DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

APPLICATION OF AN ANAEROBIC BIOMEMBRANE SYSTEM ON THE TREATMENT OF HIGH STRENGTH INDUSTRIAL WASTEWATERS

by

Yunus AKSOY

September, 2012

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APPLICATION OF AN ANAEROBIC BIOMEMBRANE SYSTEM ON THE TREATMENT OF HIGH STRENGTH INDUSTRIAL WASTEWATERS

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We have read the thesis entitled **"APPLICATION OF AN ANAEROBIC BIOMEMBRANE SYSTEM ON THE TREATMENT OF HIGH STRENGTH INDUSTRIAL WASTEWATERS"** completed by **YUNUS AKSOY** under supervision of **PROF. DR. NURDAN BÜYÜKKAMACI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Yunus AKSOY

APPLICATION OF AN ANAEROBIC BIOMEMBRANE SYSTEM ON THE TREATMENT OF HIGH STRENGTH INDUSTRIAL WASTEWATERS

ABSTRACT

In the scope of this thesis, performance of a laboratory scale side-stream anaerobic biomembrane system was evaluated. System was composed of an upflow sludge blanket reactor (UASB) and Ultrafiltration (UF) membrane. Diameter and volume of the anaerobic reactor was 20 centimeter and 10 liter, respectively. Water jacket was used to get access to mesophilic conditions in the reactor. Pall Microza SLP-1053 hollow fiber UF membrane module was used after the anaerobic reactor. Molecular weight cut-off (MWCO) and surface area of the membrane was 10 kilo Dalton and 0.1 square meters, respectively.

Synthetic wastewater consisted of diluted molasses was used. Before membrane commissioning, low organic loading rates (OLR) were applied in order to get steady-state conditions in the anaerobic reactor. After that, OLR was increased up to 15 kilogram COD per cubic meter per day step by step. As a result of the experimental studies, minimum COD removal efficiencies were obtained at lowest HRT applications. A maximum efficiency of 95 percent at OLR of 7.5 kilogram COD per cubic meter per day and HRT of 2 day was achieved. The efficiency of the system decreased with increasing organic loading rate.

At the end of the study, kinetic parameters of the system were determined by applying some biokinetic models.

Keywords: Anaerobic, membrane, bioreactor, kinetic

KONSANTRE ORGANİK KİRLİLİĞE SAHİP ENDÜSTRİYEL ATIKSULARININ ARITIMINDA ANAEROBİK BİYOMEMBRAN SİSTEMİ UYGULAMASI

ÖZ

Bu yüksek lisans tez kapsamında, yan akımlı anaerobik membran biyoreaktörlerin verimi laboratuar ölçekli bir sistem kullanılarak irdelenmiştir. Sistem, yukarı akışlı çamur yataklı anaerobik (UASB) reaktör ve ultrafiltrasyon (UF) membran modülünden oluşturulmuştur. 20 santimetre çapındaki 10 litre toplam hacme sahip anaerobik reaktörde mezofilik sıcaklık koşulları su ceketi ile sağlanmıştır. Anaerobik reaktörü takiben, 10 kilo Dalton MWCO değerine ve 0.1 metre kare yüzey alanına sahip Pall marka Microza SLP-1053 hollow fiber UF membran kullanılmıştır.

Sistem, seyreltilmiş melastan hazırlanan sentetik atıksu ile beslenmiştir. Anaerobik reaktör kararlı koşullar elde edilinceye kadar düşük organik yükleme değerlerinde çalıştırılmıştır. Kararlı koşulların elde edilmesinden sonra, membran devreye alınmış ve sisteme uygulanan organik yükleme değeri kademeli olarak arttırılarak maksimum bir günde birim hacim başına 15 kilogram KOİ uygulanmıştır. Yapılan çalışmalar neticesinde, minimum KOİ giderme verimleri düşük hidrolik alıkonma sürelerinde elde edilmiştir. Maksimum KOİ giderme verimi yüzde 95 olarak litrede 15,000 miligram KOİ konsantrasyonu ve 2 gün HRT uygulamasında (OLR = bir günde birim hacim başına 7.5 kilogram KOİ) elde edilmiştir. Organik yükleme değerleri arttırıldıkça sistem veriminde düşüş gözlenmiştir.

Deneysel çalışmaların tamamlanmasını takiben, elde edilen verilere bazı biyokinetik modeller uygulanarak sisteme ait kinetik parametreler hesaplanmıştır.

Anahtar kelimeler: Anaerobik, membran, biyoreaktör, kinetik

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CHAPTER ONE
INTRODUCTION

1.1 Introduction

Some factors such as water scarcity, strict legislation for wastewater disposal, increasing treatment costs, and reduce space availability have necessitated the research for alternative technologies instead of conventional wastewater treatment process.

The membrane bioreactor process (MBR) for wastewater treatment is an effective combination of the well known and widely applied activated sludge process with the membrane separation process.

Since membrane bioreactor technology has several advantages comparing to conventional treatment processes, it is a good alternative for several types of wastewater. MBRs provide lower footprint, lower sludge production and high-quality effluent. Due to require high investment and operational costs, this technology is still considered as a high-tech method. Unlike, MBR costs have dropped vastly since the early 1990s and the scale of installations has increased (MEDINA Project, 2007).

In the case of the biological unit is operated without oxygen and a membrane is used to separate solids from liquid simultaneously, the system is named as anaerobic membrane bioreactor (AnMBR). AnMBR were first introduced in the 1980s in South Africa and till it has less investigated compared to aerobic MBR. However, today there is a growing interest in the field of AnMBR as shown in numerous and still increasing number of studies going on. Because MBRs could operate independently in relation to the retention times, it enables to go for high organic loading rates. Therefore this became an attractive solution for low (i.e., municipal wastewater) to high strength industrial wastewater treatment with simultaneous energy recovery and less excess sludge production (Visvanathan & Abeynayaka, 2011).

AnMBRs have operated in wide range in terms of different feed concentrations, loading rates, reactor types in mesophilic as well as in thermophilic conditions. Most AnMBRs studies conducted in CSTR configuration with pressure driven mode reactors have achieved good chemical oxygen demand (COD) removal efficiencies (Bailey et al., 1994, Fakhru'l –Razi, 1994, Saddoud et al., 2007).

In this study, evaluation of an anaerobic side-stream membrane bioreactor performance for high strength wastewaters was aimed. Different organic loading rates, hydraulic retention time, and influent COD concentrations effects were examined. This study will be useful and provide guidance for spread of anaerobic membrane bioreactors which is studied very little on our country. The optimal operating parameters which were obtained from this study can use for full-scale applications of designing and operating.

CHAPTER TWO
AN OVERVIEW OF MEMBRANE BIOREACTOR TECHNOLOGY

2.1 Membrane Definition

Membrane can be primarily defined as a barrier, which separates two phases and restricts transport of various chemical in selective manner. It can be also defined as a material that separates particles and molecules from liquids and gaseous. The semi permeable membrane is used in membrane separation process. “The membrane acts as a specific filter that allows water to flow through, while it catches suspended solids and other substances” (Amri, 2010, p.29).

2.2 Types of Membrane Modules

There are many types of membrane modules used in MBR system according to the design and pore size. Membrane types according to the design are tubular, plate and frame, rotary disk and hollow fibre.

Membranes can also be classified considering pore size. There are four main types according to the pore sizes, which are Reverse Osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF) and Microfiltration (MF). Figure 2.1 shows the classification of membranes based on the pore size.

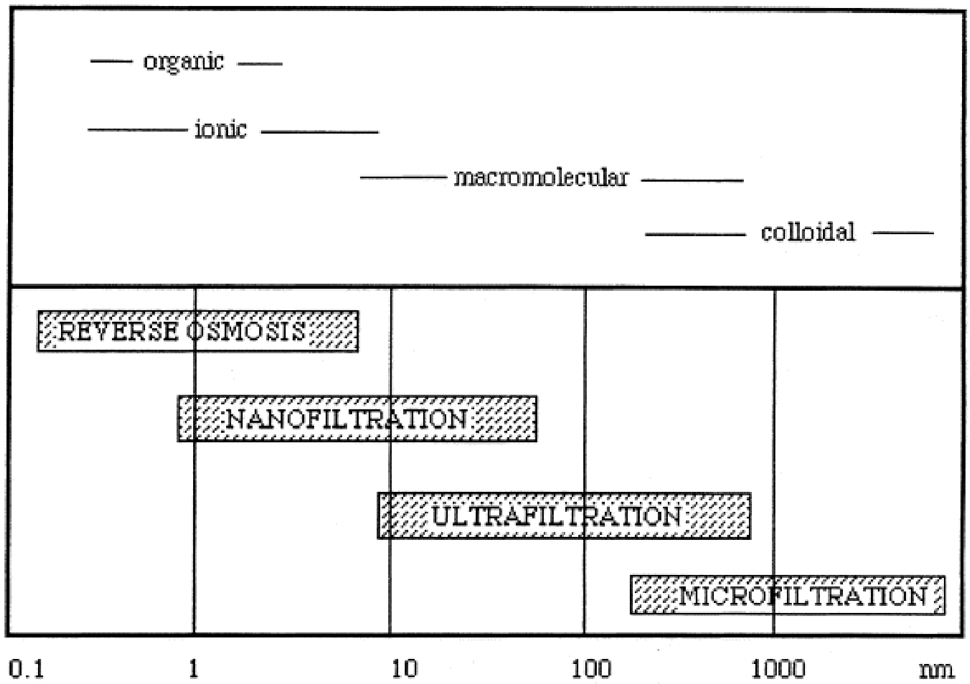

Figure 2.1 The application of membrane technology for water disinfection (Madaeni S.S, 1999)

"Membrane materials can be organics (polyethylene, polyethersulfone, polysulfone, polyolefin, etc), inorganic (ceramic) or metallic and they should be inert and non-biodegradable" (Amri, 2010, p. 31).

2.3 Membrane Bioreactor (MBR) Definition

MBRs systems are integrating biological degradation of waste products with membrane filtration. Membrane bioreactors are consisted of two mainly sections, the biological unit responsible for the biodegradation of the waste compounds and the membrane module for the physical separation of the treated water from mixed liquor (Cicek, 2003).

2.4 Membrane Bioreactor Technology Development

Ultrafiltration as a replacement for sedimentation in the conventional activated sludge process was first described by Smith et al. (1969). In the 1970s the technology entered the Japanese market through a license agreement between Dorr-Oliver and

Sanki Engineering Co. Ltd. By 1993, 39 of these external membrane bioreactor systems had been reported for use in sanitary and industrial applications. In the late 1980s Zenon Environmental continued to developing the systems for industrial wastewater treatment (Fatone, 2007).

MBR technology where the membranes were immersed directly into the biological reactor was applied by Japanese researchers, in the late 1980s. This development finally led to the introduction of various commercial, internal membrane MBR systems such as Zenon Environmental's ZeeWeed ® ZenoGem ® system and the Kubota Submerged Membrane Unit (Enegess et al., undated).

In the US, the first large-scale external membrane MBR system was constructed in Mansfield, Ohio for the treatment of industrial wastewater and the first large-scale internal membrane system was installed in 1998 for treatment of industrial wastewater (Enegess et al., undated).

In 2004, the largest MBR plant in the world was installed in Kaarst (Germany) by VA Tech Wabag Germany to serve a population of 80,000 p.e., Zenon modules were used. In March 2005, Zenon made a contract for an MBR plant to treat 144,000 m^3/d in Washington. This is very impressive development for MBR technology future (MEDINA Project, 2007).

2.5 MBR Types

MBR systems can be classified into two major groups according to membrane placement type: internal (submerged) and external (sidestream or recirculated). MBR systems can also be classified into two main groups depending on the oxygen usage: aerobic and anaerobic MBR.

2.5.1 Internal and External MBRs

The first group is the integrated (Submerged) MBR and membranes are placed into the bioreactor. The driving force across the membrane is obtained by pressurizing the bioreactor or creating negative pressure on the permeate side (Cicek, 2003).

