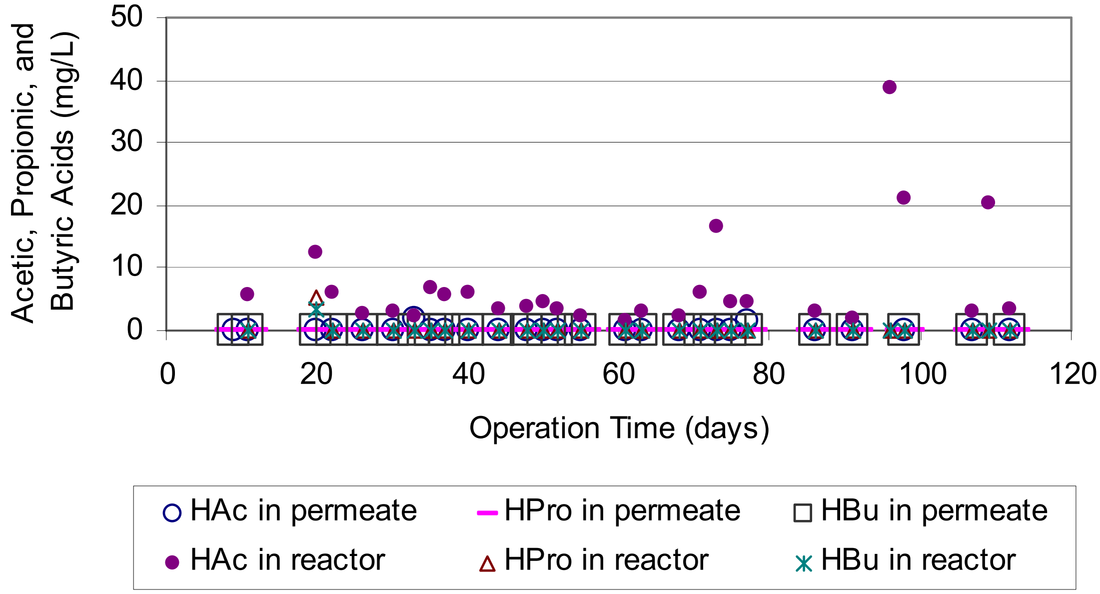


(a) AMBR 1

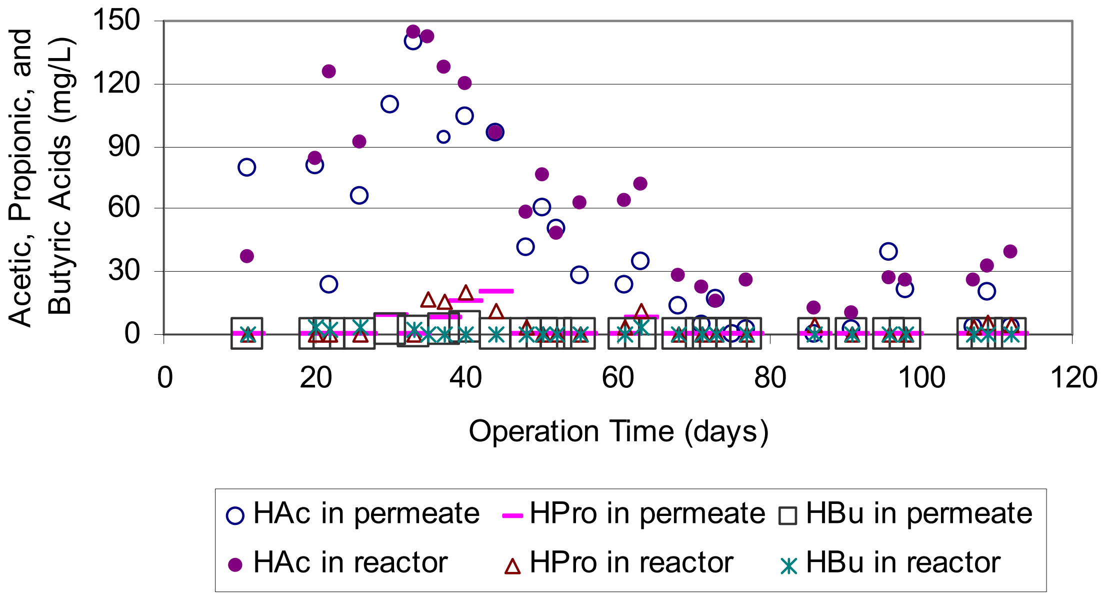


(b) AMBR 2

Figure 4-2 COD in reactor and permeate

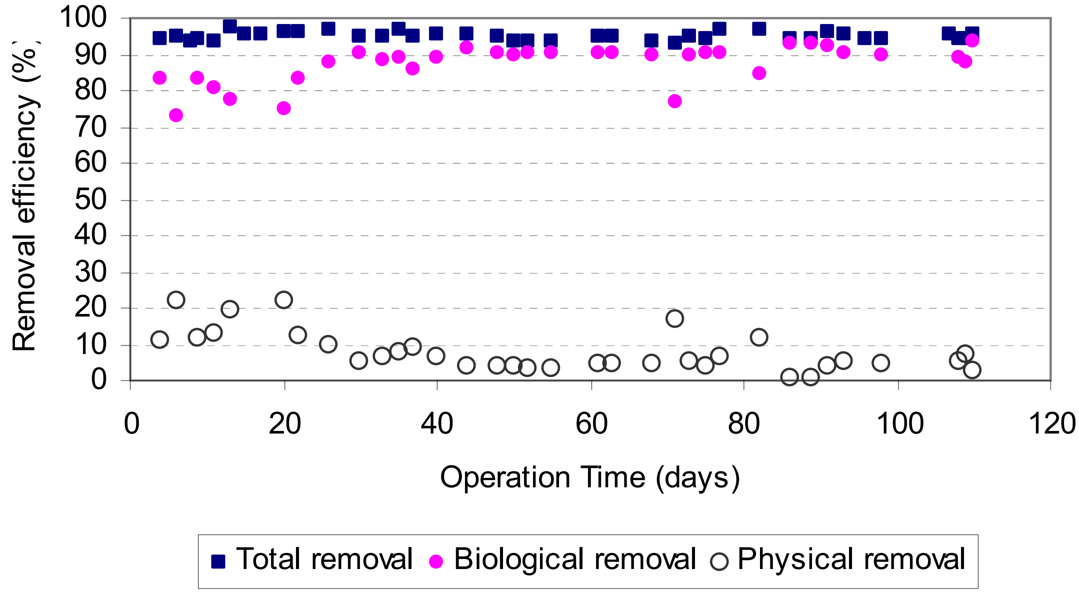


(a) AMBR 1

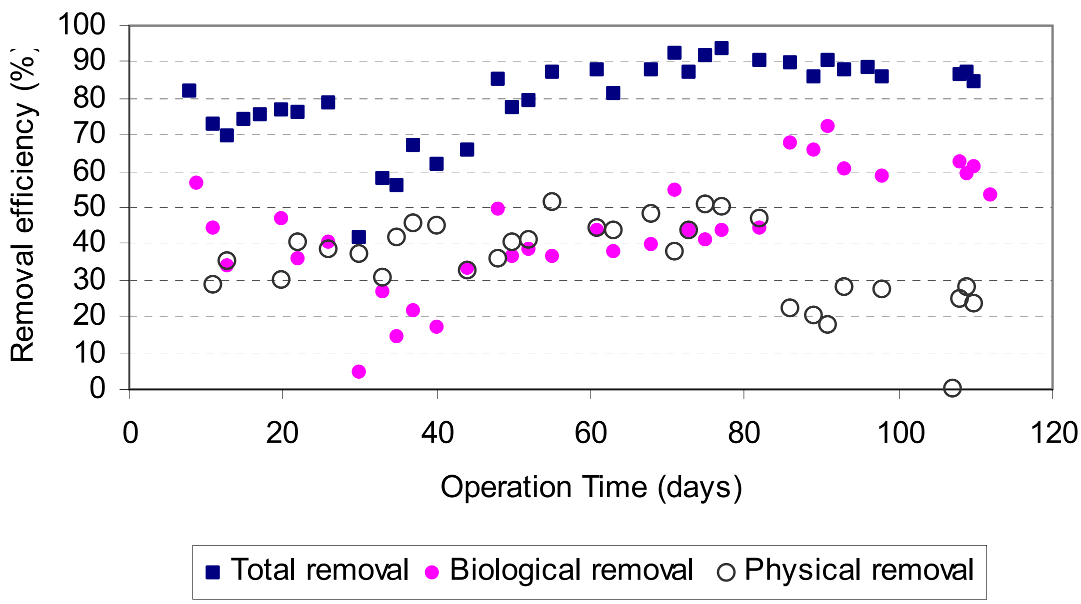


(b) AMBR 2

Figure 4-3 VFAs in reactor and permeate

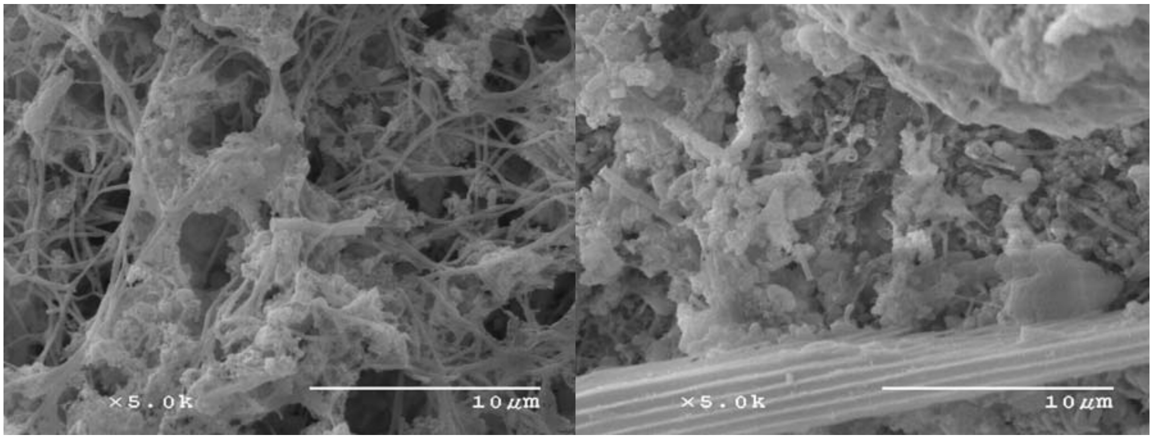


(a) AMBR 1

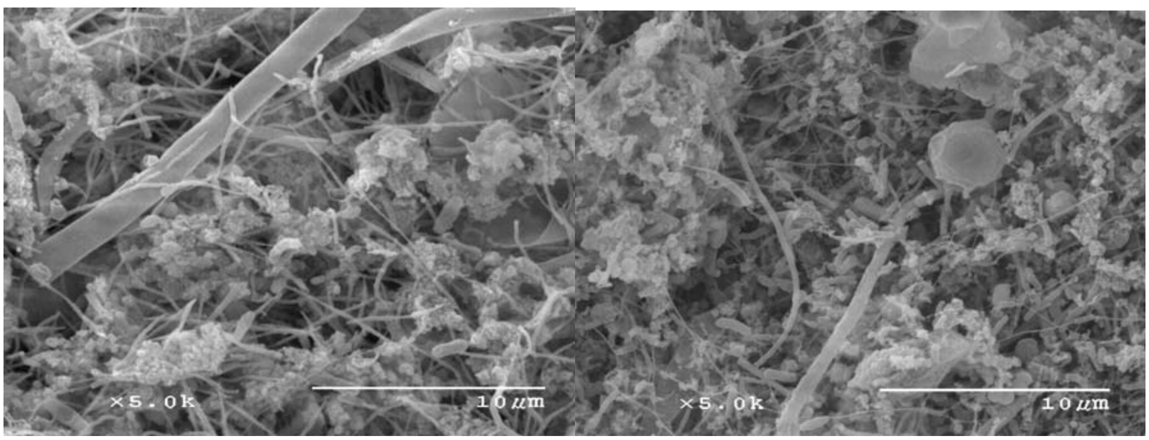


(b) AMBR 2

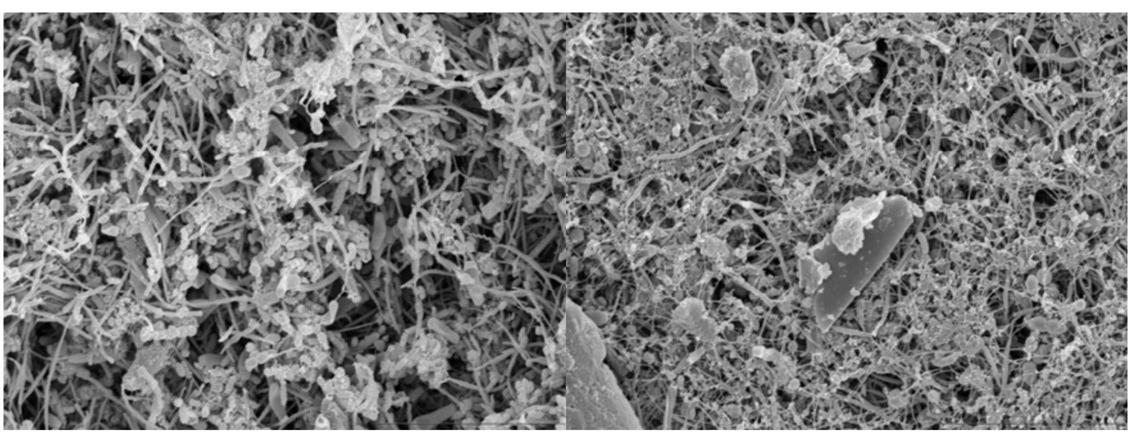
Figure 4-4 COD removal efficiency



(a) suspended sludge in AMBR 1 at day 30 (b) suspended sludge in AMBR 2 at day 30

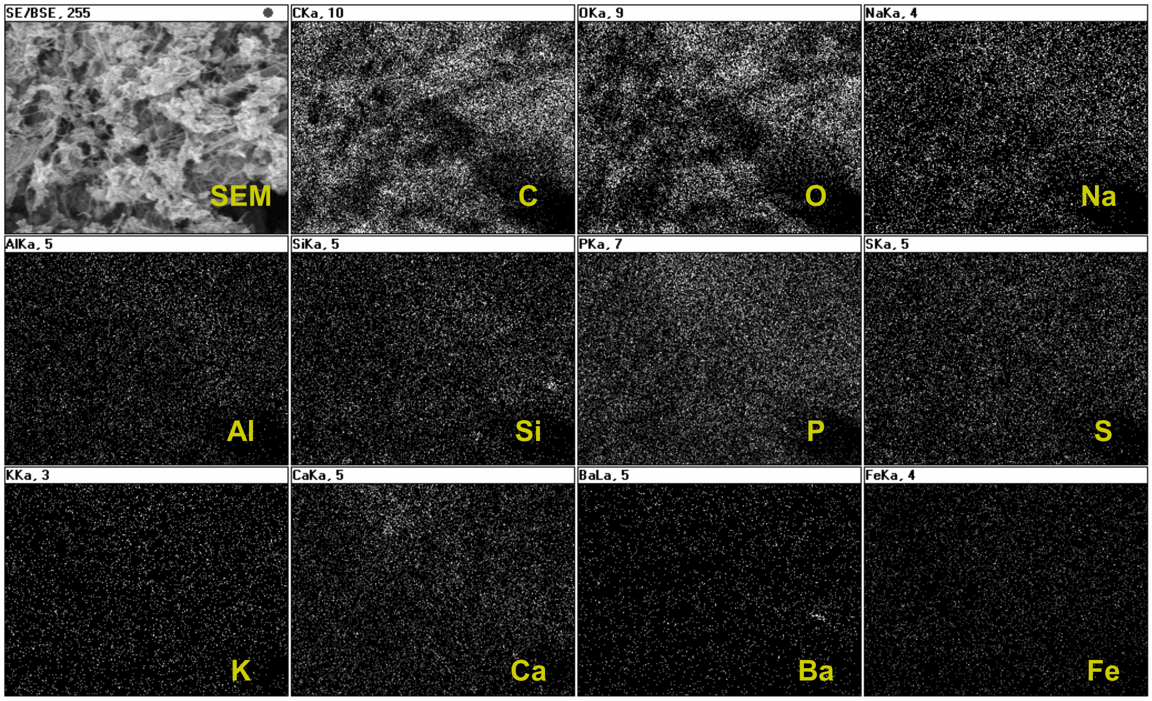


(c) attached sludge in AMBR 1 at day 30 (d) attached sludge in AMBR 2 at day 30

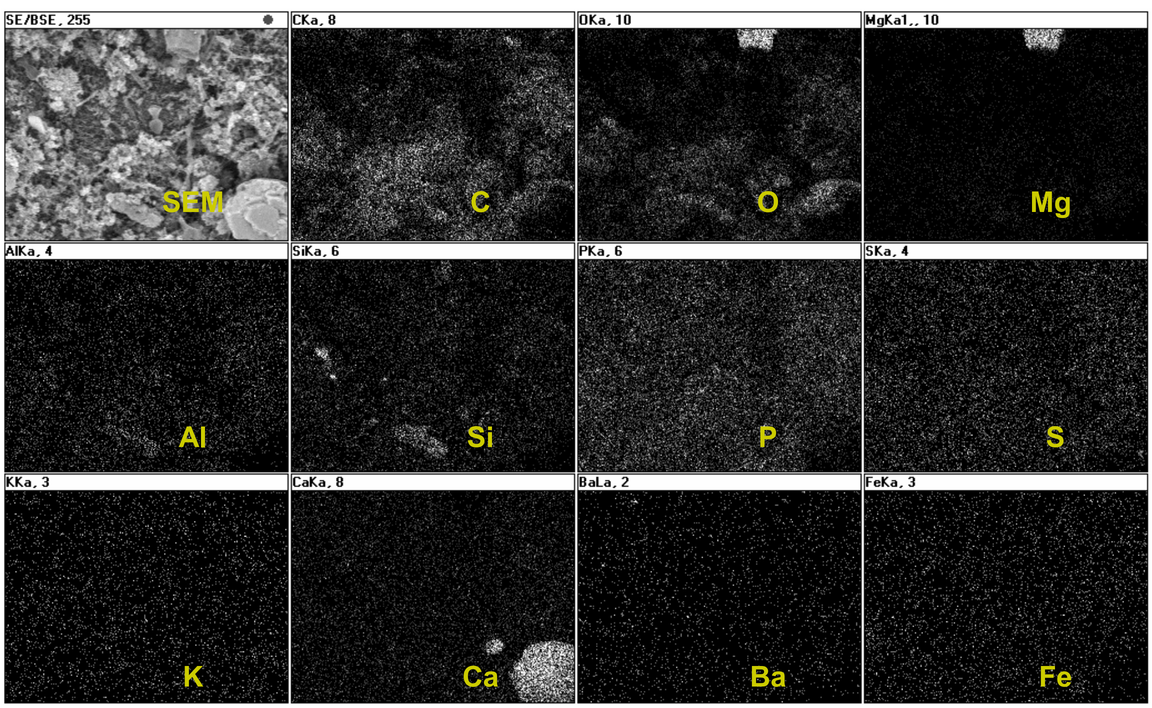


(e) attached sludge in AMBR 1 at day 60 (f) attached sludge in AMBR 2 at day 60

Figure 4-5 SEM photographs of suspended and attached sludge in AMBR



(a) cake surface of AMBR 1



(b) cake surface of AMBR 2

Figure 4-6 X-ray mapping by EDS

Table 4-1 Composition of extracted EPS

		AMBR 1		AMBR 2	
		Suspended	attached	suspended	attached
Protein (mg/g VSS)	Day 0	51.5	NA	51.5	NA
	Day 15	33.9	NA	26.0	NA
	Day 30	27.4	6.8	31.5	10.0
	Day 45	33.2	8.1	18.5	17.9
	Day 60	35.4	4.6	17.5	3.4
	Day 75	34.5	4.9	10.1	11.6
	Day 90	34.3	5.7	10.8	8.0
Carbohydrate (mg/g VSS)	Day 0	26.4	NA	26.4	NA
	Day 15	15.2	NA	8.5	NA
	Day 30	5.8	2.4	20.0	4.7
	Day 45	5.4	5.1	14.9	6.7
	Day 60	6.5	5.8	10.5	1.5
	Day 75	6.2	2.7	4.1	3.3
	Day 90	4.0	7.0	8.9	2.2
Protein / Carbohydrate	Day 0	1.9	NA	1.9	NA
	Day 15	2.2	NA	3.0	NA
	Day 30	4.7	2.8	1.6	2.1
	Day 45	6.2	1.6	1.2	2.7
	Day 60	5.5	0.8	1.7	2.2
	Day 75	5.6	1.9	2.4	3.5
	Day 90	8.5	0.8	1.2	3.7

NA: not analyzed

Table 4-2 AMBR sludge characteristics during SMA test

		Day 1	Day 15	Day 30	Day 45	Day 60	Day 75
AMBR1	*Suspended*						
	TSS (g/L)	11.2	11.9	11.6	7.5	7.2	7.1
	VSS (g/L)	7.4	8.0	8.0	5.0	4.9	5.0
	Ratio	0.66	0.67	0.69	0.67	0.69	0.71
	Attached						
	TSS (g/m^2)			23.2	42.2	30.9	18.7
	VSS (g/m^2)			17.1	33.2	24.7	15.6
	Ratio			0.73	0.79	0.8	0.84
AMBR2	*Suspended*						
	TSS (g/L)	10.7	11.3	12.3	11.7	12.4	13.0
	VSS g/L)	7.1	7.3	8.5	8.1	8.8	9.5
	Ratio	0.67	0.65	0.69	0.69	0.71	0.73
	Attached						
	TSS (g/m^2)			19.9	14.5	11.1	12.5
	VSS (g/m^2)			15.7	10.5	8.7	10.3
	Ratio			0.79	0.73	0.78	0.82

Table 4-3 Summary of SMA (ml CH_4 / g VSS d @STP) of AMBR sludge

Sludge		Temp(°C)	Day 1	Day 15	Day 30	Day 45	Day 60	Day 75
AMBR1	suspended	25	51.8	59.7	54.2	66.5	67.8	65.7
		15	NA	NA	NA	47.6	48.3	42.0
	attached	25	51.8	NA	43.9	40.7	32.0	25.4
AMBR2	suspended	25	NA	NA	NA	44.6	46.5	39.3
		15	8.1	7.0	8.7	10.9	11.2	16.5
	attached	15	8.1	NA	3.1	2.6	2.5	NA

NA: not analyzed

Table 4-4 Comparison of acetoclastic SMA in different anaerobic processes

Reactor type	Feed type	Con'c (g/L)	OLR (g/L/d)	Operation Temp. (°C)	SMA test temp. (°C)	Sludge type	SMA (ml CH_4 / g VSS day)	Reference
FBR	Sucrose + skimmed milk	2	5	30	35	Biofilm	252	Araki *et al*. (1994)
CSTR	″	20	0.67	″	″	suspended	66.5	″
AMBR	Brewery	80-90	0.7-1.5	36 ± 1	36 ± 1	Suspended	50	Ince *et al*. (1995)
UASB	Sewage	0.35	0.35	9.7 - 27.1	30	Granule	78	Sumino *et al*. (2007)
″	″	″	″	″	10	Granule	1.75	″
EGSB + AF	Whey	1	0.5-1.3	12-20	37	Granule	199.7	McHugh *et al*. (2005)
″	″	″	″	″	″	Biofilm	12.9	″
″	″	10	5-13.3	12-20	″	Granule	60.2	″
″	″	″	″	″	″	Biofilm	18.3	″
ASBR	NFDM	0.6	1.2	25	35	Granule	847	Banik *et al*., (1997)
″	″	″	″	15	″	Granule	777	″
UASB	Domestic wastewater	0.325	1.6	20.5 ± 0.4	20.5 ± 0.4	Granule	14	Álvarez *et al*., (2006)
UASB + AF	Sucrose	10	20	16 – 37	37	Granule	32.2	McHugh *et al*. (2004)
″	″	″	″	″	22	Granule	21.2	″
″	″	″	″	″	15	Granule	14.7	″
″	″	″	″	″	37	Biofilm	16.8	″
″	Acetate, ethanol, butyrate	10	20	16 – 37	37	Granule	151.7	″
″	″	″	″	″	22	Granule	59.7	″
″	″	″	″	″	15	Granule	26.4	″
″	″	″	″	″	37	Biofilm	15.5	″
AMBR	NFDM, acetate, starch	0.5	1	25	30	Suspended	114.8	This study
″	″	″	″	″	25	Suspended	65.7	″
″	″	″	″	″	15	Suspended	42.0	″
″	″	″	″	″	30	Attached	41.0	″
″	″	″	″	″	25	Attached	25.4	″

FBR: Fluidized bed reactor, CSTR: Completely stirred tank reactor, AMBR: Anaerobic membrane bioreactor: EGSB: Expanded granular sludge bed reactor, AF: Anaerobic filter, ASBR: Anaerobic sequencing batch reactor, UASB, Upflow anaerobic sludge bed reactor

CHAPTER 5. ANAEROBIC MEMBRANE BIOREACTOR TREATMENT OF SYNTHETIC MUNICIPAL WASTEWATER

A paper to be submitted to Water Environment Research

Jaeho Ho, Shihwu Sung*

Abstract

The performance of a cross-flow anaerobic membrane bioreactor (AMBR) to treat synthetic municipal wastewater was investigated at different HRTs. AMBR was operated at COD loading rates of 1-2 kg COD/m^3·d for 280 days. Permeate TCOD concentration was always less than 40 mg/L, and no noticeable VFAs were detected regardless of HRT variations, while SCOD was accumulated in the reactor with decreases in HRT. The particle size reduction was relatively less than other studies reported even after long operation time due to the low operation CFV. Approximately 30% of COD was not available for methane recovery irrespective of applied HRTs, due to the COD loss by dissolved methane, sulfate reduction, and untreated COD in the permeate. The fraction of methane recovered from the synthetic municipal wastewater decreased from 48% to 35% with the decrease of HRT from 12 to 6 h due to the increase of mixed liquor SCOD which was rejected and accumulated in the AMBR. Therefore, AMBR operation with relatively long HRT and SRT may be favorable in order to enhance methane recovery and reduce or eliminate sludge production.

Keywords: anaerobic membrane bioreactor (AMBR), hydraulic retention time (HRT), ambient temperature, methane production, synthetic municipal wastewater.

Introduction

Anaerobic process has become immensely popular for municipal and industrial sludge digestion and high strength wastewater treatment because of several inherent merits, such as high loading rates, generation of valuable methane gas, less sludge production and less energy consumption. However, anaerobic process is not a panacea for treating all types of wastewater, especially low strength wastewater at low temperatures, due to relatively low biomass yield. Recent advances in high rate anaerobic technology have expanded its applicability into low strength wastewater, which has previously been largely treated by aerobic processes. High rate anaerobic processes such as up-flow anaerobic sludge blanket (UASB), expanded granular sludge blanket (EGSB), anaerobic filter (AF), anaerobic fluidized bed reactor (AFB), and anaerobic sequencing batch reactor (ASBR) can maintain significantly higher solids retention time (SRT) irrespective of hydraulic retention time (HRT) to overcome low biomass yield. The UASB and EGSB processes have been widely adopted among all these reactor configurations due to their superior performance (Seghezzo *et al.*, 1998). Lettinga (1995) asserted that EGSB would be a sustainable alternative for a high rate anaerobic process under psychrophilic conditions due to its very high substrate affinity. There are many full scale anaerobic treatment plants in tropical countries such as India, Colombia, and Brazil. However, post-treatment of the effluent from anaerobic process is required to satisfy discharge standards (Seghezzo *et al.*, 1998). In addition, these systems require meticulous process control to achieve and maintain sludge granulation. Under unfavorable environmental conditions, granules disintegrated, which led to irreversible reactor failure (Connaughton *et al.*, 2006).

Membrane bioreactors (MBRs) are becoming increasingly popular for municipal wastewater treatment lately. In MBR, membrane modules are coupled with bioreactors in order to retain the biomass in the reactor. MBR also provides superior effluent quality for potential reuse and recycling (Melin *et al.*, 2006). MBR systems can be classified into two categories: external or cross-flow type, and internal or submersible type. The development of submersible MBR systems using coarse bubble aeration and materials improvement significantly reduced the operational cost (Yamamoto *et al.*, 1989; Judd *et al.*, 2003). There are over 500 large scale MBR systems currently in operation worldwide (Trussell *et al.*, 2005). However, anaerobic membrane bioreactors (AMBRs) have not been widely studied, mainly due to the difficulty of membrane maintenance and fouling control. Moreover, the current breakthrough in the MBR process has hindered the further development of the AMBR system. AMBR has been gaining attention as a means to treat low strength wastewater using different membrane module configurations including internal or submerged type (Chu *et al.*, 2005; Hu *et al.*, 2006), and external or cross-flow type (Baek *et al.*, 2006; Ho *et al.*, 2007). The AMBR system should adopt a suitable membrane module for easy maintenance, because the bioreactor should sustain an anaerobic condition regardless of membrane maintenance. From this point of view, external type modules could be more appropriate than the submersible membrane modules which are commonly adopted for MBR. However, operation cost for these modules is higher than for the internal type due to the circulation of mixed liquor to provide turbulent flow on the membrane surface to retard particle deposition. This study was carried out to investigate the performance of AMBR coupled with external membrane modules to treat synthetic municipal wastewater at different HRTs and ambient temperature.

Materials and Methods

AMBR set-up

A laboratory-scale anaerobic reactor (BIOFLOW 2000 FERMENTOR, New Brunswick Scientific, NJ, USA) with 4 liters of working volume was run at 25°C. The anaerobic reactor was equipped with pH and oxidation-reduction potential (ORP) monitoring units (pH2100, Mettler Toledo, Germany), and a level sensor to control permeate rate. It was coupled to a tubular poly-tetrafluoroethylene (PTFE) microfiltration membrane with a pore size of 1μm (supplied by KNH Co. Ltd., Taiwan).

Synthetic municipal wastewater

Synthetic municipal wastewater was prepared to represent municipal wastewater. The characteristics of the prepared wastewater were modified from that of Syntho, which was developed to represent pre-settled domestic wastewater (Nopens *et al.*, 2001). The synthetic municipal wastewater was composed of non-fat dry milk (NFDM) (270 mg/L), soluble starch (130 mg/L), $NaCH_3COO$ (80 mg/L), yeast extract (20 mg/L), NH_4Cl (76 mg/L), urea (43 mg/L), KH_2PO_4 (44 mg/L), and $KHCO_3$ (600 mg/L). Accordingly, the influent COD, TN, TP, and alkalinity were 500, 40, 10, and 300 mg/L, respectively. The properties of NFDM and required trace elements prepared for the synthetic municipal wastewater can be found elsewhere (Dague *et al.*, 1998). Synthetic wastewater was prepared every alternate day and stored in a 4°C cold storage room to minimize biodegradation.

Analytical Methods

Volatile fatty acids (VFAs) were measured by high performance liquid chromatography (HPLC, DX 500, Dionex, CA, USA) with a column for detecting organic acids (MethCarb 67H HPLC column, Varian, CA, USA). Chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), and sulfide were determined as per Standard Methods (APHA, 1998). To measure the mixed liquor SCOD and VFAs, mixed liquor collected from the reactor was first centrifuged at 12,000 G for 10 min. The supernatant was further filtered through a 0.22μm filter. Mixed liquor was collected in a bottle containing alkaline solution to conserve sulfide in the liquid phase to measure mixed liquor and permeate sulfide. Sulfide COD was determined by the difference between before and after desulphurization. A wet-test gas meter (Schlumberger Industries, Dordrecht, The Netherlands) was used to measure biogas production. Gas composition was analyzed using Gas Chromatography (Series 350, GOW-MAC Co., NJ, USA). The microscopic observation of the surface of the fouled membrane was carried out using a scanning electron microscope (SEM, Hitachi S2460-N, Hitachi, Japan). Particle size distribution was analyzed using a light scattering instrument (Hydro 2000, France).