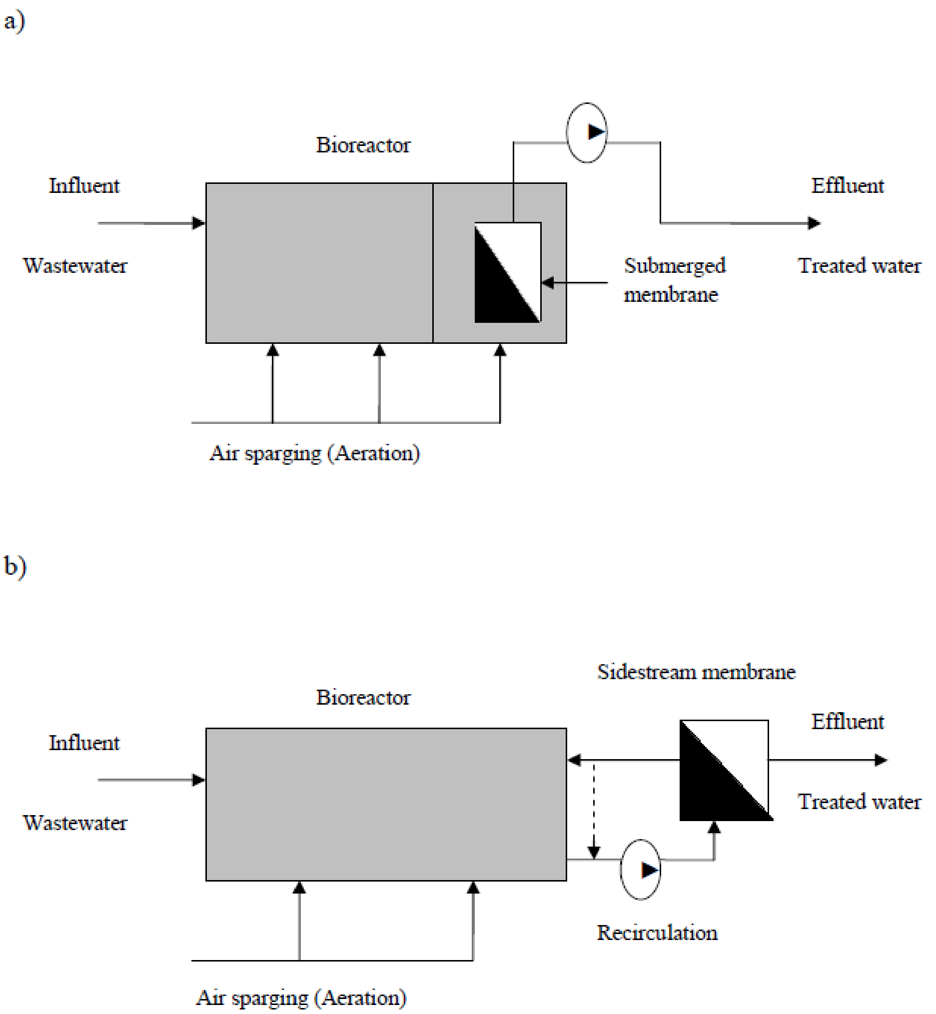

Figure 2.2 Simplified schematics of MBR configurations. a) internal MBR configuration and b) external MBR configuration (Paul et al., 2006).

In the external system (side-stream) the membrane unit is placed at the out of the biological reactor. Influent wastewater first enters to the bioreactor and biological degradation by microorganisms occurs. Then effluent from biological unit is pumped into a membrane filtration unit. In general, cross-flow membrane filtration systems are used and appropriate velocity and transmembrane pressure is obtained with the help of pumping. The membrane effluent (permeate) is the treated product and the concentrate (retentate) is continuously recycled to the bioreactor (Lew et al., 2008). Figure 2.2 shows the two types of MBR systems (Paul et al., 2006).

The determination of which type of MBR system used is made taking into account the advantages and disadvantages of each systems. Advantages and disadvantages of MBR configurations are listed below (Till, 2001):

Submerged MBR:

- High aeration costs.
- Very low liquid pumping costs (higher if suction pump used ~ 28 %).
- Lower flux.
- Higher footprint.
- Less frequent cleaning required.
- Lower operating costs.
- Higher capital costs.

Side stream MBR:

- Low aeration costs.
- High pumping costs.
- Higher flux
- Smaller footprint.
- More frequent cleaning required.
- Higher operating costs.
- Lower capital costs.

2.5.2 Aerobic and Anaerobic MBRs

2.5.2.1 Aerobic MBR$_S$

In the aerobic MBR, the biodegradation occurs in the presence of the oxygen. The aeration is used to provide oxygen to the biomass, to maintain the activated sludge, and to mitigate fouling by constant scouring of membrane surface in MBR systems. The aerobic MBR has been applied quite widely to domestic, municipal wastewater treatment instead of the conventional activated sludge system (Gander et al., 2000; Jefferson et al., 2000; Ueda and Hata, 1999 and Murakami et al., 2000). Darren et al. (2005) reported that, their laboratory-scale aerobic MBR system conducted to remove 98% of the suspended solid and gaining a notable COD removal efficiency of 96% in treating high strength synthetic wastewater. But, phosphorus removal in MBR varied from 15% (Cote et al., 1997) to 74% (Ueda and Hata, 1999). The concentration of the MLSS is reported to be 10 g/l and up to 50 g/l in some studies (Muller et al., 1995 and Scholz and Fuchs, 2000).

Aerobic MBR has been applied to treat a wide range of industrial wastewater, such as oily (Scholz and Fuch, 2000 and Seo et al., 1997) and tannery wastewaters (Yamanoto and Win, 1991). Despite the high strength of the industrial wastewater, many studies have reported high COD removal efficiencies at high organic loading rate (Scholz and Fuch, 2000; Yamanoto and Win, 1991; Kurian and Nakhla, 2006; Rozich and Bordacs, 2002). Aerobic biological process operated at high temperatures. The low yield of 0.03 g VSS/g COD, observed by Kurian and Nakhla (2006). To treatment of high strength wastewaters with the conventional systems is difficult and in these cases the aerobic MBR can be a good possible alternative (Amri, 2010).

2.5.2.2 Anaerobic MBR$_S$

Anaerobic systems have some advantages compared to aerobic systems. One of them is less biomass production which means reduced sludge treatment cost.In the anaerobic microbial systems as an electron acceptor; discard the electrons into methane instead of using them to grow more microorganisms. However, methanogenic organisms have slow growth rates and the microbial complexity of the systems make the operation of anaerobic systems difficult. Biomass retention becomes a critical factor to keep sufficient biomass within the reactor (Visvanathan & Abeynayaka, 2011).

In the AnMBR system, biological degradation occurs in the absence of oxygen and a membrane is used to obtain complete physical separation. AnMBR were first introduced in the 1980s in South Africa and till it has less investigated compared to aerobic MBR systems. However, today there is a growing interest in the field of AnMBR as shown in numerous and still increasing number of studies going on. Because MBRs could operate independently in relation to the retention times, it enables to go for high organic loading rates. Therefore this became an attractive solution for low (i.e., municipal wastewater) to high strength industrial wastewater treatment with simultaneous energy recovery and less excess sludge production (Visvanathan & Abeynayaka, 2011).

The membrane can run under pressure or under a vacuum. In the first option is external cross-flow membrane bioreactor, the membrane is out of the bioreactor and a pump push the bioreactor effluent into the membrane unit (Figure 2.3.a). The second option is submerged membrane bioreactor; membrane is directly immersed into the bioreactor and instead of direct pressure run under a vacuum (Figure 2.3.b). A pump or gravity flow due to elevation difference is used to withdraw permeate through the membrane. The vacuum driven submerged membrane may be operated in two configurations. The applications submerged MBRs for anaerobic wastewater treatment are increasing. The observation, investigation and maintenance difficulties of membranes inside a closed anaerobic reactor made the external membrane operation favorable. Membrane fouling in AnMBRs is a major drawback. To overcome fouling problems related to cake formation on the membranes, biogas is recirculated (Visvanathan & Abeynayaka, 2011).

The membrane may be immersed directly into the bioreactor or immersed in a separate chamber (Figure 2.3.c). If an external membrane used as the next diagram, a pump is required to return the retentate to the bioreactor at the next diagram. Unlike the external cross-flow membrane, the membrane here is operated under a vacuum instead of under pressure. In Figure 2.3.d, the system is operating intermittently under semi dead-end mode to reduce the continuous pumping cost and to minimize the harmful effects, such as biomass activity reduction, of sludge pumping (Visvanathan & Abeynayaka, 2011).

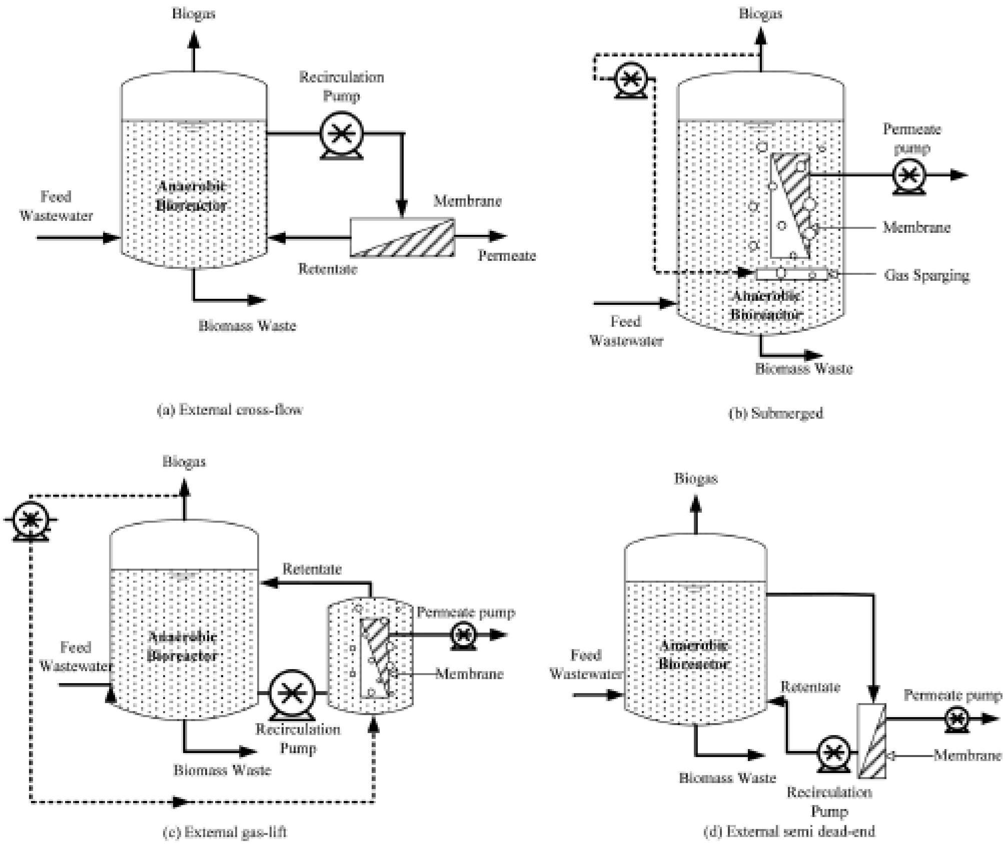

Figure 2.3 Different configurations of AnMBRs (Visvanathan & Abeynayaka, 2011).

Another AnMBR reactor configuration is the two-stage reactor configuration. In the first reactor, hydrolysis, acetogenesis and acidogenesis phases occur and this reactor is named as the hydrolytic (or acidogenic) reactor, followed by methanogenic reactor where the methanogenic process take place (Figure 2.4). The methanogenic reactor which facilitates for the methanogens operates in a strictly defined optimum pH range for the growth of the microorganisms. In a single-stage reactor, both of the processes take place inside. The biological reactions of the different species in a single stage reactor can be in direct competition with each other. In a two-stage treatment system two reactors are operating with the optimized conditions of the respective bacteria to bring maximum control of the bacterial communities living in the reactor. Acidogenic bacteria produce organic acids. They grow fast with higher biomass yield than methanogens. In addition methanogenic bacteria require stable pH and temperatures in order to optimize their performance. In the past, operation of two-stage anaerobic system was hindered by difficulties in solid-liquid separation and the maintenance of separate and distinct biomass populations in each reactor (Anderson et al., 1986). Yet the membrane coupled bioreactors provides the applicability of the two-stage anaerobic degradation both with excellent separation and high biomass retention (Visvanathan & Abeynayaka, 2011).

It is obvious that anaerobic wastewater treatment is especially suitable for high strength wastewaters and could operate in higher loading rates. Furthermore, with the advantages of biomass retention, membrane coupled anaerobic membrane bioreactors are able to operate at higher loadings conditions.

AnMBRs have operated in wide range in terms of different feed concentrations, loading rates, reactor types in mesophilic as well as in thermophilic conditions. Most AnMBRs studies conducted in CSTR configuration with pressure driven mode reactors have achieved good COD removal efficiencies (Bailey et al., 1994, Fakhru'l –Razi, 1994, Saddoud et al., 2007). Additionally, Lew et al. (2009) have studied on external configuration under gravity flow instead of having pressure pump and have achieved 88% of COD removal for domestic wastewater. This could opens new research directions so as to achieve high biomass activity and less fouling in external cross flow AnMBR applications. At an early stage of high rate AnMBR studies were conducted under external membrane configuration reactors (Bailey et al., 1994, Jeison & Lier 2006, Jeison et al., 2009 and Yejian et al., 2008). Great performances of CSTR applications would lead to the simple reactor construction and easy maintenance and operation over the complex high rate reactors in the wastewater treatment sector (Visvanathan & Abeynayaka, 2011).

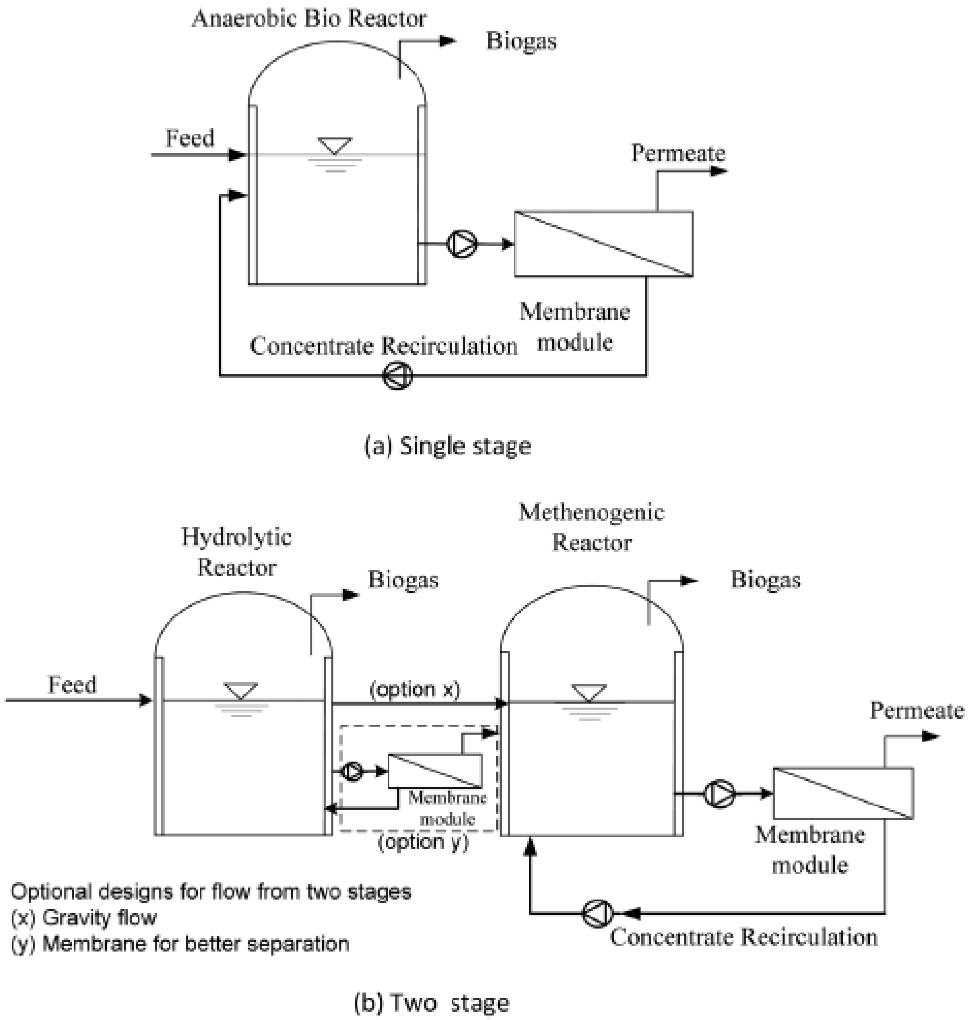

Figure 2.4 Single and two stage AnMBR configurations (Visvanathan & Abeynayaka, 2011).

Most of the studies have worked on synthetic wastewaters at the initial due to the easiness in process control. The feed solutions used in these studies were: VFA, sucrose, glucose, simulated domestic wastewater, as well as simulated high salinity wastewaters. Among those studies almost all the studies have achieved good removal efficiencies such as more than 90% (Visvanathan & Abeynayaka, 2011).

Industrial or high strength real wastewater was also studied and achieved very good removal efficiencies as well. For instance, Saddoud et al. (2007) studied with cheese whey effluent with influent COD in the range of 12-80 kg/m^3 and COD loading of 3-20 kgCOD/m^3.d. Remarkably, the study has achieved 98.5% of COD removal efficiency (Visvanathan & Abeynayaka, 2011).

Methane yield is an important parameter which reflects the performances of the anaerobic wastewater treatment systems. Since the studies on AnMBR are still under development phase, the studies on biogas yield optimization have not gained much attention. However the studies which reported the methane yield indicate around 0.27-0.36 m^3CH_4/kgCOD (Lin et al., 2011a, Wijekoon et al., 2011, Fakhru'l-Razi, 1994) with other high rate anaerobic reactors (Visvanathan & Abeynayaka, 2011).

2.6 MBR and Conventional Treatment Process Comparisons

A comparison of the different treatment processes considering organic loading rate (OLR), hydraulic retention time (HRT), and removal efficiencies is shown in Table 2.1. As seen from the table, removal efficiencies of MBR systems are usually higher than other systems. Comparing to conventional activated sludge processes (ASP), generally higher organic loading rates have been applied for MBR systems (Till, 2001).

MBR processes have advantages over conventional biological treatment especially in term of small footprint, process intensification, modular, and retrofit potential (Chaturapruek, 2003). In addition, MBR technology is able to remove pathogenic organisms, providing disinfection of the effluent (Till, 2001). Galil reports that biosolids, which had to be removed as excess sludge were characterised by a relatively low volatile to total suspended solids ratio - around 0.78. This could facilitate and lower the cost of biosolids treatment and handling. MBR can be operated at MLSS of up to 20,000 mg/L and as sludge settling is not required, submerged MBR can be up to 5 times smaller than a conventional ASP (Chaturapruek, 2003).

Table 2.1 Comparison of different treatment processes (Till, 2001)

Reactor	Organic loading rate ($kgBOD_5.m^{-3}.day^{-1}$)	HRT(h)	Percentage removal
BAF			
Downflow	1.5	1.3	93
Upflow	4	-	>93
Downflow	7.5	-	75
TF			
Low rate	0.08-0.4	-	80-90
Intermediate	0.24-0.48	-	50-70
High rate	0.48-0.96	-	65-85
ASP			
Sequencing	0.08-0.24	12-50	85-95
Conventional	0.32-0.64	4-8	85-95
Complete-mix	0.8-1.92	3-5	85-95
High-rate aeration	1.6-16	2-4	75-90
MBR			
Sub, P+F* (Kubota)	0.39-0.7	7.6	99
Sub, HF (Tech-Sep)	0.03-0.06	1	98-99
Sub, P+F	0.005-0.11	8	98
Sub, HF	1.5 (COD)	0.5	87-95
SS, ceramic	0.18	24	>95
SS, P+F	0.45-1.5 (COD)	8	88-95

* P+F: Plate & Frame, HF: Hollow Fibre, SS: Side Stream

Low sludge production is another significant advantage of MBR systems. As seen from Table 2.2, maximum of 0.3 kg/kg BOD sludge is produced in submerged MBR systems. However, in conventional activated sludge process at least two times more sludge is produced.

Table 2.2 Sludge production for various wastewater treatment processes (Till, 2001)

Treatment processes	Sludge production (kg/kgBOD)
Submerged MBR	0.0-0.3
Structured media biological aerated filter (BAF)	0.15-0.25
Trickling filter	0.3-0.5
Conventional activated sludge	0.6
Granular media BAF	0.63-1.06

Depending on the membrane types, good bacterial and viral reductions can be achieved with MBR systems. Turbidity of the effluent is less than 0.2 NTU and suspended solids are less than 3 mg per litre (Aquatec Maxcon product literature). So, high quality effluent can be obtained with this system. Table 2.3 shows the effluent quality of activated sludge and MBR system based on pilot plant study. Performance comparison of activated sludge system and MBR system is given in Table 2.4 (Coppen, 2004).

Table 2.3 Comparison of activated sludge and MBR effluent

	Activated Sludge	**MBR**
Suspended solids (mg/L)	37	2.5
COD (mg/L)	204	129
BOD (mg/L)	83	7.1

Table 2.4 Performance comparison

Parameter	**Activated Sludge**	**MBR**
Sludge age (days)	20	30
COD removal (%)	94.5	99
DOC removal (%)	92.7	96.9
TSS removal (%)	60.9	99.9
Ammonical N removal (%)	98.9	99.2
Total P removal (%)	88.5	96.6
Sludge production (kgVSS/COD/day)	0.22	0.27
Mean floc size (mm)	20	3.5

2.7 Applications of Anaerobic Membrane Bioreactors

2.7.1 Synthetic Wastewaters

The results of a number of studies which have been carried out with synthetic wastewaters are summarized in Table 2.5. Volatile fatty acids (VFA), starch, glucose, molasses, peptone, yeast, and cellulose have been used as feeding wastewater. OLRs up to 20 kg COD/m^3/d were applied and over 90% COD removal efficiencies were achieved at these studies (Liao et al., 2006).

2.7.2 Food Processing Wastewaters

Many AnMBR studies have carried out with food-processing wastewaters, as summarized in Table 2.6. AnMBRs have been tested with the treatment of effluents from field crop processing (sauerkraut, wheat, maize, soybean, palm oil), the dairy industry (whey), and the beverage industry (winery, brewery, distillery). High COD removal efficiencies (usually >90%) were achieved, but the organic loading rates are in the large 2-15 kg COD/m^3/d (Liao et al., 2006).

2.7.3 Industrial Wastewaters

Results of the studies carried out with pulp and paper and textile wastewaters are summarized in Table 2.7. Anaerobic treatment of pulp and paper wastewaters has become more common (Liao et al., 2006).

2.7.4 High-Solid-Content Waste Streams

In recent years, the AnMBR technology has been successfully tested in both pilot-and-full-scale plants for treatment of high solids wastes, as summarized in Table 2.8. AnMBRs have been tested with wastewater treatment plant sludges, pig manure, and chicken slaughterhouse effluent. Relatively high OLRs of 3-5 kg COD/m^3/d were achieved with high COD removals (80% or higher) for the manure and slaughterhouse wastewaters as compared with the usual loadings of 1-3 kg COD/m^3/d for high-solids wastes (Liao et al., 2006).

2.7.5 Municipal Wastewaters

Table 2.9 summarizes the studies on the use of AnMBRs for sewage treatment. In general, AnMBR sewage treatment had lower effluent COD (<100 mg/L) and suspended solids concentrations compared to conventional UASB treatment. In addition, the COD or BOD removal efficiency was compared to UASB treatment and very high SRTs (e.g., 150 days) could be maintained (Liao et al., 2006).

Table 2.5 Summary of AnMBR performance for treatment of synthetic wastewaters (Liao et al., 2006).

Type of wastewater	Type of reactor	Reactor volume (m^3)	Temp. (˚C)	HRT (d)	SRT (d)	OLR ($kgCOD.m^{-3}.d^{-1}$)	MLSS (gL^{-1})	Feed COD (gL^{-1})	Effluent COD (gL^{-1})	COD removal efficiency
Acetate	CSTR	0.007	35	1.0	30	8.5	10	8.5	<0.4	>95%
Acetate, lactate, propionate, butyrate	CSTR	0.24	33	3.9	100	17	12	67	0.7	99%
Glucose	2 phase CSTR+M/ CSTR+M	0.003/0.01	35	1.5/7.7	-/-	36/12	-/-	53/41	1.5	97%
Glucose,peptone,yeast extract,acetate	CSTR	0.007	30	0.5	-	20	22	9.7	<1	>90%
Starch	CSTR	0.0075	35	0.5	45	2.0	-	0.93	0.09	90%
Molasses	UASB	0.005	20	-	-	0.3-1.3	-	-	-	-
Synthetic[a]	UASB	0.009	30	0.6	-	8.3	-	5	0.05	99%
Skim milk and cellulose	CSTR	0.01	35	2.0	-	2.5	15	5	<0.08	>98%

CSTR= completely stirred tank reactor, PB= packed bed, UASB= upflow anaerobic sludge blanket, M designates the location of the membrane (no M indicates the membrane produced the final effluent)

a = Composition not reported

Table 2.6 Summary of AnMBR performance for treatment of food processing wastewaters (Liao et al., 2006).