AMBR operation

Initially, the anaerobic reactor was filled with 1 L of AMBR sludge (10 g/L) previously operated at 25°C for 9 months, and 1 L of concentrated mesophilic sludge (30 g/L) obtained from a secondary anaerobic digester in a local municipal wastewater treatment plant, after which it was finally diluted to about 10 g/L with tap water. Operation temperature was maintained at 25°C ± 1°C using a heating and cooling loop. Table 1 shows operational conditions of AMBR. HRTs decreased from 12 h to 6 h; corresponding organic loading rate increased from 1 to 2 kg COD/m^3·d. The operation flux was set to 5 L/m^2/h with a TMP of 1 to 8 psi and a CFV of 0.1 to 0.2 m/s. The mixed liquor pH was not controlled but ranged from 6.8 to 7.1. The permeate pH was somewhat higher than that of mixed liquor, and ranged from 7.3 to 7.9, as shown in Figure 1 (a). Although pH was not controlled, the pH levels in the reactor did not affect successful anaerobic degradation of organics. During the start-up period at run 1, back flushing using permeate was carried out to restore flux at every 4 to 6 days. Moreover, the cake accumulated on the membrane surface was sloughed off by brushing at every 15 days. Chemical cleaning with hypochlorite was carried out every 1-2 weeks and twice a week during run 2 and 3, respectively. Stable effluent alkalinity was observed during the operation, as shown in Figure 1 (b). Influent alkalinity was slightly higher than the alkalinity stated in the recipe of synthetic municipal wastewater, because the wastewater was prepared using tap water which contained additional alkalinity. The ORP in the reactor varied from -220 to -270mV.

Results and Discussions

Organic removal

HRT and SRT are important parameters for the operation of AMBR, which affects bioreactor performance as well as membrane performance. A couple of hours of HRT would be enough for the treatment of low strength wastewater, while a couple of days or even more than 100 days of SRT may be required for the slow-growing anaerobic microorganisms. Therefore, AMBR was operated at short HRT and prolonged SRT in this study, which is a great advantage of MBR or AMBR. Figure 1 shows the variations of mixed liquor SCOD and permeate TCOD. There is a remarkable difference between mixed liquor SCOD and permeate TCOD. The reactor SCOD increased with decreases of HRT. The permeate TCOD, however, showed relative stability regardless of the fluctuation of mixed liquor SCOD. Permeate TCOD concentration was always less than 40 mg/L regardless of HRT variations. However, mixed liquor SCOD was significantly influenced by HRT increases. Mixed liquor SCOD at 12 hr HRT was 56 mg/L, while it increased to 144 mg/L when the HRT was reduced to 6 h. Harada *et al.* (1994) also found that there was a significant difference between the mixed liquor SCOD and the permeate COD, especially at reduced HRT in a CSTR coupled with a membrane unit. Chu *et al.* (2005) also reported that additional COD was removed by membrane filtration. Membrane or cake attached to the membrane surface acts as a barrier which not only retains biomass but also adsorbs or intercepts soluble matter from mixed liquor (Chang *et al.*, 2002). Figure 4 shows the COD removal efficiency of AMBR. Total COD removal efficiency was more than 90%. Physical removal rate was 20% at the early stage, but later decreased to less than 10%. Baek *et al.* (2006) reported that the average physical COD removal rate decreased from 69% to 25% in the course of operation time. Chu *et al.* (2005) also found that an additional 10% of COD was removed physically by membrane filtration. The concentration difference between mixed liquor and permeate VFAs was smaller than the COD difference, as shown in Figure 2. Propionic and butyric acid were not detected in either mixed liquor or permeate. The concentration of acetic acid in mixed liquor was around 5 mg/L and no noticeable acetic acid was detected in permeate.

Biomass inventory

The calculated SRT, based on the sludge removed from the reactor, ranged from 90 to 360 days. Despite such a long SRT, sludge concentration was not increased due to the low growth rate as well as the relatively short operation time compared to the calculated SRT. The synthetic wastewater used in this study contained no inorganic particular matter. Therefore, the ratio of MLVSS/MLSS increased up to 0.74, while the ratio was 0.59 in the initial seed sludge. Particle size distribution of seed and AMBR sludge after 283-day operation was compared. It was expected that the low operation CFV minimized hydrodynamic shear on sludge particles. Although hydrodynamic condition is indispensable for the reduction of excess cake deposition on the membrane surface, it also produces adverse effects on the cake resistance as well as on microbial activity. Therefore, it is essential to apply CFV as low as possible in terms of a trade-off between control of flux decline and maintenance of microbial activity in a cross-flow AMBR system. The particle size reduction was relatively smaller than that reported in other studies even after long operation time (Choo *et al.*, 1998). The size distribution of both sludge in this study ranged from 2.5 to 1,096 μm, as shown in Figure 5. However, the particle size distribution of AMBR sludge shifted to the left to some degree, so that the mean particle size decreased from 50.6 to 25.3 μm after 283 days' operation. Choo *et al.* (1998) reported that there was a sharp decrease of mean particle size with the course of operation time, which contributed to the greater compactness of the cake layer. Consequently, the specific cake resistance increased due to particle size reduction from 16 to 3 μm after 12-day AMBR operation at a CFV of 0.5 m/s. However, there was no significant floc breakage in submerged AMBR with a biogas sparging rate of 5 L/min (Hu *et al.*, 2006). Particle size reduction cannot be avoided thoroughly in a cross-flow AMBR system, but decreased to a certain extent under AMBR operation with low CFV.

Table 2 shows the summary of results obtained in this study. Based on the results shown in Table 2, the kinetic constants were estimated using the Monad kinetic relationship.

$$\frac{X(HRT)}{(S - S_e)} = \frac{Ks}{k \cdot S_e} + \frac{1}{k}$$

where X is mixed liquor suspended solids, Ks is half velocity constant, S is substrate concentration in the influent, and Se is substrate concentration in the effluent. The k and Ks values were 0.26 d^{-1} and 67.4 mg/l (R^2=0.9835) respectively at 25°C. The kinetic values obtained in this research were comparable with other research. Gingh *et al.* (1996) reported that the k and Ks values of UASB to treat low strength wastewater were 0.26 d^{-1} and 149 mg/l under ambient temperature. Dague *et al.* (1998), however, found the Ks and k were 1.59 d^{-1} and 219 mg/l at 25°C.

Methane production

Figure 6 shows the biogas composition and methane yield at HRTs of 12, 8, and 6 h. The biogas is composed of 70% to 75% methane and 5% to 10% carbon dioxide. The mixed liquor pH and alkalinity ranged from 6.8 to 7.1 and from 450 to 650 mg/L, respectively, which resulted in relatively low carbon dioxide content in the biogas. It should be noted that the biogas always contained nitrogen gas up to 20 %, which partly resulted from the solubility difference at different temperatures in feed and mixed liquor. Theoretically, there would be 6.3% to 8.7% nitrogen content in the head space due to the temperature change from 4 to 25°C. The observed methane yield was 0.21 to 0.22 regardless of the applied

HRTs, which is considerably lower than the theoretical value (0.382 L CH_4/g COD removed at 25°C). Dissolved methane and sulfate in feed decreased the observed methane yield. Although methane is slightly soluble in water, this could significantly influence the methane yield in anaerobic treatment of low strength wastewater. The Henry's constant of methane is 4.13×10^4 at 25°C (Perry *et al.*, 1984). Correspondingly, the methane solubility in water is 15g/L at a methane content of 70% in the head space of the reactor, which reduced the methane production rate up to 27% at an HRT of 6 h. Sulfate in the feed also decreased the methane production rate, because it can accept electrons to be reduced to sulfide by sulfate reducing bacteria (Grady *et al.*, 1999). Two grams of COD are consumed to reduce one gram of sulfate-S to sulfide-S. The feed contained sulfate of 60 to 90 mg/L, so that a COD of 40 to 60 mg/L was theoretically not available for the methane production. The calculated methane yields after considering these two adverse effects on methane production yield were 0.31, 0.32, and 0.35 L CH_4/g $COD_{removed}$ at HRTs of 12, 8, and 6 h, respectively. Sulfide produced in an anaerobic reactor by sulfate reducing bacteria can contribute non-carbonaceous COD downstream (Grady *et al.*, 1998). If the dissolved sulfide remains in the reactor, a part of the concentration differences between the mixed liquor SCOD and permeate TCOD might result. Figure 6 shows mixed liquor and permeate sulfide concentrations and the SCOD difference before and after sulfide stripping under acidic conditions. The sulfide-S concentrations were 19.9 ± 4.2 and 5.7 ± 2.6 in the reactor and permeate, respectively. The pKa of sulfide at 25°C is around 7.0, which is very close to the reactor pH range of 6.8 to 7.1. Therefore, a part of the sulfide would be ionized and reach equilibrium in the gas phase. The COD caused by sulfide was 22.9 ± 17.8 and 5.1 ± 0.7 in the reactor and in the permeate, respectively. Although the permeate pH ranged from 7.1 to 7.8, most of the sulfide was removed through membrane filtration by either hydrogen sulfide stripping or sulfur precipitation on the outer surface of the membrane.

Figure 7 shows the COD mass balance of AMBR operated at HRTs of 12, 8, and 6 h. Total COD mass in the system consisted of COD untreated and accumulated either on the membrane surface or in mixed liquor (CODreactor), COD in permeate (CODpermeate), COD converted into methane in the gas phase (CODmethane-gas) and the liquid phase (CODmethane-liquid), and COD consumed for sulfate reduction (CODsulfate). CODmethane-liquid and CODsulfate account for 13% and 10% of the COD input in the system, which captures a significant slice of the total COD mass. CODpermeate comprised 6% to 8% of the total COD input. Therefore, approximately 30% of COD was not available for methane recovery irrespective of applied HRTs. However, the fraction of methane recovery decreased from 48% to 34.5% with a decrease of HRTs from 12 to 6 h. Maximum possible methane recovery, taking methane solubility, sulfate reduction, and cell synthesis into account, would be approximately 50% to 60% at HRTs of 12 or longer. The untreated COD which was rejected and accumulated on the membrane surface increased as the operational HRT decreased. Zero net biomass growth and no accumulation of inorganic materials were observed in an MBR with complete sludge retention at a COD loading rate of 1.2 g COD/L d after 180 days of operation and maintained for more than 150 days (Laera *et al.*, 2005). However, MBR operation with a long SRT would be costly due to the high aeration volumes (Ghyoot *et al.*, 1999). Although AMBR has been successfully operated at HRTs of 6 - 12 h, the increment of untreated COD resulted in a decrease of methane recovery in this study. From this point of view, AMBR operation with relatively long HRT and SRT can maximize methane recovery and reduce or eliminate sludge production. Long-term study is needed to evaluate the reactor and membrane performance at prolonged SRT in order to maximize methane recovery and minimize sludge production.

Conclusions

A lab-scale AMBR coupled with an external membrane module was successfully operated at relatively long SRT and low CFV, which contributed to less sludge production and less particle size reduction, respectively. The permeate quality was excellent regardless of HRT variations, with more than 90% of COD removal at an HRT of 6 h. However, the reactor performance deteriorated with decreases in HRT from 12 to 6 h due to the low k (0.26 d^{-1}) and high Ks (67.4 mg/l) values. The physical removal on the membrane surface compensated for the decreased biological removal rate up to 25% at an HRT of 6 h. The observed methane yield was 0.21 to 0.22 regardless of the applied HRTs due to the COD loss by dissolved methane and sulfate reduction. The calculated methane yields after considering COD loss were 0.31, 0.32, and 0.35 L CH_4/g $COD_{removed}$ at HRTs of 12, 8, and 6 h, respectively. The fraction of methane recovered from the synthetic municipal wastewater decreased with the decrease in HRT due to the increase of accumulated SCOD in the reactor. Maximum possible methane recovery, taking methane solubility, sulfate reduction, and cell synthesis into account, would be approximately 50% to 60% at HRT of 12 h or longer.

References

American Public Health Association/American Water Works Association/Water Environmental Federation (1998) Standard Methods for the Examination of Water and Wastewater, 20th ed., Washington DC, USA.

Baek, S.H., Pagilla, K.R., 2006. Aerobic and anaerobic membrane bioreactors for municipal wastewater treatment. *Wat. Environ. Res*. 78, 133-140.

Chang, I.-S., Clech, P. L., Jefferson, B., Judd, S., 2002. Membrane fouling in membrane bioreactors for wastewater treatment. *J. Environ.Engr*. 128, 1018-1029.

Choo, K.H., and Lee, C.H. (1998) Hydrodynamic behavior of anaerobic biosolids during crossflow filtration in the membrane anaerobic bioreactor. *Wat. Res*. 32, 3387-3397.

Chu, L.-B., Yang, F.-L., Zhang, X.-W. (2005) Anaerobic treatment of domestic wastewater in a membrane-coupled expended granular sludge bed (EGSB) reactor under moderate to low temperature, *Process Biochemistry*, 40, 1063-1070.

Connaughton, S., Collins, G., O'Flaherty, V., 2006. Development of microbial community structure and activity in a high-rate anaerobic bioreactor at 18 °C. *Wat. Res*. 40, 1009-1017.

Dague, R.R, Banik, G.C., and Ellis, T.G. (1998) Anaerobic sequencing batch reactor treatment of dilute wastewater at psychrophilic temperatures. *Wat. Environ. Res*.,70, 155-160.

Ghyoot, T., Verstraete, W. (1999) Reduced sludge production in atwo-stage membrane-assisted bioreactor, *Wat. Res*., 34, 205-215.

Grady, C.P., Daigger, G.T., and Lim, H.C. (1999) Biological wastewater treatment. Marcel Dekker, Inc. New York, NY.

Harada, H., Momonoi, K., Yamazaki, S., Takizawa, S. (1994) Application of anaerobic-UF membrane reactor for treatment of a wastewater containing high strength particular organics, *Wat. Sci. Tech*., 12, 307-319.

Hu, A. Y., Stuckey, D. C. (2006) Treatment of diluted wastewater using a novel submerged anaerobic membrane bioreactor, *J. of Environ. Engr*., 190- 198.

Judd, S. and Jefferson, B. (2003) Membranes for industrial wastewater recovery and reuse. Elsevier Science Ltd., UK.

Laera, G., Pollice, A., Saturno, D., Giordano, C., Lopez, A. (2005) Zero net growth in a membrane bioreactor with complete sludge retention, *Wat. Res*., 39, 5241-5249.

Melin, T., Jefferson, B., Bixio, D., Thoeye, C., De Wilde, W., De Koning, J., van der Graaf, J., Wintgens, T. (2006) Membrane bioreactor technology for wastewater treatment and reuse, *Desalination*, 187, 271-282.

Nopens, I., Capalozza, C., and Vanrolleghem, P.A. (2001) Technical Report: Stability analysis of a systematic municipal wastewater. Dept. Applied Mathematics, Biometrics and Process Control, Universiteit Gent, Gent, Belgium.

Perry, R. H., Green, D. W., Maloney, J. O. (1984) Perry's Chemical engineers' handbook, McGraw-Hill, Inc., NY, USA.

Seghezzo, L., Zeeman, G., van Lier, J.B., Hamelers, H.V.M., and Lettinga, G. (1998) A review: The anaerobic treatment of sewage in UASB and EGSB reactors. *Bioresource Technology*., 65, 175-190.

Singh, K.S., Harada, H., and Viraraghavan, T. (1996) Low-strength wastewater treatment by a UASB reactor. *Bioresource Technology*, 55, 187-194.

Trussell, R. S., Adham, S., and Trussell, R. R. (2005) Process limits of municipal wastewater treatment with the submerged membrane bioreactor, *J. Environ. Engr*., 131, 410-416.

Yamamoto, K., Hiasa, M., Mahmood, T., and Matsuo, T. (1989) Direct solid-liquid separation using hollow fiber membrane in an activated sludge aeration tank, *Wat. Sci. Technol*., 21, 43-54.