Type of wastewater	Type of reactor	Reactor volume (m^3)	Temp. (˚C)	HRT (d)	SRT (d)	OLR ($kgCOD.m^{-3}.d^{-1}$)	MLSS (gL^{-1})	Feed COD (gL^{-1})	Feed TSS (gL^{-1})	Effluent COD (gL^{-1})	COD removal efficiency
Acid whey permeate	CSTR	0.3	35	5.7	27	9.6	37	52	0.1	0.5	99%
Sauerkraut brine	CSTR	0.007	30	6.1	-	8.6	55	52.7	0.5	0.5	99%
Wheat starch	2 phase UFAF+M/ UASB+M	-	-	-	-	-	-	36	17	8.8	76%
Maize	CSTR	2610	35	5.2	-	2.9	21	15	-	0.4	97%
Soybean	2 phase UFAF+M/ UFAF	1.0/2.0	30	3.5/7.0	-	3.0	-	1.3/0.9	0.5/0	0.1	92%
Soybean	2 phase CSTR+M/ FB+M	-	-	-	-	-	-	10	4.3	0.9	91%
Alcohol distillery	CSTR	0.004	54	13	-	3.3	2.0	38	0	3.8	90%
Brewery	CSTR	0.12	35	4.0	59	19.7	38	84	-	3.1	96%

CSTR= completely stirred tank reactor, FB= fluidized bed, UFAF= upflow anaerobic filter, UASB= upflow anaerobic sludge blanket, M designates the location of the membrane (no M indicates the membrane produced the final effluent)

Table 2.7 Summary of AnMBR performance for treatment of industrial wastewaters (Liao et al., 2006).

Type of wastewater	Type of reactor	Reactor volume (m^3)	Temp. (˚C)	HRT (d)	OLR ($kgCOD.m^{-3}.d^{-1}$)	MLSS (gL^{-1})	Feed COD (gL^{-1})	Feed TSS (gL^{-1})	Effluent COD (gL^{-1})	COD removal efficiency
Kraft bleach plant effluent	CSTR	0.015	35	1.0	0.04[b]	7.6-15.7	0.04[b]	-	0.016[b]	61%[b]
Kraft pulp effluent	UFAF	5	-	0.5	35[a]	9.4	19.2[a]	-	1.5[a]	93%[a]
Pulp and paper effluent	FB	7	-	-	-	-	28	15	1.1	96%
Evaporator condensate (methanol)	UFAF	5	53	0.5	35.5[a]	7.6	17.8[a]	<0.003	1.2[a]	93%[a]
Wool scouring	UFAF	4.5	37	6.8	15	-	102.4	30.5	51	50%

CSTR= completely stirred tank reactor, FB= fluidized bed, UFAF= upflow anaerobic filter, M designates the location of the membrane (no M indicates the membrane produced the final effluent)

a =Units are BOD instead of COD

b = Units are AOX (adsorbable organic halogen)

Table 2.8 Summary of AnMBR performance for treatment of high solids content wastes (Liao et al., 2006).

Type of wastewater	Type of reactor	Reactor volume (m^3)	Temp. (˚C)	HRT (d)	SRT (d)	OLR ($kgCOD.m^{-3}.d^{-1}$)	MLSS (gL^{-1})	Feed COD (gL^{-1})	Feed TS (gL^{-1})	Effluent COD (gL^{-1})	COD removal efficiency
Primary sludge	Upflow mixed	0.12	35	20	-	1.06	22-35	40.2	44.4	18	54%
Coagulated raw sludge	VFA fermenter CSTR	0.076	35	0.5	10	4.6[b]	34	2.3[b]	6.8	1.3[b]	43%[b]
Screened sludge	Semi continuous CSTR	1.8	-	14	26	-	55	-	-	-	-
Sewage sludge	CSTR	0.004	25-40	6.7-20	-	0.17-1.35[a]	20-40	-	-	<0.3	-
Pig manure	CSTR	200	35	10	-	3	-	30	20	2.4	92%
Pig manure	2phase CSTR+M/Hybrid	3/3	20/25	1-2/1-2	-/-	2.8-5.5/-	-/-	5.5	0.6	1.1	80%
Chicken slaughterhouse	CSTR	0.007	30	1.2	-	4.3	22	5.2	2.4-4.7	<0.5	90%

CSTR= completely stirred tank reactor, Hybrid= UASB with anaerobic filter instead of a solids/liquid/gas separator, Mdesignates the location of the membrane (no M indicates the membrane produced the final effluent)

a= Units are VSS instead of COD

b= Units are TOC instead of COD

Table 2.9 Summary of AnMBR performance for treatment of municipal wastewaters (Liao et al., 2006).

Type of wastewater	Type of reactor	Reactor volume (m^3)	Temp. (˚C)	HRT (d)	SRT (d)	OLR ($kgCOD.m^{-3}.d^{-1}$)	MLSS (gL^{-1})	Feed COD (gL^{-1})	Feed TSS (gL^{-1})	Effluent COD (gL^{-1})	COD removal efficiency
Night soil (heat-treated and hydrolyzed)	UASB	0.4	-	-	-	-	-	25.5	2.6	2.0	92%
Heat-treat liquor	CSTR	0.2	37	0.6	-	15.4	21.4	10.3	0.3	2.0	81%
Primary effluent	CSTR	0.01	3	0.5	217	1.6	7	0.08	0.12	0.02	68%
Sewage	Hydrol CSTR/UASB+M	-/5.4	-	-	-	-	-	1.1	0.5	0.07	94%
Sewage	Hydrol CSTR+M/FB+M	2.0/5.4	35/-	3/0.27	-	5.7	7/40	0.49	0.3	0.08	83%
Domestic wastewater	Hybrid	0.018	20	0.25	150	0.4-10	16	0.1-2.6	0.1-0.8	<0.03	>92%

CSTR= completely stirred tank reactor, FB= fluidized bed, Hybrid= UASB with anaerobic filter instead of a solids/liquid/gas separator, Hydrol= side-stream suspended solids hydrolysis reactor plus methanogenic reactor for combined hydrolysate and primary clarifier effluent, UASB= upflow anaerobic sludge blanket, M designates the location of the membrane (no M indicates the membrane produced the final effluent)

CHAPTER THREE
MATERIALS AND METHODS

3.1 Laboratory Scale AnMBR System

Experimental studies were carried out by using a lab scale AnMBR model reactor consisted of an anaerobic bioreactor connected to a side-stream ultrafiltration unit (UF). Wastewater was introduced to the anaerobic reactor at the bottom and effluent was withdrawn from the top of the reactor and pumped to the UF unit (Figure 3.1).

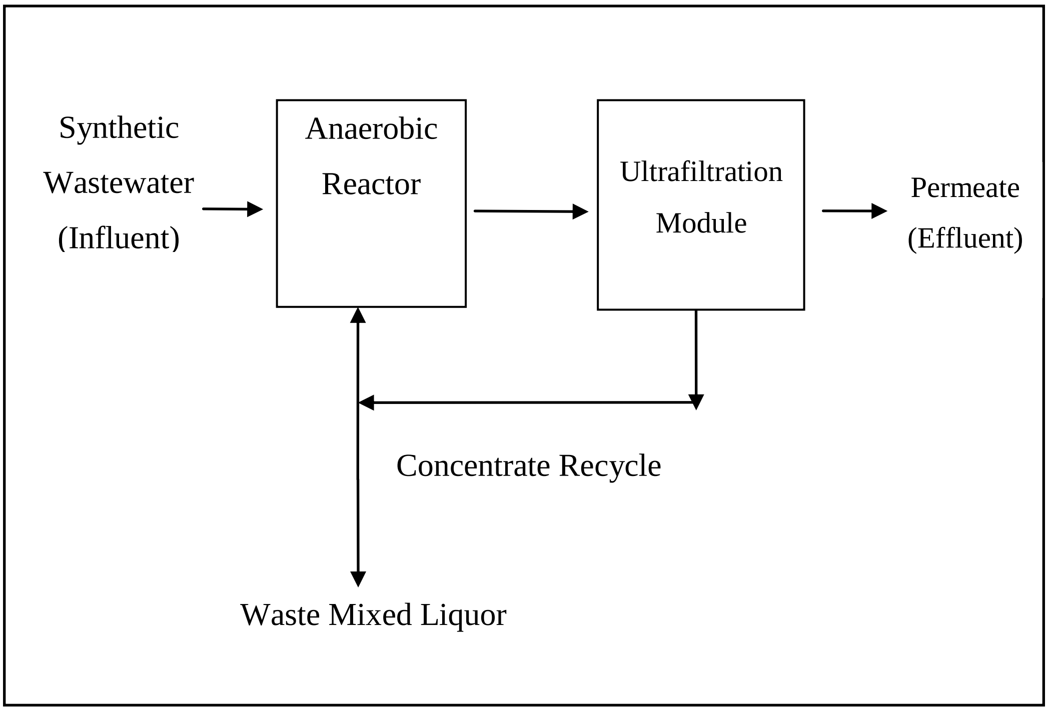

Figure 3.1 Schematic diagram of the laboratory scale AnMBR system

Feeding tank, anaerobic reactor, and hot water tank was made of stainless steel. With a total volume of 10 liters the anaerobic reactor is equipped with inlet and outlet valves, sampling valves, and gas and sludge outlet valves.

The anaerobic reactor was operated under mesophilic (37 ºC) conditions and the temperature kept constant by circulating hot water through the reactor jacket. At the beginning of the study, the anaerobic reactor was operated as completely mixed reactor. Mixing in the reactor was obtained with a recirculation pump. In this case, there was a lot of solid leakage at the effluent.

Giving a water which has such intense solids to the UF membrane system at the next stage, will create enormous clogging problems and considering of a decline of the lifetime of the membrane, the anaerobic reactor which is considered as a completely mixed reactor, has started to run as up-flow sludge bed reactor (UASB) by stopping the mixture. The photo of the anaerobic model reactor is given in Figure 3.2 .

Figure 3.2 The view of the model reactor system used in experimental studies. (Tank on the left: feed tank, the tank in the middle: anaerobic reactor, the right tank: hot water tank)

Effluent of the anaerobic reactor was subjected to the UF module. In this study, hollow fiber membrane in Pall's Microza module (SLP-1053) was used. The cartridge specifications and operating parameters is given in Table 3.1.

Table 3.1Cartridge specifications and operating parameter

Module Type	MWCO (Dalton)	Water Flux (l/hr)	Area (m^2/ft^2)	Module Lenght (mm/in)	Module Outside Diameter (mm/in)	Max. Inlet Pressure (bar/psi)	Max. ΔP (bar/psi)
SLP-1053	10,000	40	0.1/1.1	347/13.7	42/1.7	3/45	3/45

A peristaltic pump was used for wastewater pumping to the membrane. Inlet and outlet pressure was measured using pressure measurement devices attached to the module. Although the maximum inlet pressure of the system is given as 3 bar (45 psi) during the experiments the inlet pressure was kept constant at 1.5±0.2 bars. The maximum wash and backwash pressures for the UF membrane were 1.7 and 2.5 bar, respectively. In Figure 3.4 and 3.5, photo of the UF module structure and photo of the laboratory scale anaerobic membrane bioreactor system are given, respectively.