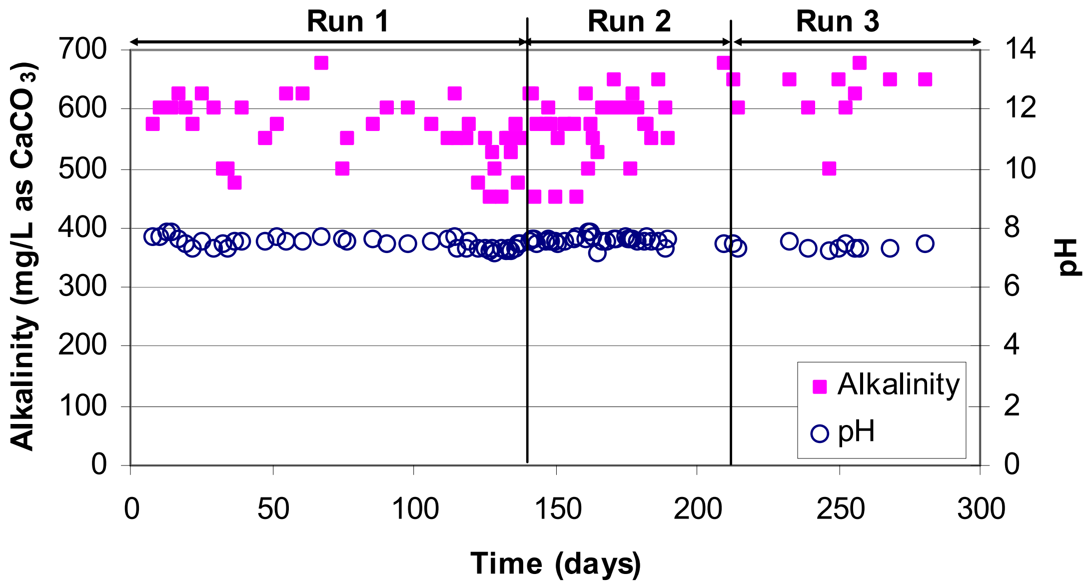
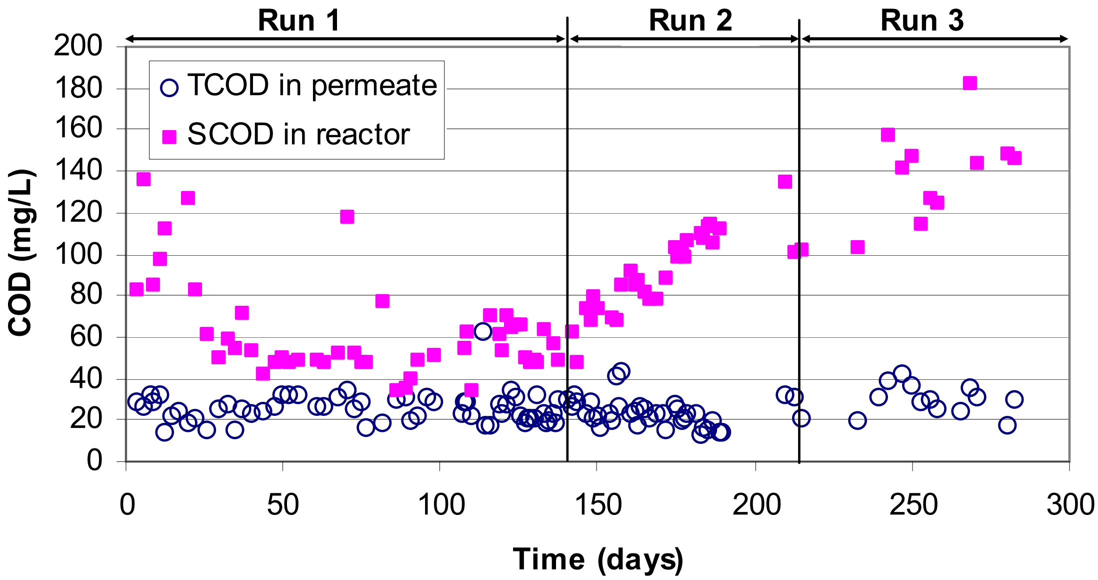
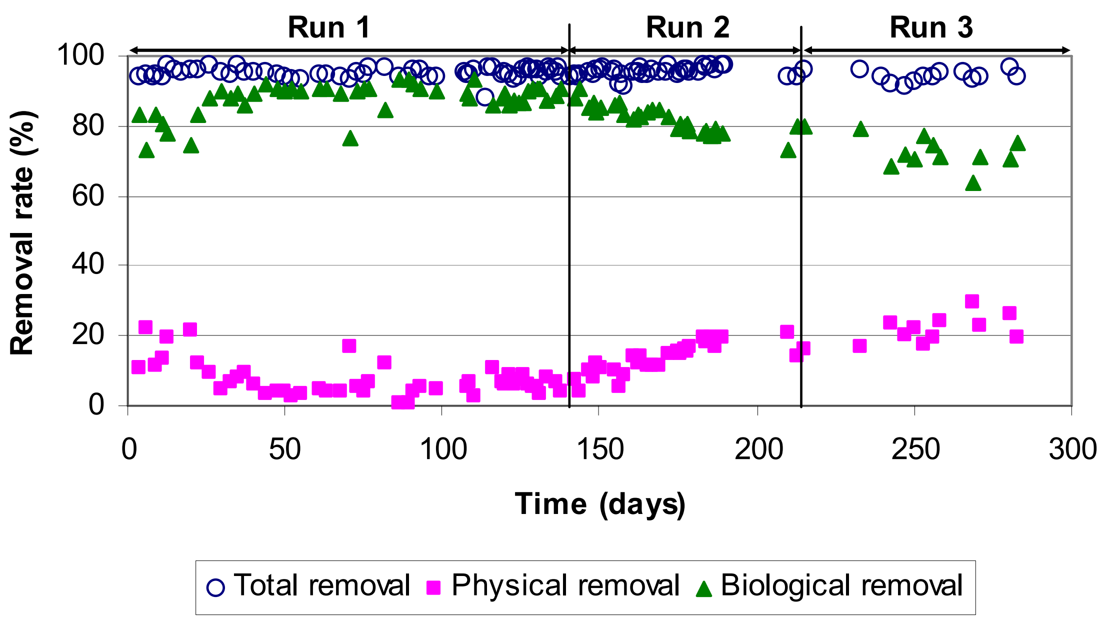


Figure 5-1 Permeate pH and alkalinity



(a) Mixed liquor SCOD and permeate TCOD



(b) Physical and biological removal rate

Figure 5-2 COD removal

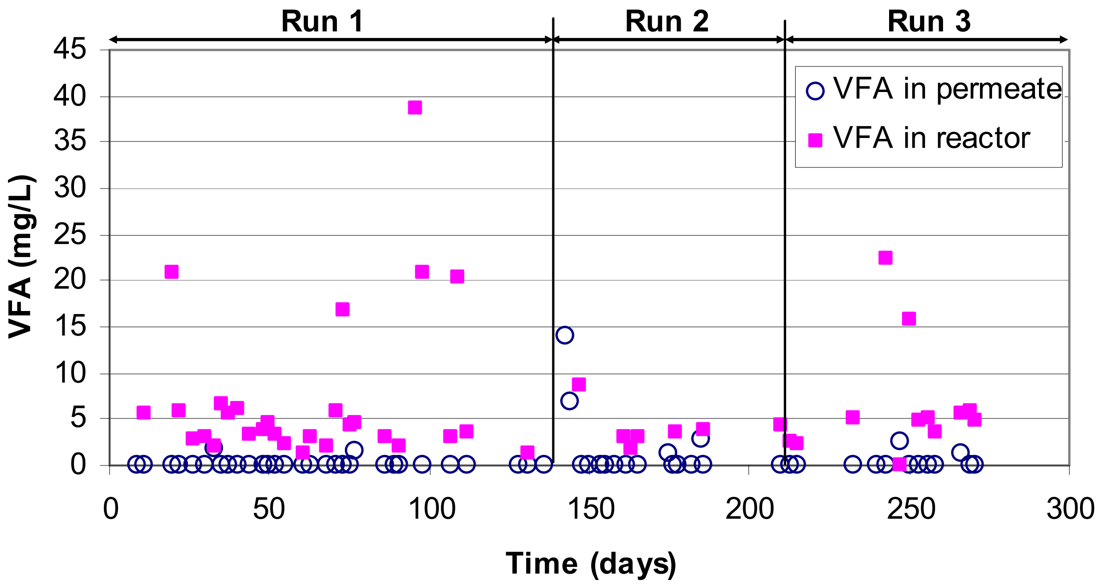


Figure 5-3 Mixed liquor and permeate VFAs

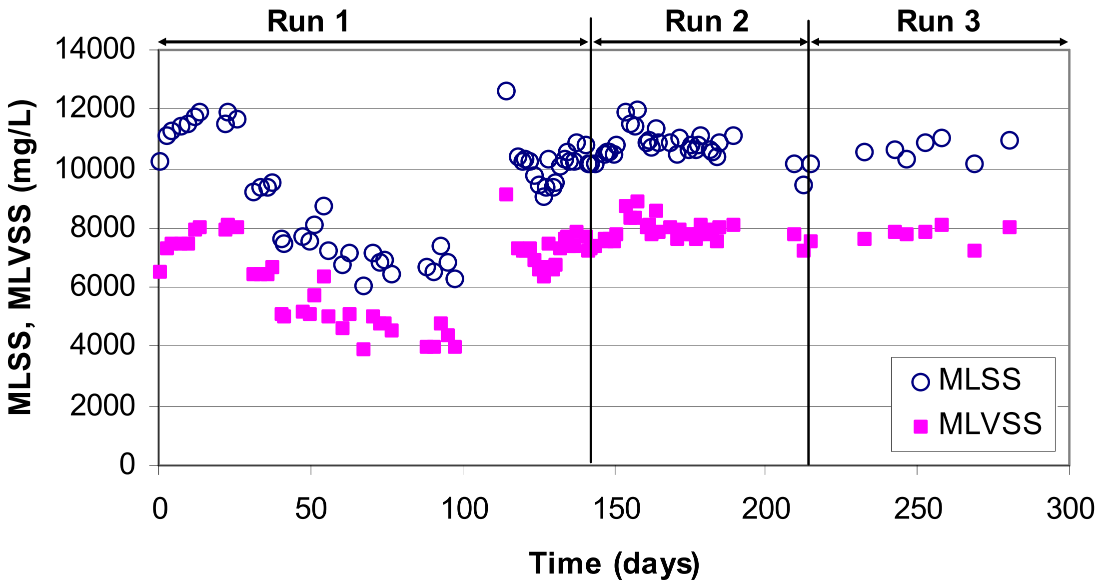


Figure 5-4 MLSS and MLVSS variation

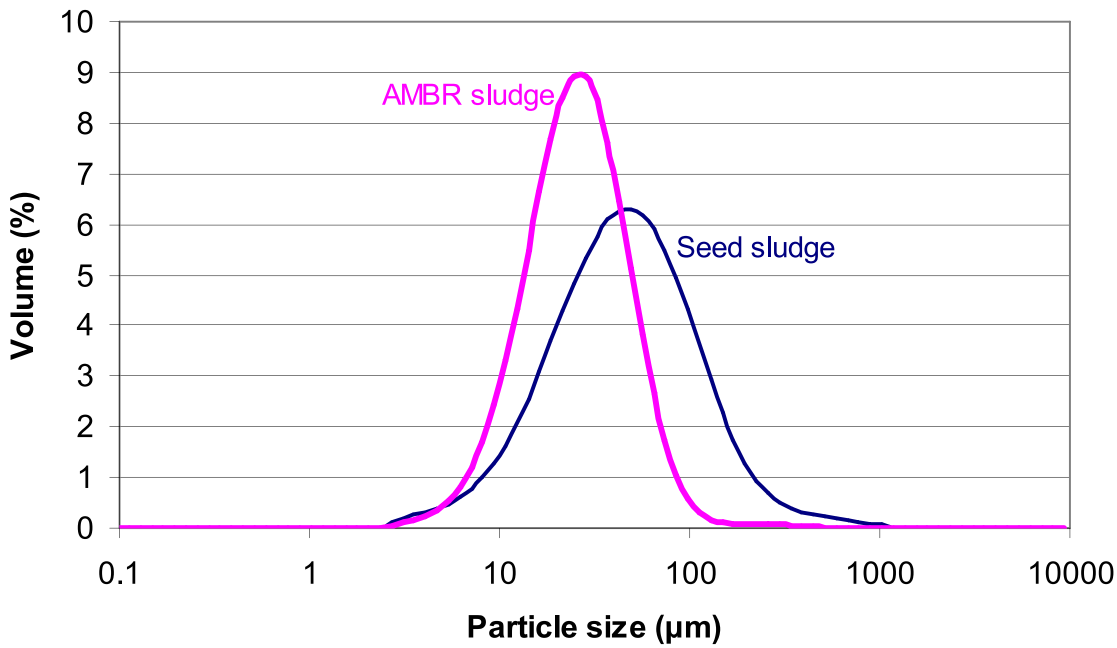


Figure 5-5 Particle size distribution

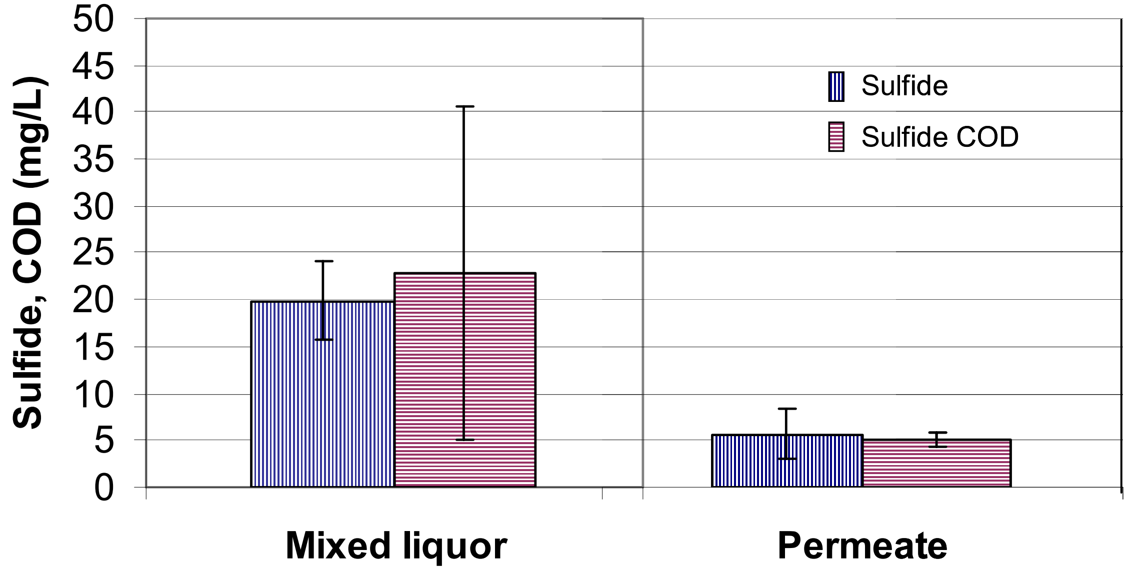


Figure 5-6 Sulfide and sulfide COD

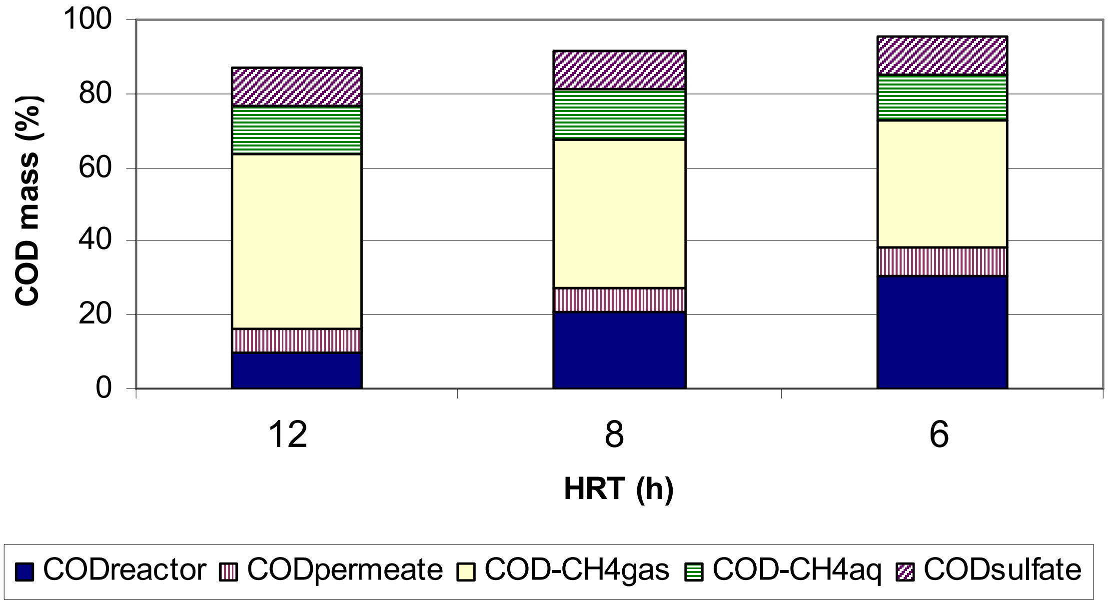


Figure 5-7 COD mass balance

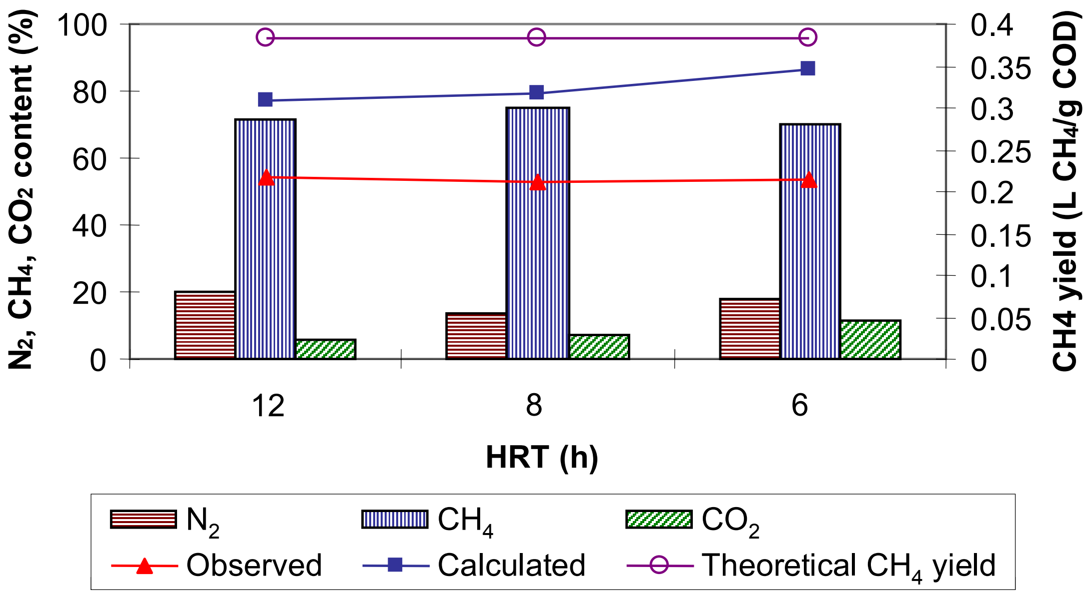


Figure 5-8 Methane production rate

Table 5-1 Operation conditions for AMBRs

	Run 1	Run 2	Run 3
Operation time (days)	1 ~ 141	142 ~ 215	216 ~ 283
HRT (h)	12	8	6
OLR (kg/m^3·d)	1	1.5	2
Flux (L/m^2/h)	5	5	8
TMP (psi)	< 5	< 5	< 8
Filtration area (m^2)	0.09	0.12	0.12

Table 5-2 Summary of AMBR performance

	Run 1	Run 2	Run 3
HRT (h)	12	8	6
MLSS (mg/L)	10,370 ± 444	10,660 ± 220	10,610 ± 360
MLVSS (mg/L)	7,490 ± 310	7,780 ± 190	7,780 ± 310
Mixed liquor SCOD (mg/L)	55.9 ± 7.3	103.2 ± 4.7	143.7 ± 10.6
Permeate TCOD (mg/L)	24.9 ± 3.9	20.4 ± 5.1	30.1 ± 9.4
Total removal rate (%)	95.0 ± 0.8	95.9 ± 1.0	93.8 ± 1.9
Biological removal (%)	88.8 ± 1.5	79.4 ± 0.9	70.4 ± 4.4
Physical removal (%)	6.2 ± 2.2	16.5 ± 1.7	23.4 ± 4.4

CHAPTER 6. EFFECTS OF SOLID CONCENTRATIONS AND CROSS-FLOW HYDRODYNAMICS ON SLUDGE FILTRATION IN AN ANAEROBIC MEMBRANE BIOREACTOR

A paper to be submitted to Journal of Membrane Science

Jaeho Ho and Shihwu Sung

Abstract

The filtration characteristics of anaerobic sludge suspension containing different solid contents were investigated. The initial rapid flux decline was in good agreement with standard blocking filtration law, while the latter gentle flux decline is attributable to the cake filtration law, which represented a Class II type dynamic membrane. The highest pseudo-steady state flux and lowest normalized flux reduction were observed at TS concentration of 13-17 g/L. Consequently, the lowest plugging constant of cake filtration (K_c) was observed at around 13 to 20 g/L TS. The influence of CFV on flux was somewhat different depending on the TS concentration. The highest initial flux was observed at 30 g/L regardless of CFV. However, the increased CFV influenced the pseudo-state flux more significantly at low or high TS concentration. Anaerobic sludge suspension which had been filtered previously at CFV of 0.1-0.7 m/s had a lower flux than fresh anaerobic sludge suspension at the same CFV, because the higher shear force increased the concentration of SMP and decreased the mean particle size in anaerobic sludge suspension. The extractable EPS content in anaerobic sludge, however, was not changed regardless of applied CFV.

KEYWORDS: filtration law, cross-flow velocity (CFV), extracellular polymeric substances (EPS), soluble microbial products (SMP), anaerobic membrane bioreactor (AMBR)

Introduction

Membrane bioreactors (MBRs) are becoming increasingly popular for municipal wastewater treatment. Since 1990, the development of a submersible MBR system using coarse bubble aeration significantly reduced operational costs [1]. There are over 500 large-scale MBR systems currently in operation worldwide [2]. However, membrane fouling hinders widespread use of MBR processes, because membrane fouling in the MBR process is complex and different in each case. Fouling in MBR for wastewater treatment has been extensively reviewed [3, 4, 5, 6, 7]. There are many variables affecting membrane fouling, e.g., membrane properties, solid content, solid retention time (SRT), hydraulic retention time (HRT), organic loading rate, trans-membrane pressure (TMP), and cross-flow velocity (CFV). Membrane fouling results from physicochemical interactions between membrane material and particles or solutes in the liquid. The main interactions are adsorption and deposition of particles and macromolecular matters on the membrane surface or inside the pore. Membrane fouling is classified into organic and inorganic fouling according to what the fouling material is. In general, organic fouling results from particle adsorption or deposition on or into the membrane, and inorganic membrane fouling is caused by the precipitation of inorganic materials such as struvite and calcium carbonate. Membrane fouling can also be divided into reversible and irreversible fouling according to flux recovery after cleaning. Reversible fouling is easily removed by suitable physical cleaning methods depending on the strength of adhesion. However, irreversible fouling is only removed by chemical cleaning.

Thus, there are two strategies to minimize membrane fouling. One is maintenance cleaning by regular or irregular short-term back flushing with or without chemicals. The other is recovery cleaning by long-term cleaning with chemicals. Sodium hypochlorite and citric acids are widely used for organic and inorganic fouling control respectively [5].

Many researchers have attempted to understand the fundamentals of flux decline and fouling mechanism in microfiltration [8,9,10,11,12] and in ultrafiltration [13,14]. Flux decline in cross-flow filtration appears to be due to two distinct independent mechanisms: pore plugging and cake deposition. The initial rapid flux decline is mainly due to pore reduction by particle adsorption on the membrane wall, and the latter gentle flux decline is due to cake deposition on the membrane surface [8]. In general, the shear force generated at the higher CFV reduced pore plugging and cake deposition. Although the increased CFV leads to higher flux, it may influence biomass characteristics, e.g. particle size, extracellular polymeric substances (EPS), and soluble microbial products (SMP), which may cause an adverse effect on membrane performance, because EPS and/or SMP have been considered major foulants in the MBR process due to their functional role related to adhesion to surfaces [15,16]. However, it is difficult to examine the true effect of operational conditions on membrane performance in the MBR process operation, because biological reaction also influences the physical properties of biological suspension. The goal of this study was to investigate the effect of solid content and hydrodynamic conditions on sludge filtration in an anaerobic membrane bioreactor.

Material and Methods

Flux test

A tubular poly-tetrafluoroethylene (PTFE) microfiltration membrane with a pore size of 1µm and total filtration surface area of 0.015m^2 (supplied by KNH Co. Ltd., Taiwan) was used in this study. Fresh anaerobic sludge stored in a refrigerator was placed in a warm water bath to adjust the temperature to 25°C before conducting the flux test. The anaerobic sludge was continuously stirred at 150 rpm and circulated through a membrane module by a peristaltic pump with a variable-speed modular drive (I/P modular pump, Cole-Parmer, IL). The flux test was performed at various TS concentrations ranging from 2 to 36g/L, CFVs of 0.1-0.7 m/s, TMP of 0.9 psi, and temperature of 25°C. The membrane was cleaned using hypochlorite after every set of flux tests. Permeate flow rate was manually measured using a graduated cylinder and a stopwatch.

Analytical Methods

Chemical oxygen demand (COD), total solids (TS), and volatile solids (VS) were determined as per Standard Methods [17]. Mixed liquor collected from the reactor was centrifuged at 12,000 g for 10 min, and then the supernatant was further filtered through a 0.22 µm microfiltration cartridge to measure SMP. EPS was extracted using CER (Dowex Marathon C, Na+ form, Dow North America, MI, USA) extraction method [18]. Collected sludge was centrifuged at 2000 g for 15 min and resuspended using nano pure water. The CER (70g CER/g VSS) was added to a bottle with a 200 ml sludge sample. The sample was stirred at 600 RPM and 4°C for 2 h. The supernatant was centrifuged at 12,000 g for 10 min to remove CER and particles. Carbohydrates and protein were measured by Anthrone and

Lowry methods with glucose and bovine serum albumin (BAS) as the standards, respectively, which were described by Frølund *et al.*[18].

Results and Discussion

Filtration model

Table 1 shows mathematical expressions of various filtration laws including complete blocking, standard blocking, intermediate blocking, and cake filtration [19,20], which were derived from a common differential equation for constant pressure filtration:

$$\frac{d^2t}{dV^2} = K\left(\frac{dt}{dV}\right)^n$$

where K and n are constant related to the mode of filtration and the operation conditions respectively, t is the filtration time, and V is filtrate volume. Filtration mode can be examined by plotting the rearranged experimental data which is the appropriate form for each filtration model shown in Table 1. These filtration laws were developed under the specific assumptions of pore plugging [14]. In practice, however, the filtration behavior is too complex to be expressed by one single filtration model [1]. Blocking filtration started with a standard law followed by complete, intermediate, and cake filtration laws, where the pore size was greater than the particle size [10]. Although the nominal pore size of the PTFE membrane used in this study was similar to the smallest particle size in the anaerobic broth, the actual pore opening estimated based on scanning electron micrograph (SEM) observation was larger than the nominal pore size measured by bubble point method. Therefore, it was assumed that the pore blocking by complete, standard, or intermediate blocking caused the initial rapid flux decline, and cake filtration governed the latter gradual flux decline. Figure

1 shows plots of rearranged experimental data for complete blocking (a), standard blocking (b), and intermediate blocking (c) at the initial filtration period, and cake filtration mode (d) at the latter filtration period. The standard blocking model which is displayed on a plot of the filtration time (t) versus filtration time/filtrate volume (t/V) is linear at short durations, while the cake filtration model, which is represented by a plot of filtrate volume (V) versus filtration time/filtrate volume (t/V) fits well at long durations. The results clearly indicate that fouling occurs by standard blocking filtration, which accounts for the initial sharp decline and cake filtration which leads to a pseudo steady-state flux. Tanny [21] also reported that pore reduction by either standard or intermediate blocking filtration causes an initial flux decline, and the latter flux behavior follows cake filtration law for Class II type dynamic membranes, which occurs where the membrane pore size is larger than the size of the particles being filtered. Flux decline was modeled from two flux decline curves which were plotted using the initial standard blocking filtration and the latter cake filtration as shown in Figure 2(a). The modeled cumulative filtrate volume was in good agreement with the collected filtration data over the different TS concentrations as shown in Figure 2(b).

Effect of solid content on flux

The flux and fouling tests at TMP of 6.2 kPa and CFV of 0.1 m/s with different solid contents showed that TS concentration affected the initial and pseudo steady-state flux decline (Figure 3). The initial flux decreased abruptly from 70 to 28 L/m^2/h with the increase in TS concentration to 6 g/L. It leveled off to around 25 L/m^2/h at TS of 15 g/L or below, while it increased to 35 L/m^2/h at TS of 15 g/L TS or above. The stabilized flux after 6h filtration, on the contrary, gradually improved to 30-32 L/m^2/h with the increase in TS concentration. The highest pseudo steady-state flux was observed at a TS concentration of 17 g/L. The normalized flux reduction in terms of J_{6h}/J_0 also showed that the lowest flux reduction occurred at around 15 g/L TS. After 6h filtration, the flux decreased to as low as 15% of the initial flux at low and high TS concentrations, while it maintained more than 40% of the initial flux at around 15 g/L TS. No matter how high the initial flux may be, the stabilized flux after initial rapid flux decline is more important for AMBR operation and maintenance. From this point of view, the optimal solid content for AMBR operation in terms of stabilized flux would be around 15 g/L TS. Figure 4 shows plugging constants of standard blocking law (K_s) and cake filtration law (K_c) at different TS concentrations, which clearly support that the standard filtration law governs the flux decline mechanism at TS concentrations of 10 g/L or below and cake filtration law dominates the flux decline at higher TS concentrations above 25 g/L. Watanabe *et al.* [22] also reported that irreversible fouling increased with F/M ratio due to pore blocking at lower TS levels, while reversible fouling increased due to increased viscosity at higher TS levels. As previously stated, the lowest K_s and K_c were observed at around 15 to 20 g/L TS. The particles seem to behave as individual particles at diluted TS concentrations as high as 10 g/L, while they are more likely to act as agglomerated particles via a bridging effect through particle-particle interactions at concentrated TS levels. However, the severe cake formation on the membrane surface at TS concentrations of 20 g/L or above caused a gradual decrease in flux.

Effect of hydrodynamics on flux decline

The filtration test at different CFVs showed that the flux increased as the CFV was raised, but there was no significant evidence of filtration characteristics change. The experimental data plotted in Figure 5 shows that the filtration characteristics followed standard filtration law over the initial filtration period and cake filtration over the latter period. Therefore, the retardation of particle plugging and deposition could be the main effect of an increase in the flux. The influence of CFV on flux was somewhat different depending on the TS concentration. The highest initial flux was observed at 30 g/L regardless of CFV as shown in Figure 6. However, the increased CFV influenced the pseudo-state flux more significantly after 6 h filtration at low and high TS concentration. The highest pseudo steady-state flux at CFV of 0.1 m/s was examined at a TS of 18 g/L, while the lowest flux at CFV of 0.7 m/s was also observed at 18 g/L TS. The results clearly indicated that the increased CFV could improve flux more effectively at a TS concentration at which standard or cake filtration is predominant, due to the reduced pore clogging and cake deposition. Therefore, the pseudo steady-state flux at a TS of 6 g/L and 36 g/L was more than 4 times higher at a CFV of 0.7 m/s than at a CFV of 0.1 m/s. As a general rule, the cake layer deposited on the membrane surface at low CFV (0.5 m/s) caused a severe cake fouling compared to that which occurred at high CFV (4 m/s) [23]. However, the flux behavior of suspension containing a higher portion of large particles did not improve or even deteriorated compared to the smaller particle system due to the higher cake resistance associated with the finer particle deposition at higher CFV [8]. Therefore, the degree of hydrodynamic effect on membrane performance may be somewhat different depending on the membrane and particle characteristics, which appears to be shown in this study. Figure 7 shows the variations in plugging constants of standard blocking law (K_s) and cake filtration law (K_c) at different hydrodynamic conditions. Although both constants became smaller as the applied CFV increased, the increased CFV appeared to affect K_c to a greater extent than

K_s associated with the initial flux decline. The amount of cake deposited on the membrane surface decreased with the increase in shear stress at the wall [10]. Tardieu *et al.* [23] reported that no cake deposition was observed at sufficiently high hydrodynamic conditions, and the fouling rate decreased with CFV increase. However, changing the hydrodynamic conditions on the membrane surface may influence the physical properties of the biological suspension, such as particle size, SMP, and EPS. Therefore, these properties in anaerobic sludge suspension, exposed at different hydrodynamic conditions, were measured. The influence of CFV on the physical properties of sludge suspension is shown in Figure 8. As expected, the concentration of SMPp, SMPc, and SCOD in anaerobic sludge suspension increased with an increase in CFV. However, the extractable EPS content in anaerobic sludge did not change regardless of applied CFV. Many MBR studies have reported that EPS and/or SMP are the major foulants in MBR [25,26]. The SMPc concentration in anaerobic sludge suspension with a TS of 18 containing 13 mg carbohydrate/L initially increased to 56 mg carbohydrate/L after 6h filtration at a CFV of 0.7 m/s, while the SMPp increased from 33 to 55 mg carbohydrate/L under the same conditions. Although it is not clear which one is more related to membrane fouling, SMPc was released more than twice as frequently compared to SMPp in this study. Lesjean *et al.* [27] reported that membrane fouling in MBR was more attributable to SMPc in biological suspensions. Soluble matter contributed more than 50% of the total resistance [28]. Although EPS is also believed to play a role in membrane fouling in MBR [15,29], there was no significant effect of the CFV on the EPS content in this study. Each gram of anaerobic sludge contained 12.6 mg EPSp and 7.2 mg EPSc before filtration, and about 11-13 mg EPSp and 5-6 mg EPSc after 6h filtration at CFV of 0.1-0.7 m/s. The anaerobic sludge used in this study was stored in a refrigerator, which may lead to a lower EPS yield.