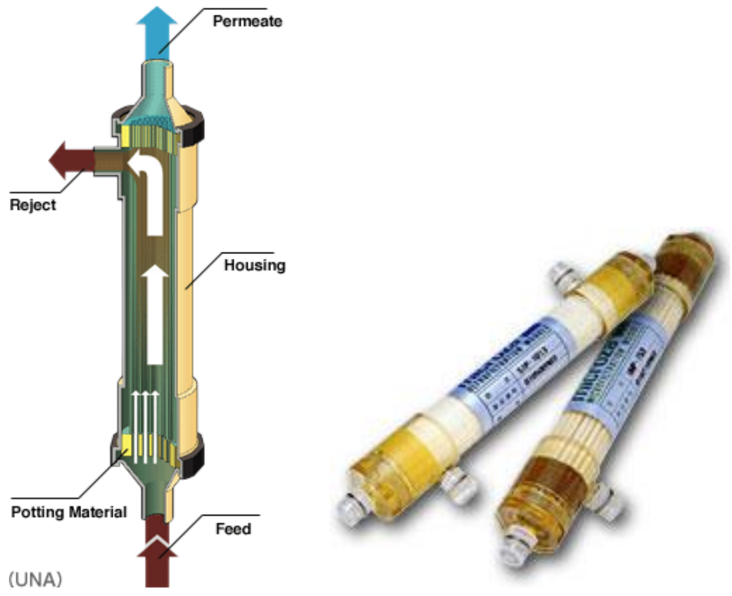

Figure 3.4 The UF module structure

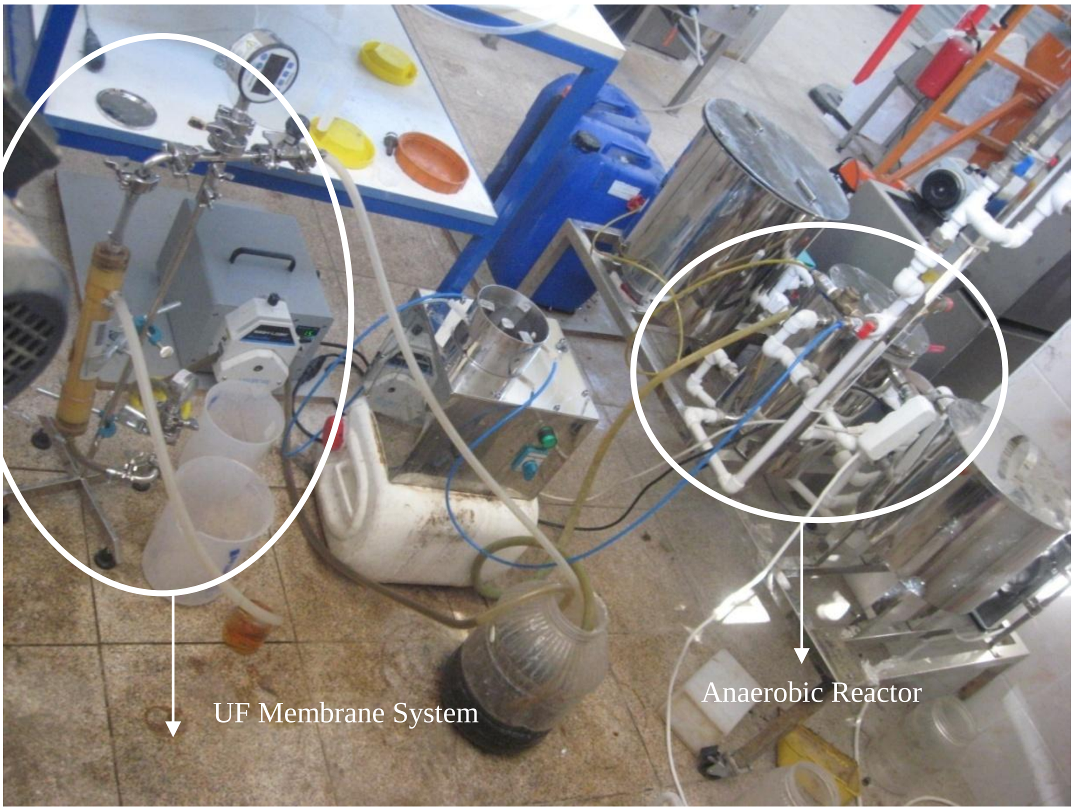

Figure 3.5 Photograph of the laboratory scale AnMBR system

3.2 Wastewater Properties

Synthetic wastewater consisted of diluted molasses was used in this study. COD concentration of molasses is about 1,000,000 mg/L; and it was diluted according to applied influent COD concentration. Vanderbilt mineral medium was used as a mineral environment (Speece, 1996).

In order to provide anaerobic conditions Sodium Thioglikolat was added to low the redox potential of the environment.

Alkalinity and pH is provided by addition of appropriate amounts of $NaHCO_3$. The composition of the synthetic wastewater ($COD_{influent}$ = 15,000 – 20,000 mg/L) is shown in Table 3.2.

Table 3.2 The composition of the synthetic wastewater

Parameter	Range
COD, mg/L	15,000-20,000
TS, mg/L	15,528-22,076
TVS, mg/L	12,788-18,696
TSS, mg/L	124-372
TVS, mg/L	16-152
Total nitrogen, mg/L	26-27
Phosphate, mg/L	0.69-2.4
pH	5-8.7

TS, TVS, TSS, TVS, Total nitrogen and phosphate values in the Table 3 were measured after commissioning the membrane.

3.3 Analytical Procedure

In the experimental studies following analyses were carried out:

Feeding water: Chemical oxygen demand (COD), total nitrogen (TN), phosphate (P), alkalinity, total solids (TS), total volatile solids (TVS), total suspended solids (TSS), volatile suspended solids (VSS), pH, and electrical conductivity (EC).

Anaerobic reactor and membrane effluent samples: Chemical oxygen demand (COD), total nitrogen (TN), phosphate (PO_4-P), alkalinity, total solids (TS), total volatile solids (TVS), total suspended solids (TSS), volatile suspended solids (VSS), volatile fatty acids, pH, and electrical conductivity (EC).

EC and pH were measured by using WTW model 340i multi analyzer. TN and P analyses were done by using test kits (Merck 14537 – 14543). The analyses of the other parameters were carried out according to procedures given in Standard Methods (APHA, AWWA, WEF, 2005).

Total solid concentration of the sludge and the organic material fraction of the solid material measurements were carried out according to Standard Methods (APHA, AWWA & WEF, 1992). Dewatering property of the sludge analysis was done by using TRITON type 304M CST-meter.

The composition of the biogas (CH_4, CO, CO_2, H_2S) was measured by using Dräger X AM 7000 multi gas measurement device. Total biogas and methane production volume were also measured with liquid displacement methods. Total biogas was measured by using saturated NaCl and H_2SO_4 2%, and methane gas productions were measured by using NaOH 3% (w/v) containing distilled water.

3.4 Operational Conditions

Experimental studies were carried out by using AnMBR consisted of an UASB without Gas/Liquid/Solid separation system and ultrafiltration unit (UF). In order to appropriate microbiological growth in the anaerobic reactor, the system was inoculated by adding 4 L of sludges taken from the anaerobic reactors of Izmir PAKMAYA Baker's Yeast Company's Wastewater Treatment Plant.

Rate for solid material of this sludge was 10% and the content of the organic material of the solid material was measured as 32%. At start-up phase of the anaerobic reactor, in order to adapt the microorganisms to the environment, low organic loading rate was used. The water jacket was used to provide mesophilic temperature conditions in the anaerobic reactor. Thus, the temperature in the reactor was fixed at 37 ºC.

During the experiments, the inlet pressure of the UF module was kept constant at 1.5±0.2 bar. The UF module was operated 2 times in a day totally 1 hour. The concentrate was returned to the anaerobic reactor by a peristaltic pump with 15±1 L/d flow rate. The anaerobic reactor effluent was pumped to the UF module by a peristaltic pump with a 0.5±0.1 L/min flow rate. In order to prevent membrane from clogging, it was backwashed with distilled water and it was stored wet by using 0.025 % Sodium Hydroxide solution.

Continuous feeding of the reactor was started with an initial organic loading rate (OLR) of 0.4 kg COD/ m^3.day and hydraulic retention time (HRT) of 5 day. The HRT and COD concentration was maintained constant throughout the start-up period. The influent COD concentration was 2,000 mg/L for the first 29 days, and then it was increased stepwise to 20,000 mg/L from 29 to 295 days. The experiments, carried out for 295 days, comprised 7 stages; the applied operational conditions are shown in Table 3.3. Due to problems in purchasing the membrane, UF membrane could be operated with anaerobic reactor after Phase 4. So, the anaerobic reactor was operated alone between Phase 1 – 4.

Table 3.3 Applied operational conditions

	COD, mg/L	**HRT, day**
Phase 1	7,500	4
Phase 2	10,000	4
Phase 3	10,000	3
Phase 4	15,000	3
Phase 5	15,000	2
Phase 6	15,000	1
Phase 7	20,000	2

CHAPTER FOUR
RESULTS AND DISCUSSIONS

4.1 Start-up Phase

Anaerobic model reactor has been commissioned on 04.10.2010. In order to appropriate microbiological growth in the system, the model reactor was inoculated by adding 4 L of sludges taken from the anaerobic reactors of Izmir PAKMAYA Baker's Yeast Company's Wastewater Treatment Plant. The dry solids content of the sludge and the organic matter content in the solid material were 10% and 32%, respectively,

During the start-up phase of the anaerobic reactor, in order to adapt the microorganisms to the environment, low organic loading rate was applied. Continuous feeding was started with an initial organic loading rate (OLR) of 0.4 kg COD/m^3.day and hydraulic retention time (HRT) of 5 day. The COD concentration and HRT was maintained constant throughout the start-up period. The influent COD concentration was 2,000 mg/L for the first 29 days, and then it was increased stepwise to 20,000 mg/L from 29 to 295 days.

Methane producing bacteria are sensitive to pH levels, which should optimally be between 6.5 and 7.6. During the start-up period, there were small pH fluctuations and it generally remained between 6 and 7. Because acidification phase is dominant at the beginning of the study, pH sometimes dropped to the lower levels. The lowest pH was measured as 5.17 and NaOH was used to adjust pH at that case. After then, pH values remained at the desired levels without any interference.

Removal efficiencies of the organic material were monitored by COD parameter. After commissioning the system synthetic wastewater with a COD concentration of 2,000 mg/L was fed and COD removal efficiencies were not taken into consideration at the first 10 days. After then, COD analyses were carried out at least twice a day. COD removal efficiencies increased from 11% to 90% in 29 days of operation.

After this period, influent COD concentration was gradually increased to 7,500 mg/L by assuming the system reaches stable conditions, and at the same time hydraulic retention time (HRT) was reduced from 5 days to 4 days. Thus, the organic loading rate (OLR) applied to the system was increased to the value of 1.88 kg COD/m^3.day.

4.2 pH, Alkalinity, VFA and EC Results

4.2.1 pH

The pH of the anaerobic reactor effluent and permeate were measured regularly in order to control the system.

4.2.1.1 Anaerobic Reactor Effluent

The microbial community in an anaerobic reactor is very sensitive to pH changes. In order to protect methanogens from pH fluctuations, the pH of the anaerobic reactor content was maintained in required levels.

pH changes in the anaerobic reactor effluent during the AnMBR system operation are shown in Figure 4.1. As seen from the figure, there was no significant fluctuation at the pH level of the reactor. The average pH levels of the anaerobic reactor effluent were 6.6. The minimum value of the pH was 5.17 while the maximum was 7.93. The pH level in the reactor did not reach to inhibition level of the activity of microorganisms.

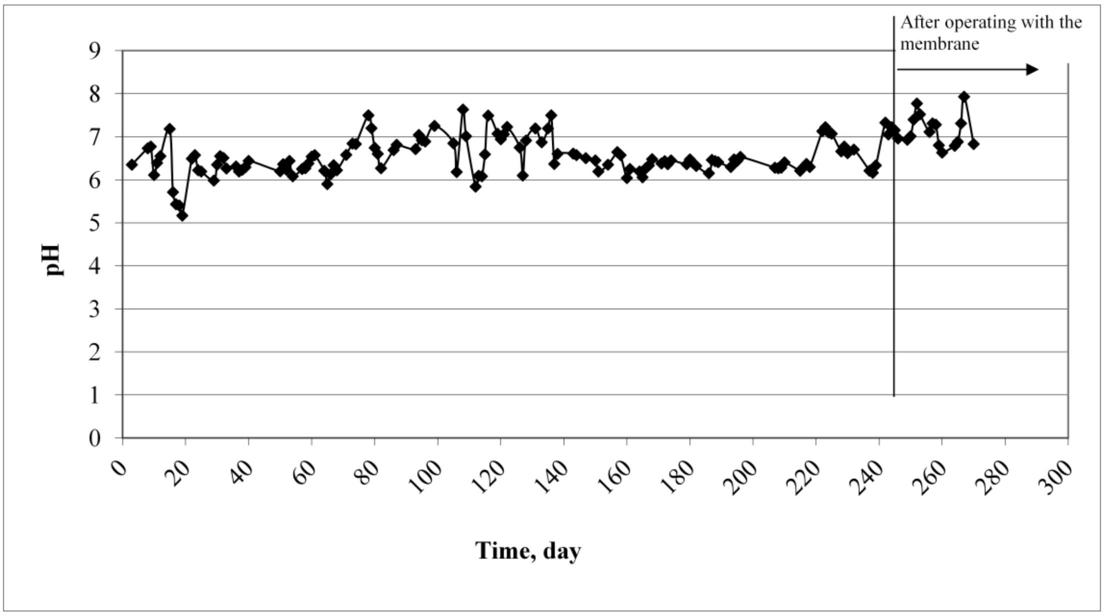

Figure 4.1 pH variations in the anaerobic reactor effluent during the operation

4.2.1.2 Membrane Effluent (Permeate)

After commissioning the UF module, the anaerobic reactor and membrane worked together. Anaerobic reactor effluent was pumped to the UF membrane and then permeate was collected from the membrane effluent. A little bit higher pH values were measured in permeates than anaerobic reactor effluent. The variations in permeate pH are shown in Figure 4.2. The average pH levels of permeates were 7.25. The minimum value of the pH was 6.13 while the maximum was 8.48.