Another important parameter associated with membrane performance at different hydrodynamic conditions is particle size distribution in the feed stream. In general, the particles in MBR break down into finer particles due to the shear force, and then form a denser cake layer [28]. A significant decrease in mean particle size was observed due to high shear stress on the membrane surface [28,30]. The particle distribution curve shifted toward the left with CFV, as shown in Figure 9. Consequently, the mean particle size of anaerobic sludge decreased from 56 to 44 μm after 6h filtration at CFV of 0.7 m/s. However, the particle size reduction was relatively smaller than other studies reported [28,30]. Each anaerobic sludge suspension used for the 6h filtration test at CFVs of 0.1, 0.3, 0.5, and 0.7 m/s was filtered again at CFV of 0.1 m/s to examine the effect of CFV on the permeate flux. An anaerobic sludge suspension which had been filtered previously at CFV of 0.1-0.7 m/s had a lower flux than a fresh anaerobic sludge suspension (Figure 10). The permeate flux difference became larger as the applied CFV increased. The change of physical properties in anaerobic sludge suspension due to the applied CFV had more consequence for the initial flux difference, which implies that the smaller particles and macromolecular matter (SMP) produced by shearing forces generated at the higher CFV increased initial pore plugging. However, the permeate flux of both suspensions before and after filtration at higher CFV became closer with filtration time, because the pseudo steady-state flux was more attributable to cake filtration than standard blocking filtration by macromolecular matter.

Conclusions

The permeate flux decline was modeled from two filtration laws: standard blocking filtration for the initial flux decline and cake filtration for the latter flux decline. The standard filtration law governs the flux decline mechanism at TS concentrations of 10 g/L or below and cake filtration law dominated the flux decline at higher TS concentrations above 25 g/L. Particles seem to behave as individual particles at diluted TS concentrations as high as 10 g/L, while they are more likely to act as agglomerated particles by a bridging effect through particle-particle interactions at concentrated TS levels. However, severe cake formation on the membrane surface at TS concentrations of 20 g/L or above caused a gradual decrease in flux. The increased CFV improved pseudo steady-state flux more significantly at TS concentrations at which standard or cake filtration are predominant due to reduced pore clogging and cake deposition. However, the increased CFV for scouring the membrane surface reduced the mean particle size and increased SMP content in anaerobic sludge suspension. Membrane fouling was more attributable to SMP rather than EPS.

Reference

[1] S. Judd, and B. Jefferson (2003) Membranes for industrial wastewater recovery and reuse. Elsevier Science Ltd., UK.

[2] R. S. Trussell, S. Adham, and R. R. Trussell (2005) Process limits of municipal wastewater treatment with the submerged membrane bioreactor, *J. Environ. Engr*., 131, 410-416.

[3] G. Belfort, R. H. Davis, and A. Zydney (1994) The behavior of suspensions and macromolecular solutions in crossflow microfiltration, *J. Membrane Science*, 96, 1-58.

[4] I.-S. Chang, P. L. Clech, B. Jefferson, and S. Judd, Membrane fouling in membrane bioreactors for wastewater treatment. *J. Environ.Engr*., 128 (2002), 1018-1029.

[5] P. Le-Clech, V. Chen, and T. A. G. Fane (2006) Fouling in membrane bioreactors used in wastewater treatment, *J. Membrane Science*, 284, 17-53.

[6] A. O. Schwarz, B. E. Rittmann, G. V. Crawford, A. M. Klein, and G. T. Daigger (2006) Critical review on the effects of mixed liquor suspended solids on membrane bioreactor operation, *Separation Science and Technology*, 41, 1489-1511.

[7] P. R. Berube, E. R. Hall, P. M. Sutton (2006) Parameters governing permeate flux in an anaerobic membrane bioreactor treating low-strength municipal wastewaters: A literature review, *Water Environment Research*, 78, 887-896.

[8] E. S. Tarleton, and R. J. Wakeman (1993) Understanding flux decline in crossflow microfiltration: Part I – Effects of particle and pore size, *Trans IChemE*, 71, 399-410.

[9] E. S. Tarleton, and R. J. Wakeman (1994) Understanding flux decline in crossflow microfiltration: Part II – Effects of process parameters, *Trans IChemE*, 72, 431-439.

[10] W. R. Bowen, J. J. Calvo, and A. Hernandez (1995) Steps of membrane blocking in flux decline during protein microfiltration, *J. Membrane Science*, 101, 153-165.

[11] H. H. P. Fang, and X. Shi (2005) Pore fouling of microfiltration membranes by activated sludge, *J. Membrane Science*, 264, 161-166.

[12] A. L. Lim and R. Bai (2003) Membrane fouling and cleaning in microfiltration of activated sludge wastewater, *J. Membrane Science*, 216, 279-290.

[13] A. R. Costa, M. N. de Pinho, and M. Elimelech (2006) Mechanisms of colloidal nature organic matter fouling in ultrafiltration, *J. Membrane Science,* 281, 716-725.

[14] J. P. F. De Bruijn, F. N. Salazar, and R. Boroquez (2005) Membrane blocking in ultrafiltration - A new approach to fouling, *Trans IChemE, Part C, Food and Bioproducts Processing*, 83, 211-219.

[15] I-S. Chang, and C-H. Lee (1998) Membrane filtration characteristics in membrane-coupled activated sludge system-the effect of physiological states of activated sludge on membrane fouling, *Desalination*, 120, 221-223.

[16] S. Rosenberger, I. T. Miettinen (2002) Filtrability of activated sludge in membrane bioreactor, *Desalination*, 146, 373-379.

[17] American Public Health Association/American Water Works Association/Water Environmental Federation, 1998. Standard Methods for the Examination of Water and Wastewater, 20th edn,, Washington DC, USA.

[18] B. Frølund, P. Palmgren, K. Keiding, P. H. Nielsen (1996) Extraction of extracellular polymers from activated sludge using a cation exchange resin. *Wat. Res*. 30, 1749-1758.

[19] H. P. Grace (1956) Structure and performance of filter media, *A.I.Ch.E. Journal*, 2, 307-336.

[20] J. Hermia (1982) Constant pressure blocking filtration laws-application to power-law no-newtonian fluids, *Trans IChemE*, 60, 183-187.

[21] G. B. Tanny (1978) Dynamic membranes in ultrafiltration and reverse osmosis, *Separation and purification methods*, 7, 183-220.

[22] Y. Watanabe, K. Kimura, and T. Itonaga (2006) Influence of dissolved organic carbon and suspension viscosity on membrane fouling in submerged membrane bioreactors, *Separation Science and Technology*, 41, 1371-1382.

[23] E. Tardieu, A. Grasmick, V. Geaugey, and J. Manem (1998) Hydrodynamic control of bioparticle deposition in a MBR applied to wastewater treatment, *J. Membrane Science*, 147, 1-12.

[24] E. Tardieu, A. Grasmick, V. Geaugey, and J. Mamem (1999) Influence of hydrodynamics on fouling velocity in a recirculated MBR for wastewater treatment, *J. Membrane Science*, 156, 131-140.

[25] F. Fawehinmi, P. Les, T. Stephenson, F. Rogalla, and B. Jefferson (2004) The influence of operating conditions on EPS, SMP and bio-fouling in anaerobic MBR, Proceeding of the Water Environemnt-Membrane Technology Conference, Seoul, Korea.

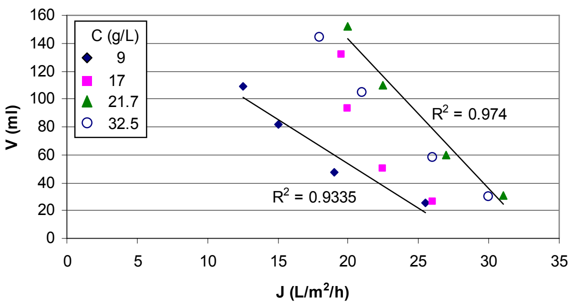
[26] C. Cabassud, A. Masse, M. Espinosa, and M. Sperandio (2004) Submerged membrane bioreactors: interactions between membrane filtration and biological activity, Proceeding of the Water Environemnt-Membrane Technology Conference, Seoul, Korea.

[27] B. Lesjean, S. Rosenberger, C. Laabs, M. Jekel, R. Gnirss, and G. Amy (2005) Correlation between membrane fouling and soluble/colloidal organic substances in membrane bioreactor for municipal wastewater treatment, *Wat Sci. Technol*., 51, 1-8.

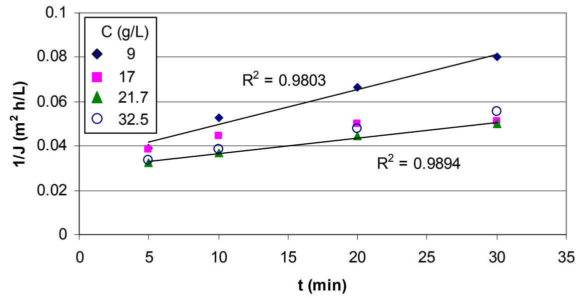
[28] C. Wisniewski, and A. Grasmick (1998) Floc size distribution in a membrane bioreactor and consequences for membrane fouling, *Colloids and Surface A: Physicochemical and Engineering Aspects*, 138, 403-411.

[29] H. Nagaoka, S. Ueda, and A. Miya (1996) Influence of bacterial extracellular polymers on the membrane separation activated sludge process, *Wat. Sci. Tech*. 34, 165-172.

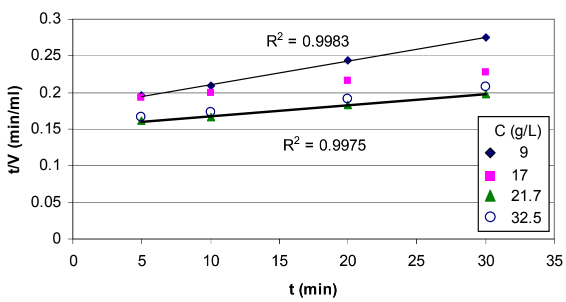
[30] K. H. Choo, and C. H. Lee, Hydrodynamic behavior of anaerobic biosolids during crossflow filtration in the membrane anaerobic bioreactor. *Wat. Res*. 32 (1998), 3387-3397.



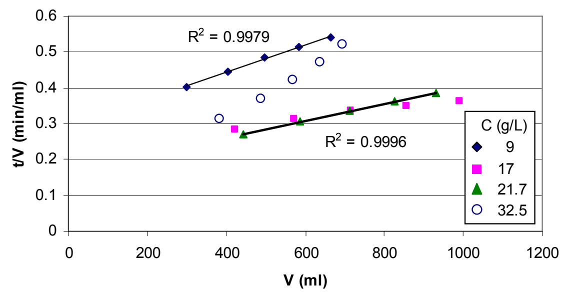
(a) complete blocking filtration



(b) intermediate blocking filtration

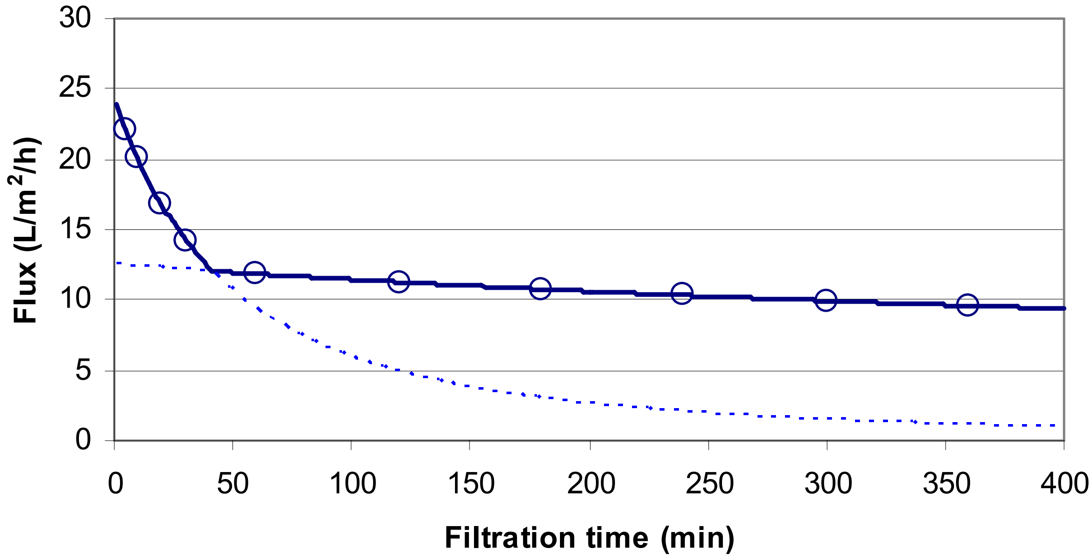


(c) standard blocking filtration

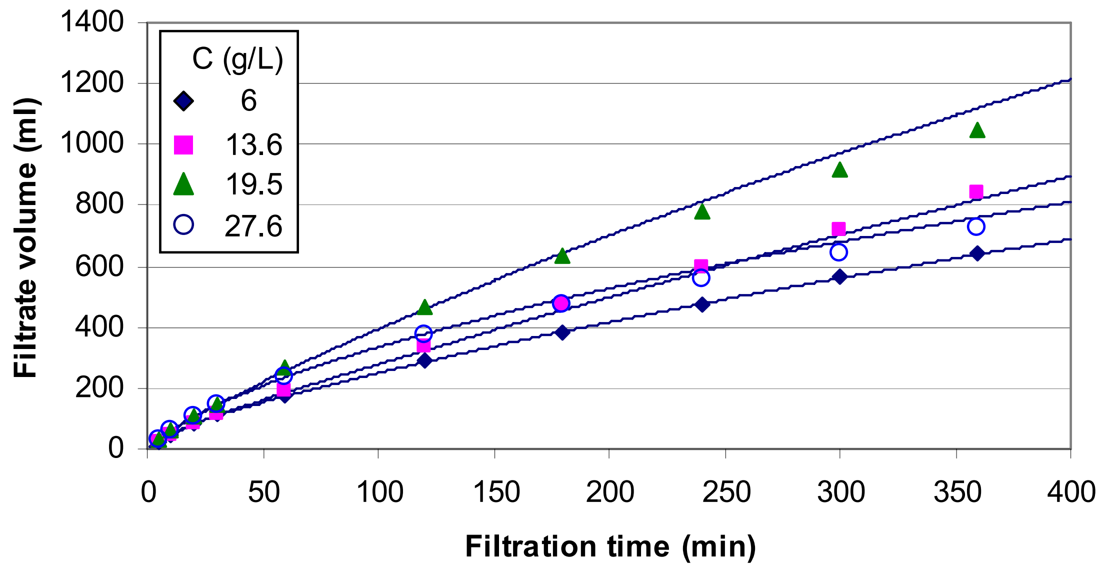


(d) cake filtration

Figure 6-1 Flux decline date for anaerobic sludge filtration at different TS concentration