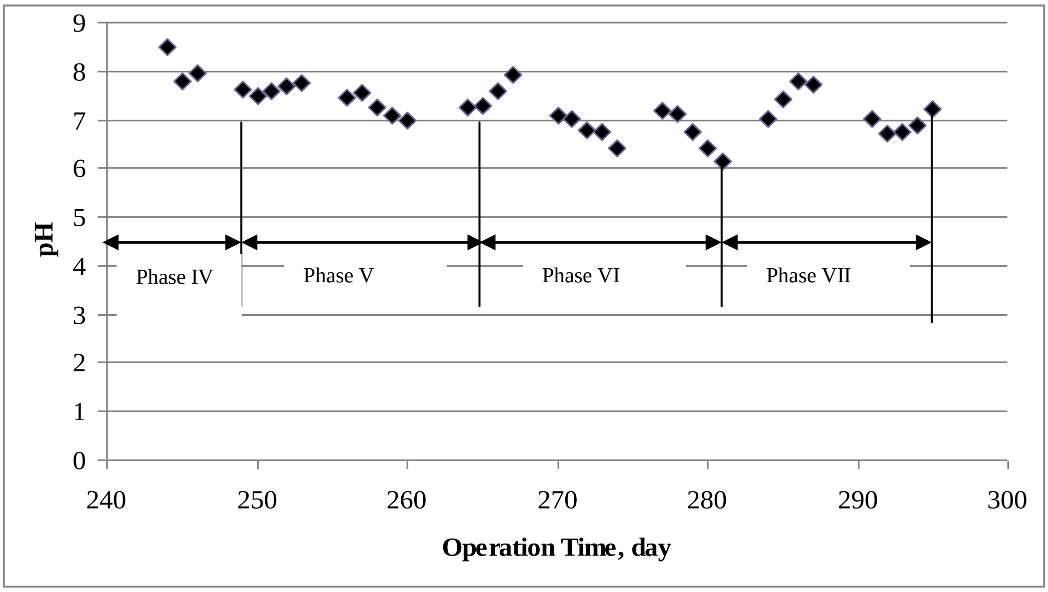

Figure 4.2 Changes in the permeate pH during the membrane operation

4.2.2 Alkalinity and VFA

Alkalinity and the total volatile fatty acids (VFA_S) concentration were regularly measured in the anaerobic reactor and in permeate.

4.2.2.1 Anaerobic Reactor Effluent

2,000 to 3,000 mg $CaCO_3$/L of alkalinity concentrations are needed in anaerobic processes to keep an adequate pH. The principal consumer of alkalinity in a digester is carbon dioxide, and not volatile acids as is commonly believed (Speece, 2001). Carbon dioxide is produced in the fermentation and methanogenesis phases of digestion process. Due to partial pressure of gas in a digester, the carbon dioxide solubilizes and forms carbonic acid, which consumes alkalinity requirements (Tchobanoglous & Burton, 1991). The optimum VFA for better operation of anaerobic system should be below 250 mg/L and alkalinity should be in the range of 1,000-5,000 mg/L (Speece, 1996).

Total alkalinity and VFA measurements in the anaerobic reactor were done once a week. It is known that the alkalinity should not be below 1,000 mg/L and also the pH should not be below 6.5 levels. The values of alkalinity were measured between 940 and 4,430 mg/L as $CaCO_3$. Figure 4.3 shows the alkalinity values of feed wastewater and anaerobic reactor effluent. As seen from the figure, the level of alkalinity in the reactor decreased just one time under 1,000 mg/L, which is the critical value.

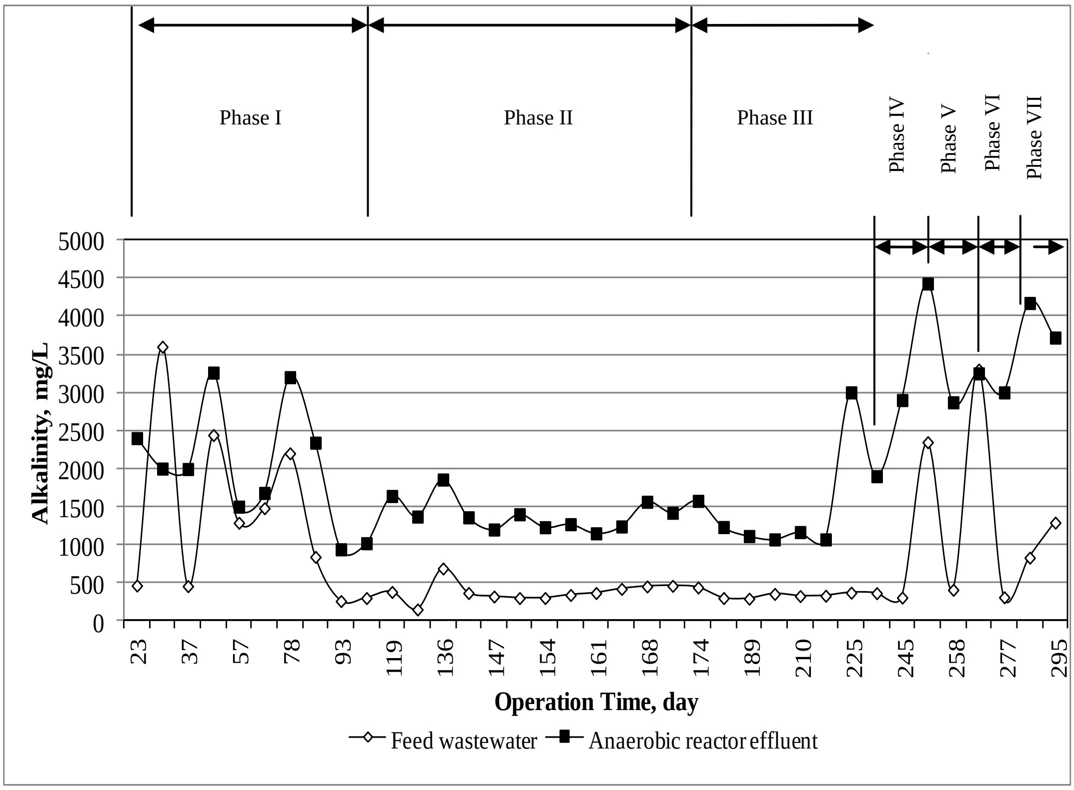

Figure 4.3 Feed wastewater and anaerobic reactor effluent alkalinity values

VFA analysis results are given in Figure 4.4. As shown from the figure, during the operation the average VFA concentration in the anaerobic reactor was around 1,300 mg/L. VFA concentrations increased with the 20,000 mg/L influent COD concentrations applications.

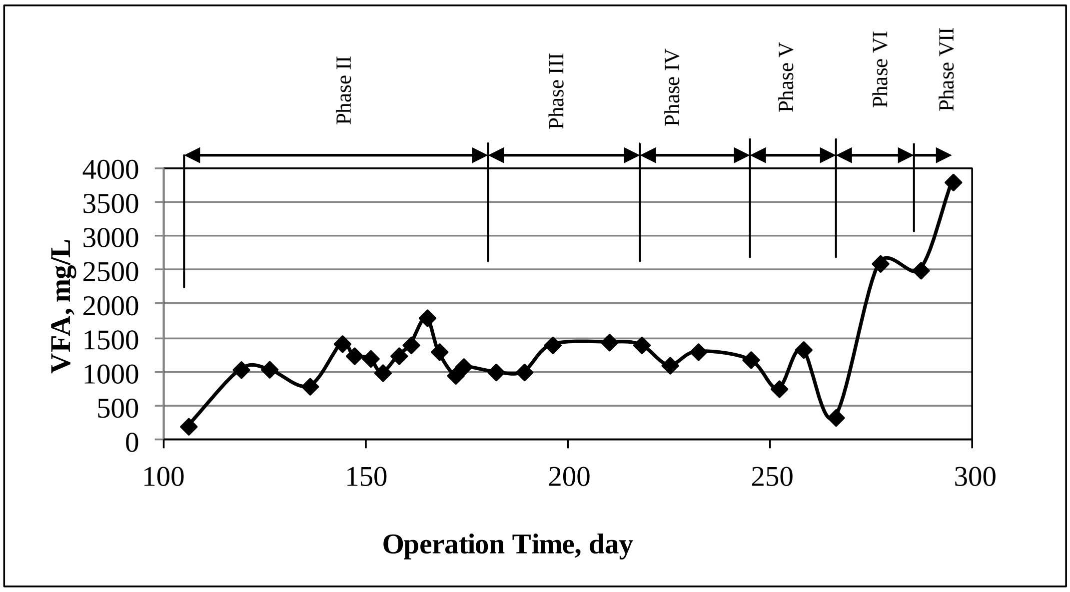

Figure 4.4 VFA concentrations in anaerobic reactor effluent

The VFA and alkalinity, separately, is not a good indicator for evaluating the process stability of the anaerobic reactor since total alkalinity reflect both levels of VFA and bicarbonate, and unstable conditions increased VFA reduced the bicarbonate resulting in constant total alkalinity (Wijetunga, S. et al., 2006). So, the ratio of VFA to alkalinity is the best option to monitor process stability in anaerobic systems. As reported by Zhao and Viraraghavan (2004) if the ratio of VFA to alkalinity exceeds 0.8, the inhibition of methanogens occurs and the process failure is apparent and increase above 0.3 - 0.4 indicate the system instability and a proper ratio is between 0.1 and 0.2. On contrary, Sanchez et al. (2005) and Malpei et al. (1998) have stated that optimum ratio of VFA to alkalinity should be less than 0.3 or 0.4.

Figure 4.5 shows variations in VFA/Alkalinity ratio. It shows that the ratio varied between 0.1 and 1.45. As seen in Figure 4.5 the ratios of VFA to alkalinity were generally above the limit value of 0.4. Despite this undesirable situation, the level of alkalinity in the reactor decreased just one time under 1,000 mg/L and although some pH values were under 6.5, the pH levels remained 6.74 as the average value. These results showed that acidification did not become a problem in the reactor.

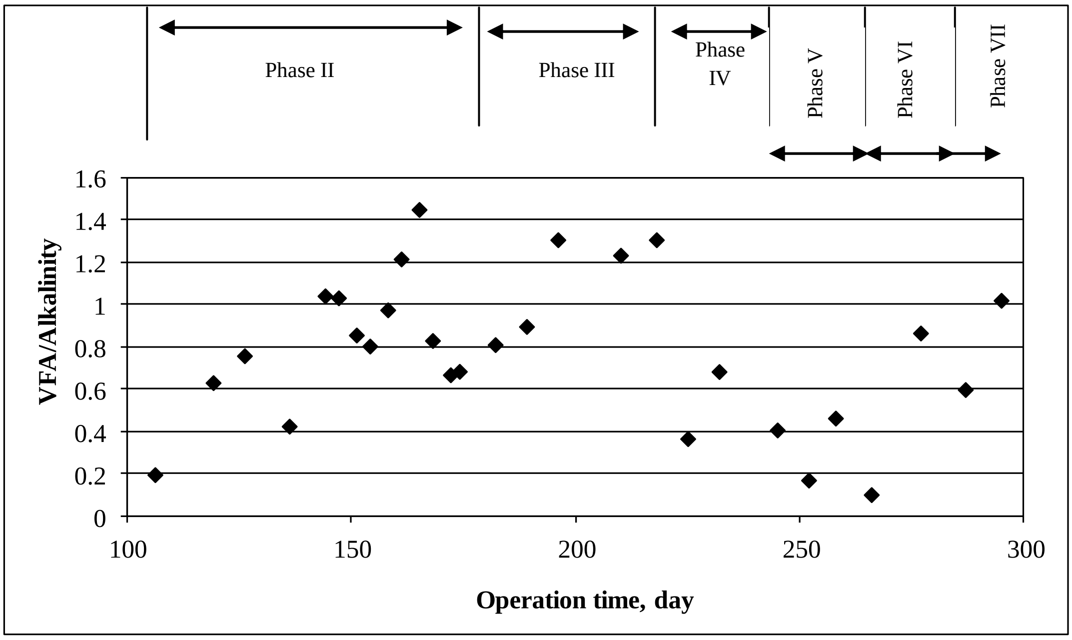

Figure 4.5 VFA/Alkalinity ratios in the anaerobic reactor.