(a) flux decline



(b) cumulative permeate volume

Figure 6-2 Permeate flux and cumulative permeate volume (solid curves are model calculation using standard blocking and cake filtration law)

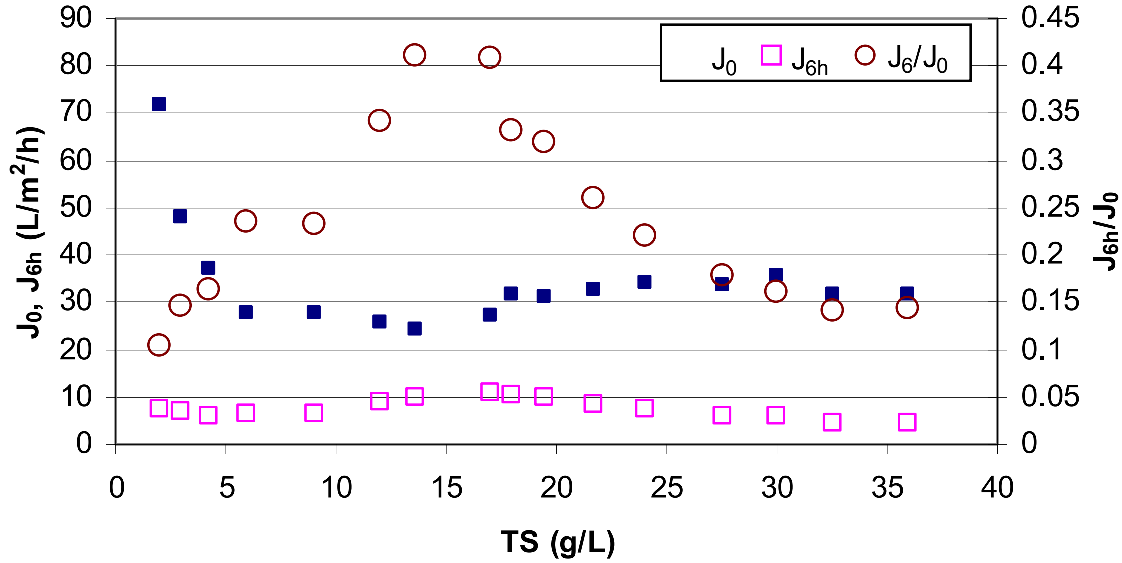


Figure 6-3 Initial and pseudo steady-state flux and normalized flux reduction

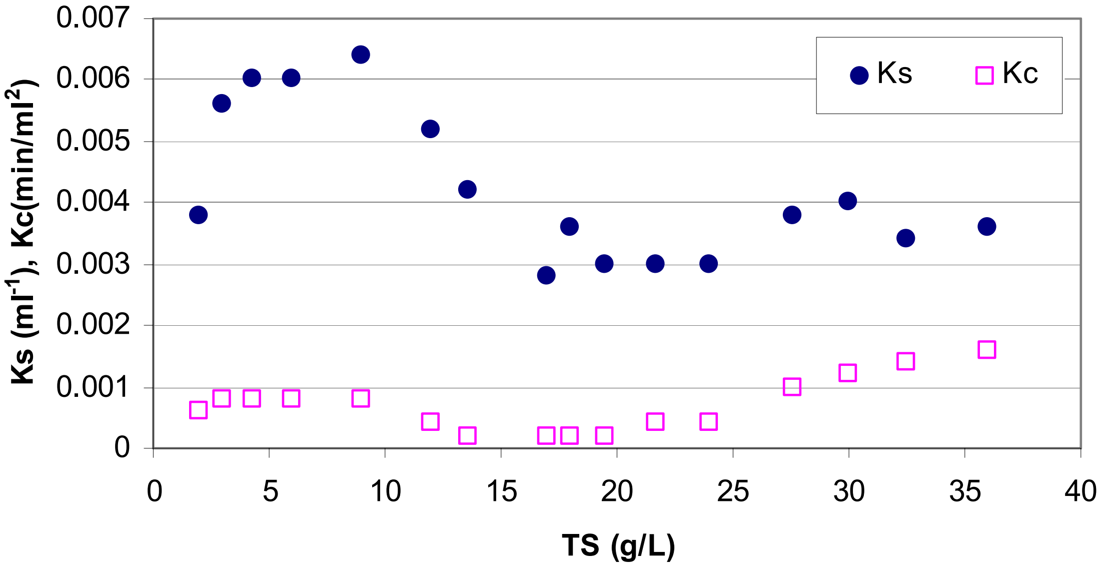
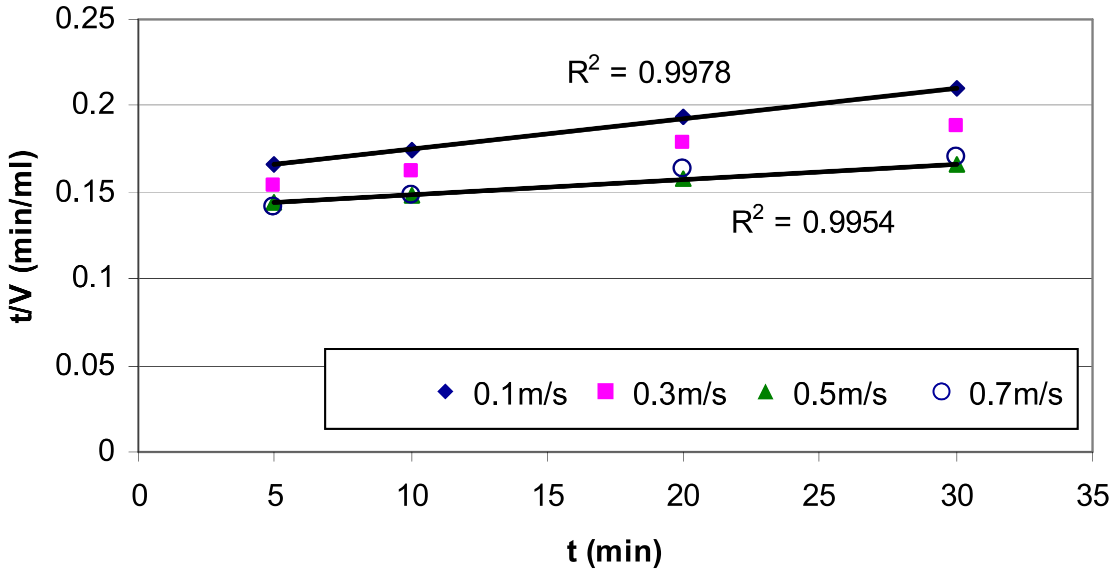
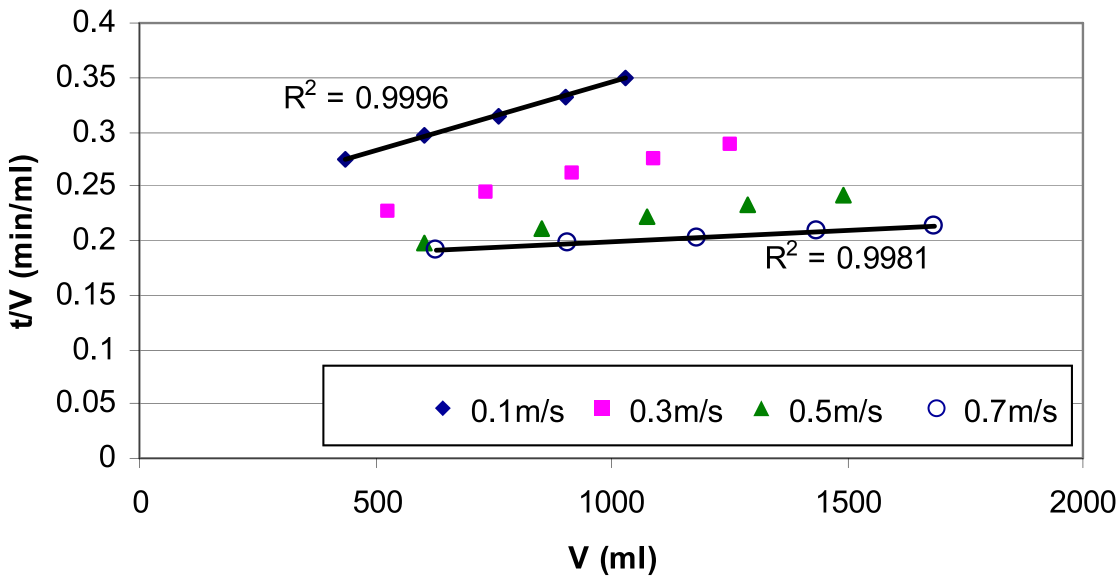


Figure 6-4 Plugging constants variation at different TS concentrations

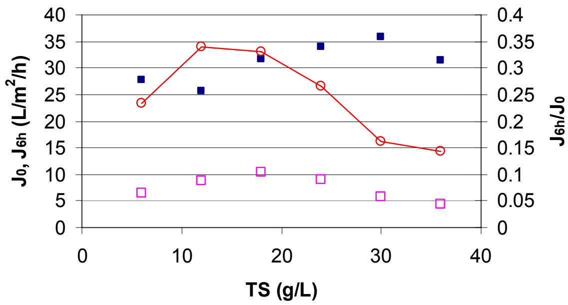


(a) standard blocking filtrationmodel

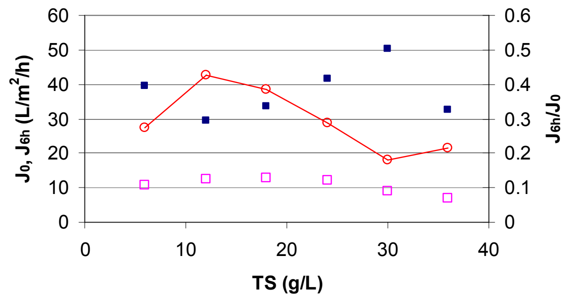


(b) cake filtration model

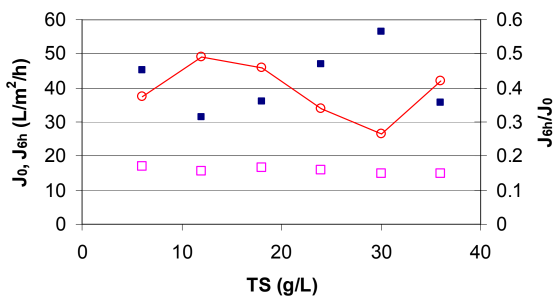
Figure 6-5 Flux decline date for anaerobic sludge filtration at different CFVs



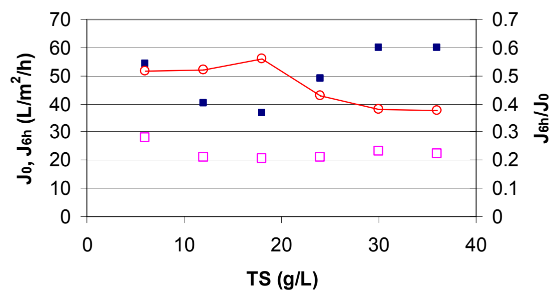
(a) CFV = 0.1 m/s



(b) CFV = 0.3 m/s

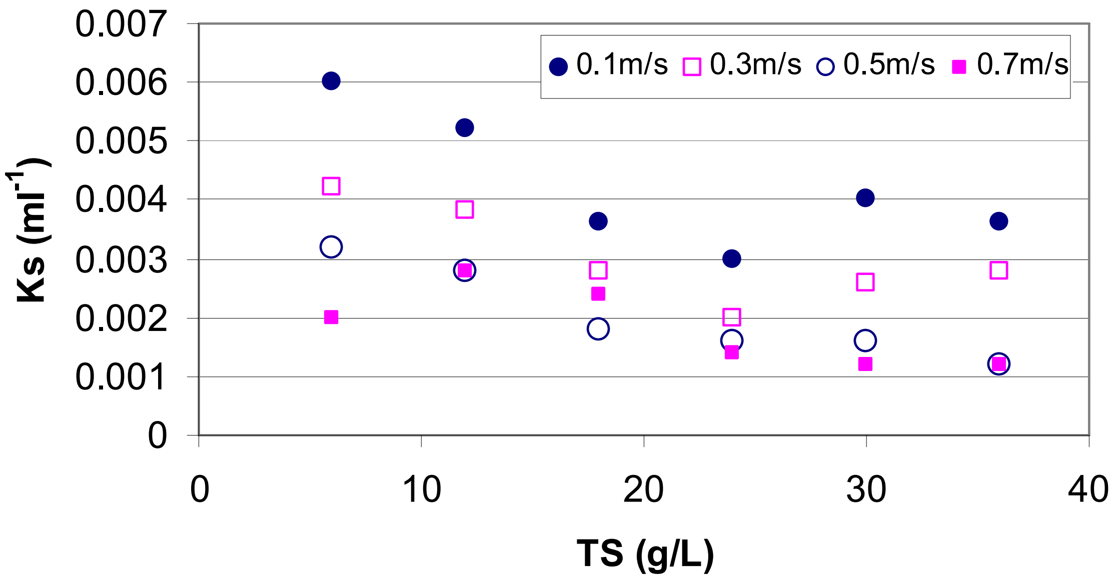


(c) CFV = 0.5 m/s

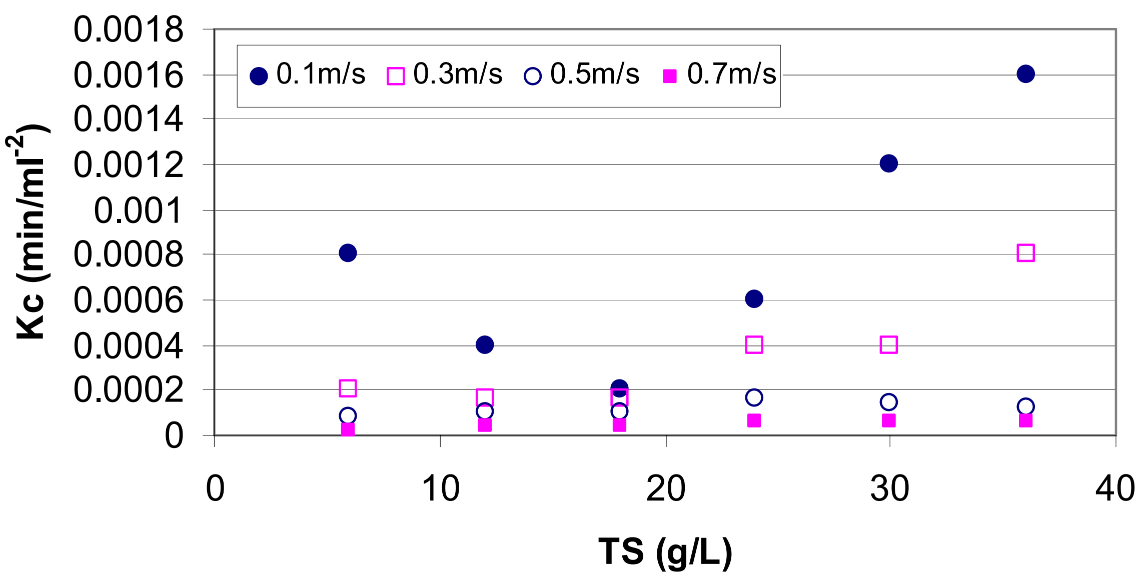


(d) CFV = 0.7 m/s

Figure 6-6 Initial and pseudo steady-state flux and normalized flux reduction at different CFVs

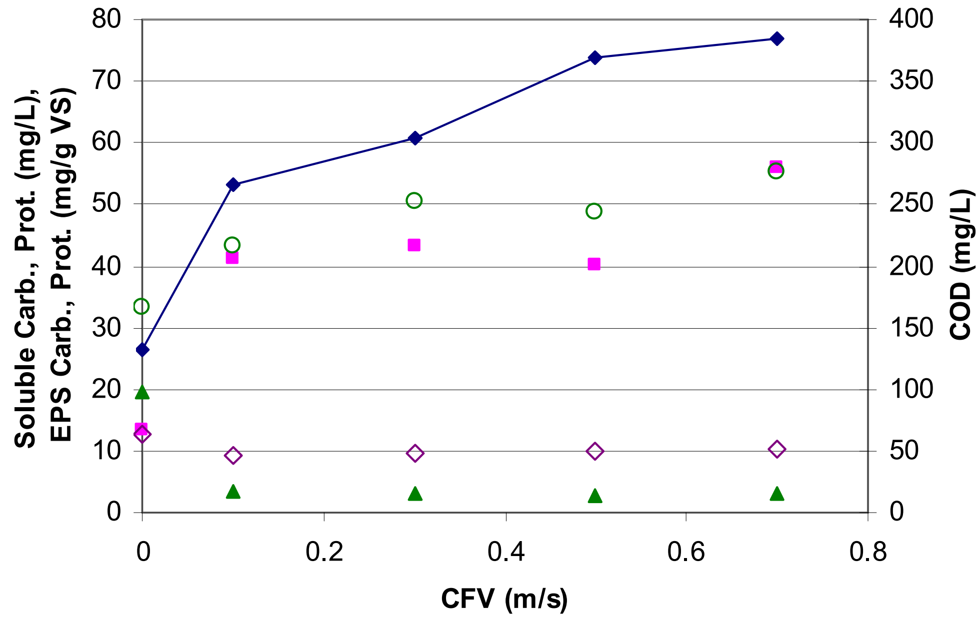


(a) standard blocking filtration

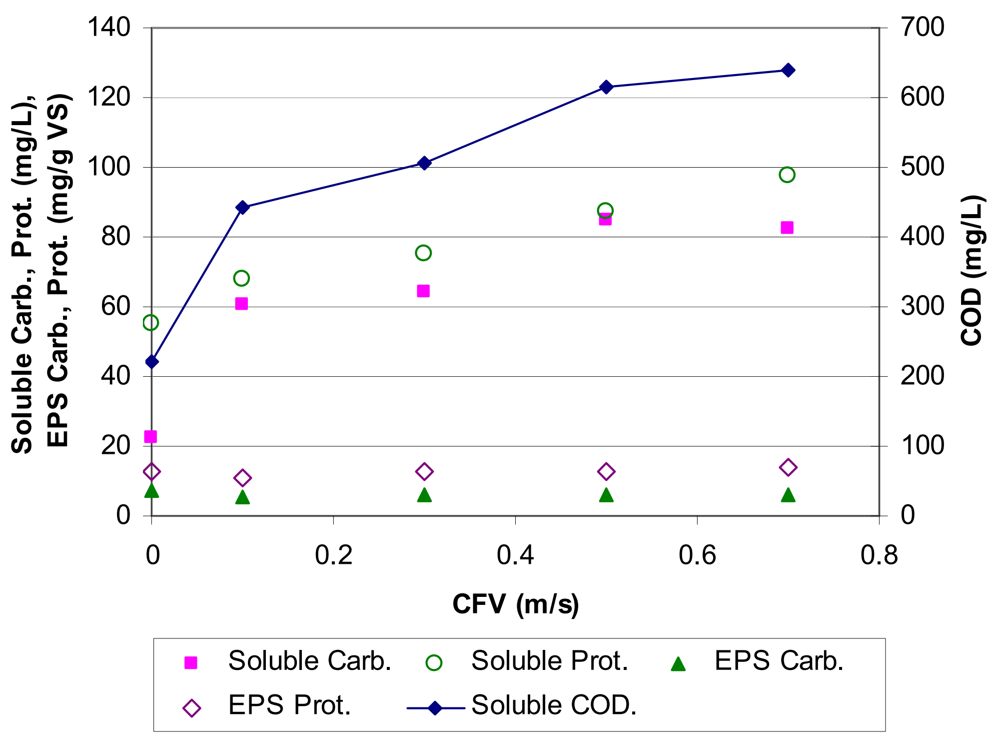


(b) cake filtration

Figure 6-7 Plugging constants at different CFVs



(a) TS = 18 g/L



(b) TS =30 g/L

Figure 6-8 EPS and SMP at different CFVs

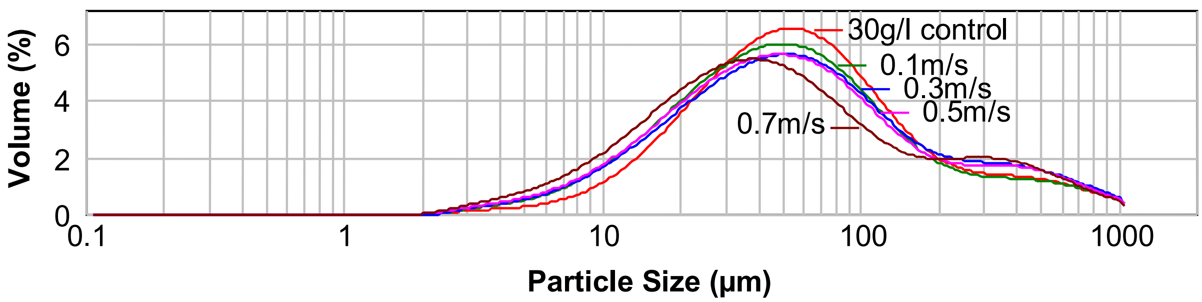
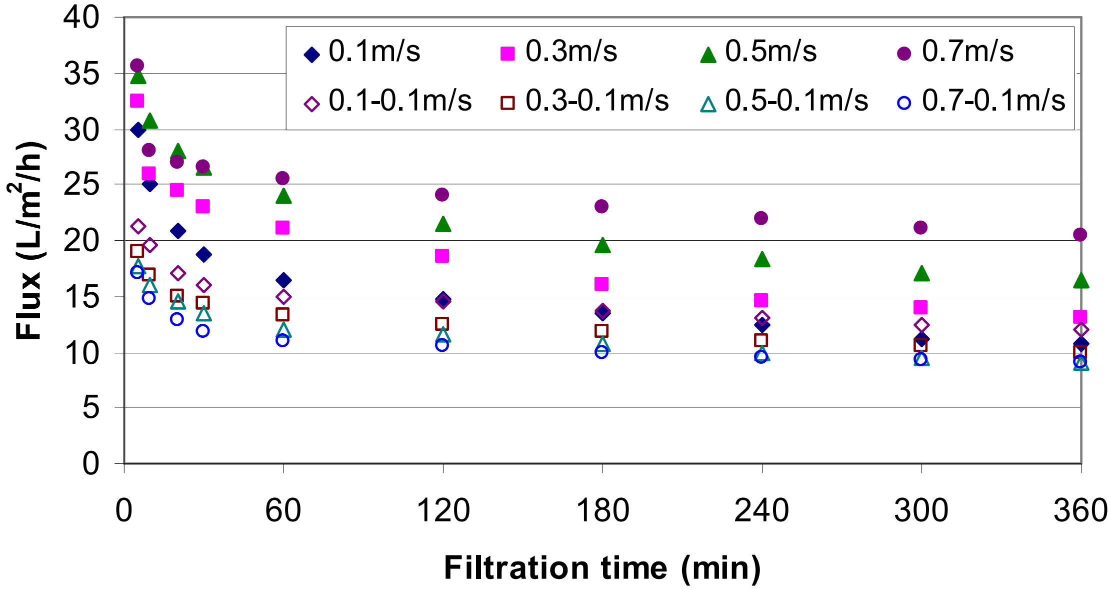
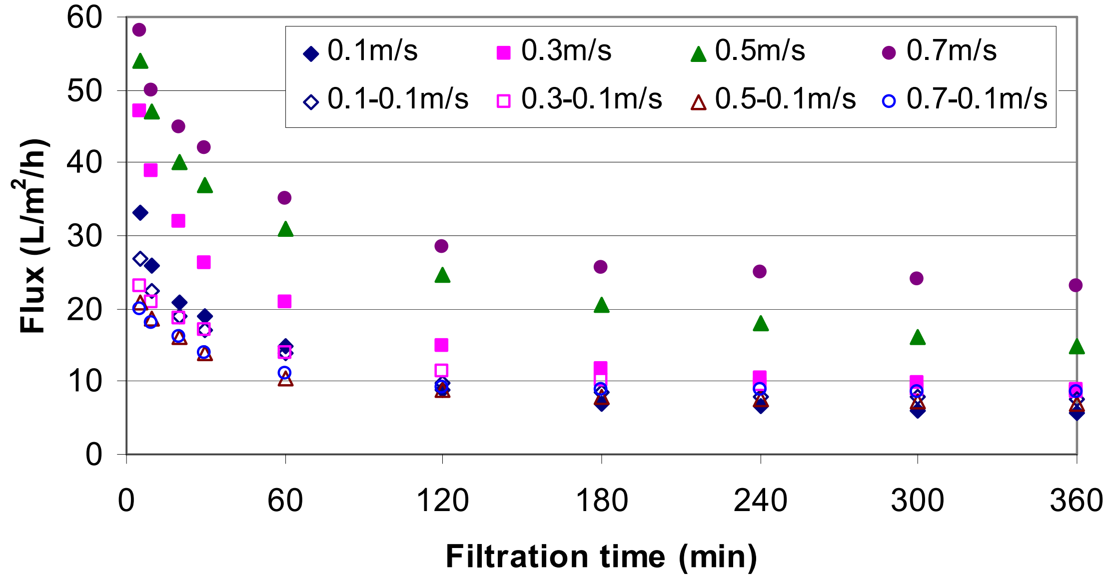


Figure 6-9 Particle size distributions at different CFVs



(a) TS = 18 g/L



(b) TS = 30 g/L

Figure 6-10 Permeate flux decline before and after filtration at higher CFVs

Table 6-1 Filtration modes

Complete blocking	Standard blocking	Intermediate blocking	Cake filtration
n = 2	n = 3/2	n = 1	n = 0
$J = J_0 - K_b V$	$\frac{t}{V} = \frac{K_s}{2} \cdot t + \frac{1}{q_0}$	$\frac{1}{J} = K_i \cdot t + \frac{1}{J_0}$	$\frac{t}{V} = \frac{K_c}{2} \cdot V + \frac{1}{q_0}$

CHAPTER 7. GENERAL CONCLUSIONS

General Discussion

This research investigated the fundamentals of the AMBR for the treatment of low strength wastewater including module configuration, membrane fouling, microbial activity dynamics, and reactor performance at ambient temperature. Main conclusions obtained from this research are summarized as follows:

The inside-to-out flow configuration module with PTFE laminated non-woven filter could be an alternative for microfiltration membrane. Low CFV and TMP were applied to reduce operation cost as well as to minimize shear stress. Therefore, thin anaerobic sludge cake accumulated on the PTFE laminated non-woven filter acted as a dynamic membrane. These secondary membranes improved permeate quality, even though the membrane pore size was larger than sludge particle size. Class 2 type of secondary membrane cake captured inside of the non-woven fabric matrix and accumulated on the PTFE membrane surface could substitute for the membrane and cake in the commercial membrane system.

Both yield pseudoplastic and pseudoplastic model were fit for anaerobic sludge with TS concentration of 10g/L or above. The rheological characteristics of anaerobic sludge became more non-Newtonian as sludge concentration increased. The minimum CFV to produce turbulent flow (Reynolds number ~ 2,100) increased almost linearly to 0.5-0.8 m/s at TS concentration of 10-20 g/L. The highest pseudo-steady state flux was observed at TS concentration of 15 g/L. The bridging effect of concentrated anaerobic sludge improved the flux at MLSS concentration of 15-20 g/L. However, the lower particle concentration does not necessarily yield the higher flux due to the internal fouling by dispersed particles.

Moreover, the higher particle concentration also caused a gradual deterioration in flux due to the severe cake fouling.

Membrane in AMBR system is likely not only to retain all biomass in the reactor, but also complement decreased biological removal efficiency by rejecting soluble organics. Methanogenic activity of attached sludge was far lower than suspended, which indicates that it is suppressed under the harsh environmental conditions, i.e. shear stress by CFV and decreased temperature. The lower EPS content in attached sludge on the membrane surface, especially by protein decrease, may be related to the decreased methanogenic activity of AMBR at low temperature. The cake accumulated on the membrane surface is more likely to act as a physical secondary barrier through lack of biological activity.

A lab-scale AMBR coupled with an external membrane module was successfully operated at relatively long SRT and low CFV, which contributed to less sludge production and less particle size reduction, respectively. The permeate quality was excellent regardless of HRT variations, with more than 90% of COD removal at an HRT of 6 h. The physical removal on the membrane surface compensated for the decreased biological removal rate up to 25% at an HRT of 6 h. The observed methane yield was 0.21 to 0.22 L CH_4/g $COD_{removed}$ regardless of the applied HRTs due to the COD loss by dissolved methane and sulfate reduction. The calculated methane yields after considering COD loss were 0.31, 0.32, and 0.35 L CH_4/g $COD_{removed}$ at HRTs of 12, 8, and 6 h, respectively. The fraction of methane recovered from the synthetic municipal wastewater decreased with the decrease in HRT due to the increase of accumulated SCOD in the reactor. The k and Ks values were 0.26 d^{-1} and 67.4 mg/l, respectively, at 25°C. Maximum possible methane recovery, taking methane solubility, sulfate reduction, and cell synthesis into account, would be approximately 50% to 60% at HRT of 12 h or longer.

The permeate flux decline was modeled from two filtration laws: standard blocking filtration for the initial flux decline and cake filtration for the latter flux decline. The standard filtration law governs the flux decline mechanism at TS concentrations of 10 g/L or below and cake filtration law dominated the flux decline at higher TS concentrations above 25 g/L. Particles seem to behave as individual particles at diluted TS concentrations as high as 10 g/L, while they are more likely to act as agglomerated particles by a bridging effect through particle-particle interactions at concentrated TS levels. However, severe cake formation on the membrane surface at TS concentrations of 20 g/L or above caused a gradual decrease in flux. The increased CFV improved pseudo steady-state flux more significantly at TS concentrations at which standard or cake filtration are predominant due to reduced pore clogging and cake deposition. However, the increased CFV for scouring the membrane surface reduced the mean particle size and increased SMP content in anaerobic sludge suspension. Membrane fouling was more attributable to SMP rather than EPS.

Recommendations for Future Research

Anaerobic treatment is getting attention as a sustainable technology due to its tremendous advantages over aerobic. However, AMBR has not been widely studied, because maintaining microbial activity as well as preventing fouling is more complicated than MBR process. Current MBR breakthrough also blocks the AMBR development. Therefore, the knowledge with respect to AMBR to treat low to medium strength wastewater is far from complete at this point. Several issues for future study may be recommended from this study.

Microbial community structure

Methanogenic activity was significantly suppressed at low temperature. Moreover, methanogenic activity of attached sludge was far lower than suspended due to the shear stress by CFV and. Microbial community structure and population are strongly influenced by environmental conditions. Therefore, understanding of microbial community may be essential to make effective control of AMBR to treat low strength wastewater at ambient temperature.

Membrane fouling in long-term operation

Membrane fouling in AMBR was found to be more related to SMP rather than EPS in anaerobic sludge suspension. The increased CFV for scouring the membrane surface reduced the mean particle size and increased SMP, which increased membrane fouling potential. However, there was limitation to examine the effect of operation conditions, e.g. SRT, MLSS, and CFV, on membrane fouling in AMBR for long-term operation. Future study is therefore needed to investigate SMP fouling and accumulation in AMBR at different operating conditions.

Expand to municipal sewage

AMBR system was able to treat synthetic municipal wastewater at HRT as low as 6h with effluent quality better than the conventional activated sludge process. Therefore, it may be reasonable to expect that it would be able to treat municipal sewage as well. After more through study on AMBR to treat municipal sewage in lab, it may extend its application to small wastewater as a more environment-friendly system.

ACKNOWLEDGEMENTS

I would like to acknowledge my major professor, Dr. Shihwu Sung, who stimulated and encouraged me to complete this dissertation. Special thanks are extended to the committee members, Dr. Robert C. Brown, Dr. Say-Kee Ong, Dr. Hans van Leeuwen, and Dr. Samir K. Khanal for their invaluable helps and comments to this study. I thank the National Science Foundation (award number OISE-0422898), and Institute for Physical Research and Technology at Iowa State University for supporting this work.

I would like to express my gratitude to my parents for the patient, encouragement, and faith through my life. Finally, I am also most grateful to Youngah, my wife, and Yoonseo and Jinseo, my lovely sons, for their patient and love.