4.2.2.2 Membrane Effluent (Permeate)

Total alkalinity and VFA measurements in permeate were done once a week after commissioning the UF module. Figure 4.6 shows the alkalinity results.

The values of alkalinity were measured between 2,700 and 4,000 mg/L as $CaCO_3$. As is shown in the figure the permeate alkalinities were generally a little bit less than the anaerobic reactor effluent alkalinities. So it can be said that the UF module could not reject alkalinity, CO_3^-/ HCO_3^- ions crossed through the membranes with permeate. The alkalinity decline affected the total buffering capacity of the anaerobic system.

The variations of VFA concentrations in permeate is shown in Figure 4.7. VFA concentrations in permeate has shown a small reduction compared with that of the anaerobic reactor effluent, which could be due to removal of VFA across the membrane.

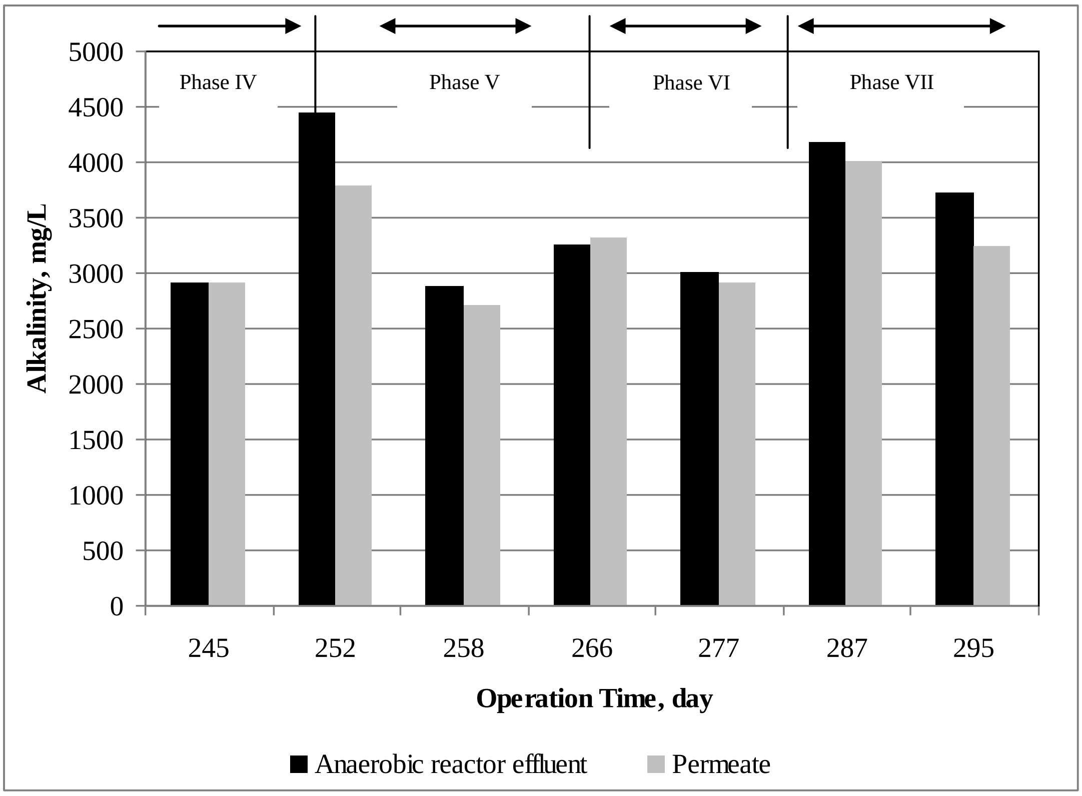

Figure 4.6 The anaerobic reactor effluent alkalinity and permeate alkalinity values

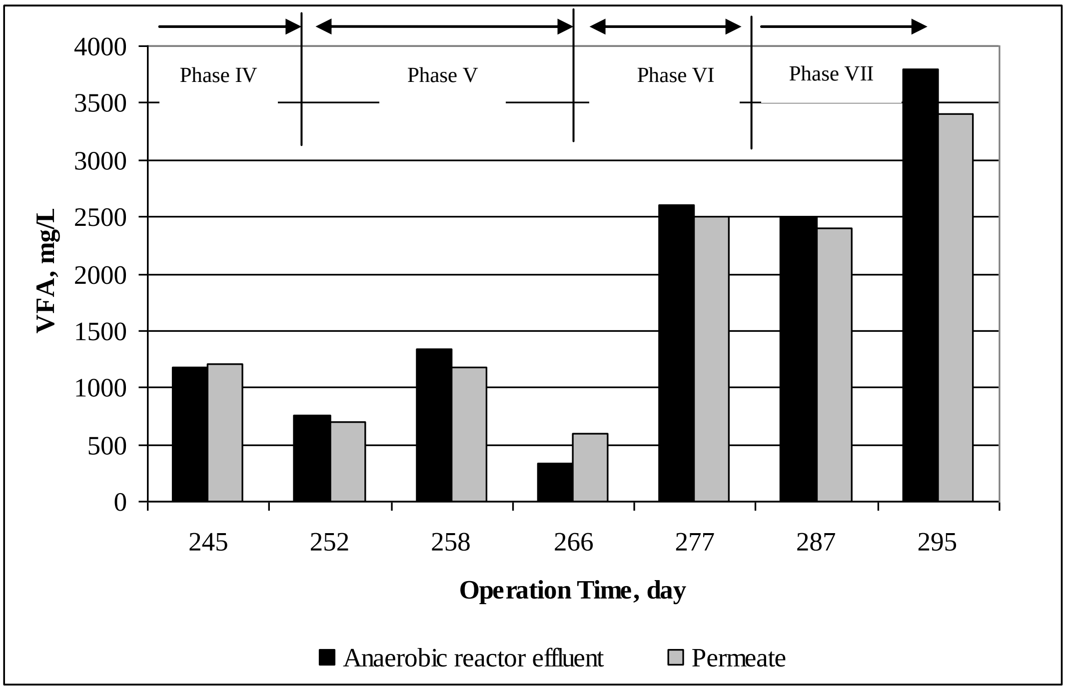

Figure 4.7 Variations of VFA concentrations in the permeate during the study operation

4.2.3 EC

Electrical conductivity parameter is generally used to estimate salinity level. The diameter of ions causing salinity is lower than 0.001 microns. However Ultrafiltration (UF) membranes remove particles from 0.005 to 0.05 microns. Therefore significant salinity removal with UF membrane cannot be achieved. Anyway salinity levels of permeate were determined with EC analyses in this study. EC analyses were carried out daily after commissioning the UF module and the results are shown in Figure 4.8. The values of EC were measured between 4.01 and 8.7 mS/cm.

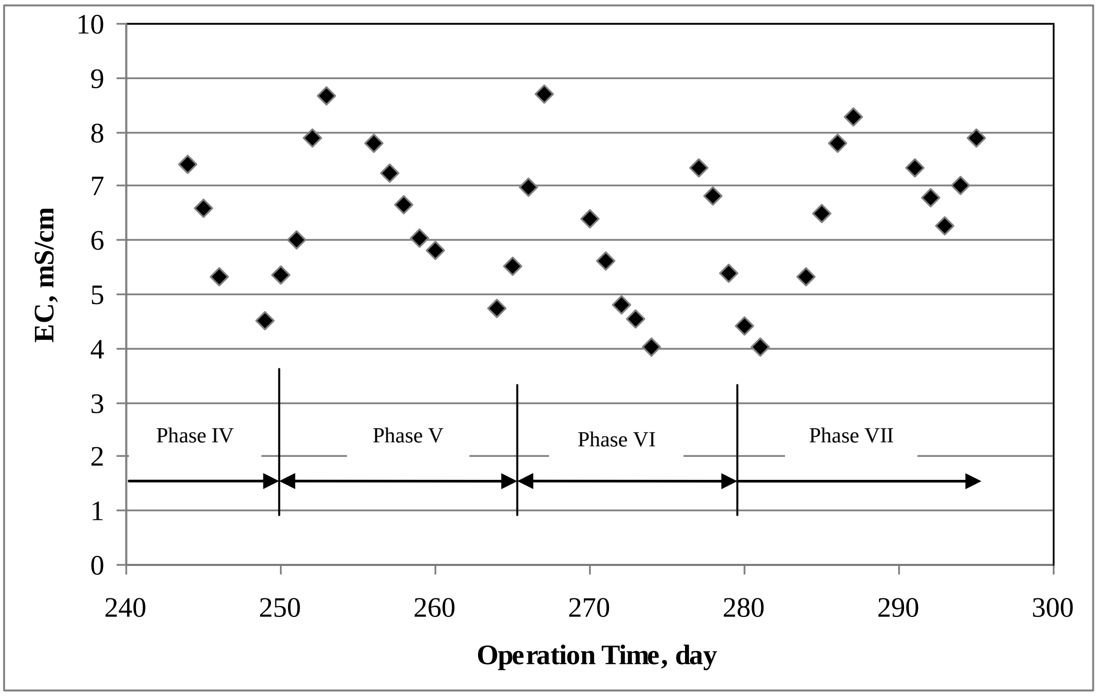

Figure 4.8 Changes in the permeate EC during the operation time

4.3 Effects of Operational Conditions on Organic Material Removal

The Chemical Oxygen Demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water and it is an important parameter for treatment efficiency of biological processes. In these experimental studies, COD parameter is used to determine the amount of organic material. COD removal efficiencies were monitored for the anaerobic reactor, membrane system, and overall system.

Seven different operational conditions were applied during 295 days of operation and applied operational conditions are shown in Table 4.1. Due to problems in purchasing the membrane, UF membrane could be operated with anaerobic reactor after Phase 4. So, the anaerobic reactor was operated alone between Phase 1 – 4.

Table 4.1 Applied operational conditions

	COD, mg/L	HRT, day	OLR, kg COD/m^3.d
Phase 1	7,500	4	1.88
Phase 2	10,000	4	2.5
Phase 3	10,000	3	3.33
Phase 4	15,000	3	5
Phase 5	15,000	2	7.5
Phase 6	15,000	1	15
Phase 7	20,000	2	10

Influent COD concentrations changed from 7,500 mg/L to 20,000 mg/L and hydraulic retention time was decreased from 4 days to 1 day. Depending on these conditions, organic loading rate changed between 1.88 kg COD/m^3.d and 15 kg COD/m^3.d.

4.3.1 Anaerobic Reactor

COD removal efficiencies of the anaerobic reactor were carried out twice a week according to Standard Methods (APHA, AWWA, WEF, 2005). COD removal efficiencies of the anaerobic reactor depending on organic loading rates are shown in Figure 4.9.

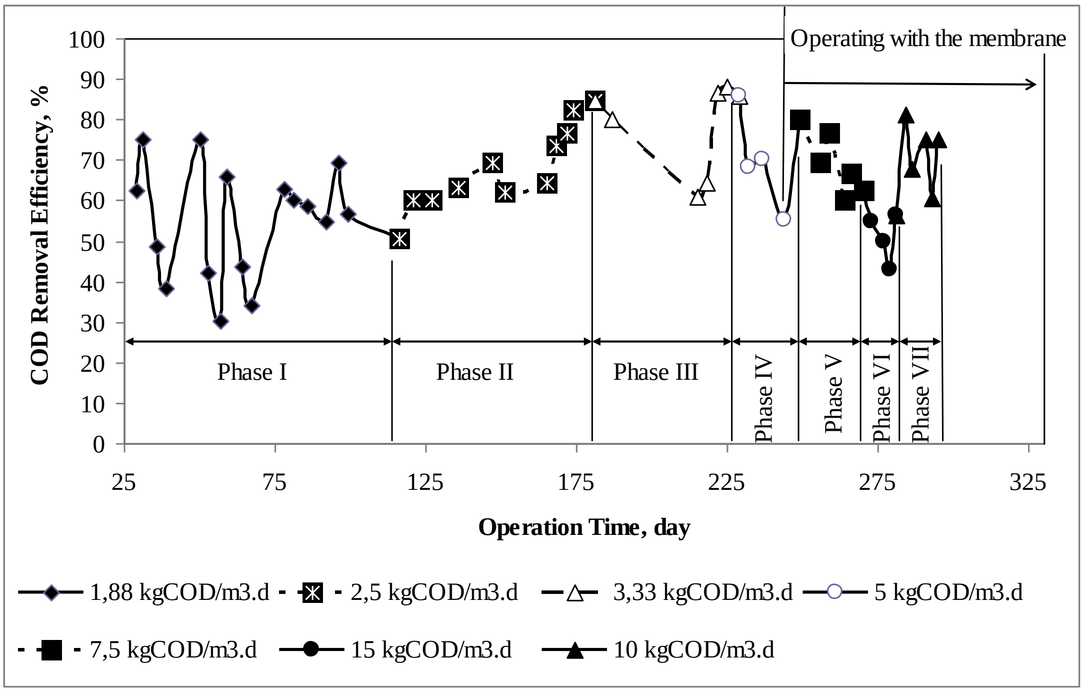

Figure 4.9 COD removal efficiencies of the anaerobic reactor depending on organic loading rates

As seen from Figure 4.9, average COD removal efficiencies were 55 %, 67.87 %, 78.68 %, 71.78 %, 69.18 %, 53.27 %, and 69.35 % at 1.88 kg COD/m^3.d, 2.5 kg COD/m^3.d, 3.33 kg COD/m^3.d, 5 kg COD/m^3.d, 7.5 kg COD/m^3.d, 15 kg COD/m^3.d and 10 kg COD/m^3.d of organic loading rate applications, respectively.

Without operating UF module, maximum COD removal efficiency of 88.24 % was achieved at OLR of 3.33 kg COD/m^3.d and HRT of 3 day. Comparing to 4 days of HRT application, 13.24% higher removal efficiency was achieved at 3 days of HRT. Decreasing HRT and increasing organic loading rate caused significant organic material removal until 15000 mg/L of influent COD concentration application.

After commissioning of the membrane, HRT was reduced from 3 day to 1 day while COD concentration kept constant at 15,000 mg/L and at these conditions maximum organic loading rate of 15 kg COD/m^3.d was applied to the system. Organic material removal efficiency adversely affected from the decreasing HRT to 1 day and increasing of organic loading rate to 15 kg COD/m^3.d and 23.21% lower COD removal efficiency was obtained comparing to HRT of 3 days application.

After UF applications, maximum 81.25% COD removal efficiency was achieved at 10 kg COD/m^3.d OLR and HRT of 2 day with a COD concentration of 20,000 mg/L.

Experimental studies results showed that UF membrane application after anaerobic reactor did not give significant effect on COD removal efficiency.

4.3.2 Membrane System

The MBR system is capable of achieving COD removal by both physical and biological mechanisms. The membrane filter offers the physical barrier against particulates and some soluble organic carbon and inert fractions of mixed liquor (Chay et al., 2001). The biological COD removal increases with the time, but the physical COD removal by the membrane decreases over time because of the age of the membrane and sloughing of some biomass on permeate side of the membrane (membrane fouling).

After commissioning the UF module, the anaerobic reactor effluent was pumped to the UF membrane system. COD removal efficiencies of UF membrane system were determined twice a week and the results are shown in Figure 4.10.

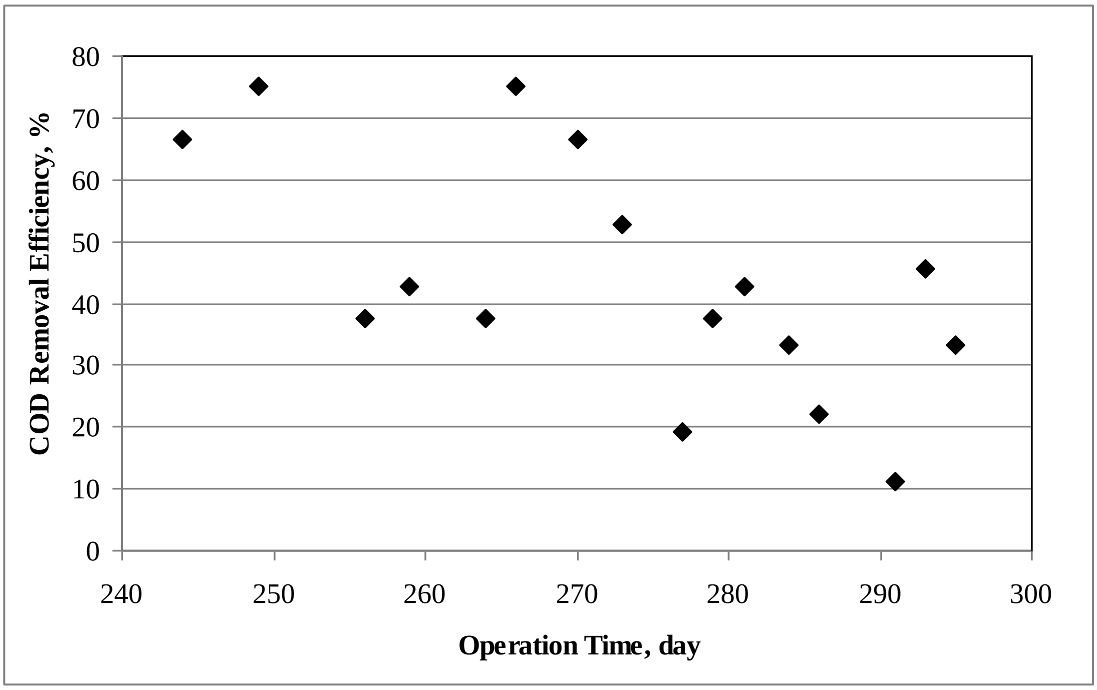

Figure 4.10 COD removal efficiencies of the UF module

Maximum 75% COD removal efficiency was obtained with UF membrane system and average COD removal efficiency was about 45%. This result was not a surprise. UF is very effective for the removal of bacteria and suspended particles; however removal of organics is generally low. This is because organics that are smaller than the pore size can pass through the membrane. Arnal et al. (2008) obtained the COD rejections in the range of 35–50% with a 4-inch spiral-wound UF membrane module (IRIS 3028 10 kDa). In another study, although almost 100% COD removal efficiencies were obtained with NF, it was not possible to decrease COD with UF membranes of 5 to 100 kDa MWCO (Bes-Piá et al., 2002).

4.3.3 Overall System (AnMBR)

COD removal efficiencies of the overall system including the anaerobic reactor efficiency and membrane system efficiency together (AnMBR) were also evaluated. The results are shown in Figure 4.11.

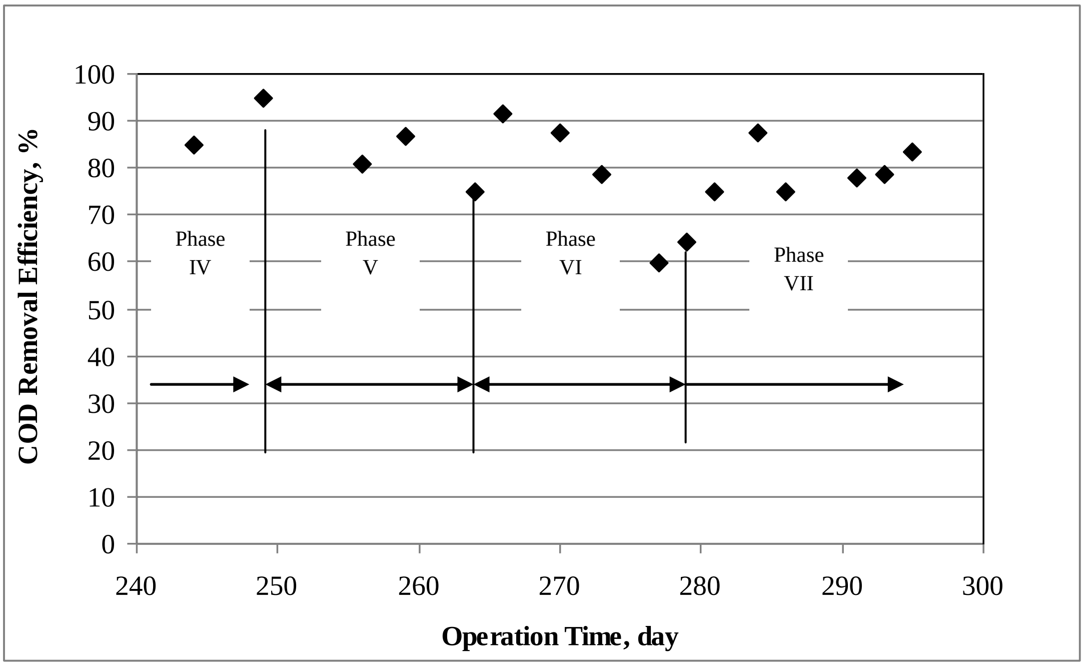

Figure 4.11 COD removal efficiencies of the overall system after membrane commissioning

As shown in Figure 4.11, maximum 95% COD removal efficiency was obtained with AnMBR system at 15,000 mg/L influent COD concentration and HRT of 2 day (OLR = 7.5 kg COD/m^3.d). 85.94%, 72.99%, and 79.53% of average COD removal efficiencies were obtained at 7.5 kg COD/m^3.d, 15 kg COD/m^3.d, and 10 kg COD/m^3.d organic loading rates applications, respectively.

The changes in HRT relatively influence the COD removal in the MBR. Darren et al. (2006) observed slightly difference in overall COD removal efficiencies of MBR_s treating the same wastewater at different HRT_s.

The results demonstrated that although membrane did not play an important role at COD removal of anaerobic reactor, a little bit more removal efficiencies were obtained after membrane application when the overall system efficiencies are taken into consideration.

4.4 Methane Production Performance of the Anaerobic Reactor

The composition of the biogas (CH_4, CO_2) was determined by using Dräger X-AM7000 multi gas measurement device. This device measures the methane percentage of produced biogas as LEL % and it could be used only for 168 days of study. After then, the amount of produced total biogas and methane gas were measured with liquid displacement methods. Total biogas was measured by using saturated NaCl and 2% H_2SO_4, and methane gas productions were measured by using 3% NaOH (w/v) containing distilled water.

The results of methane and carbon dioxide gas analyses carried out with Dräger device and the amount of produced total biogas and methane gas determined with liquid displacement method are shown in Figure 4.12 and 4.13, respectively.

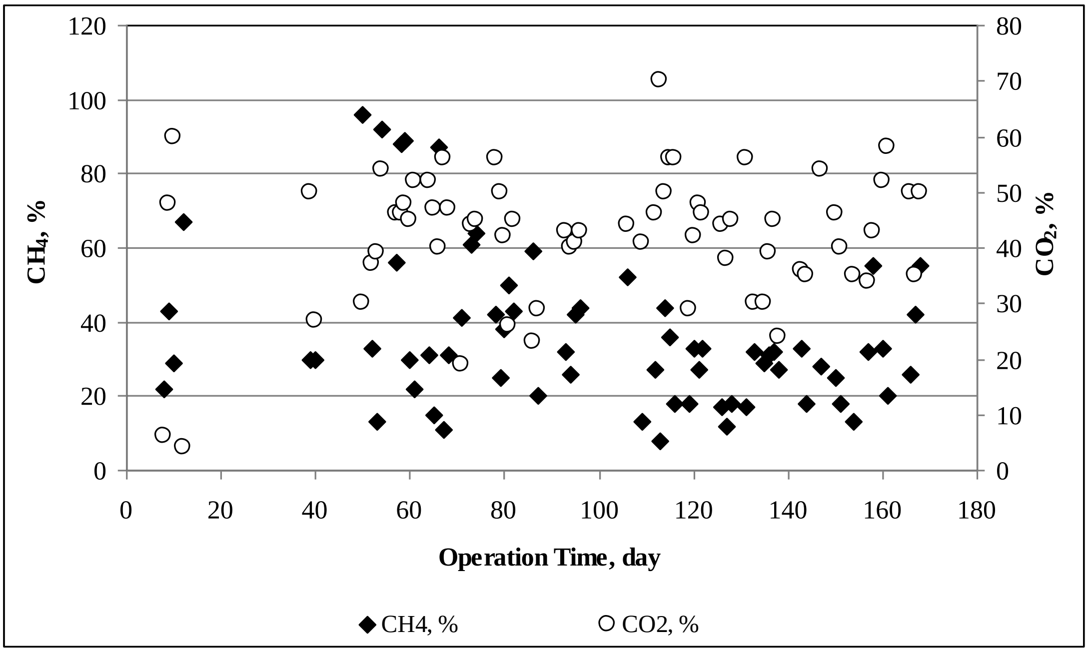

Figure 4.12 Composition of biogas (up to 168th day)

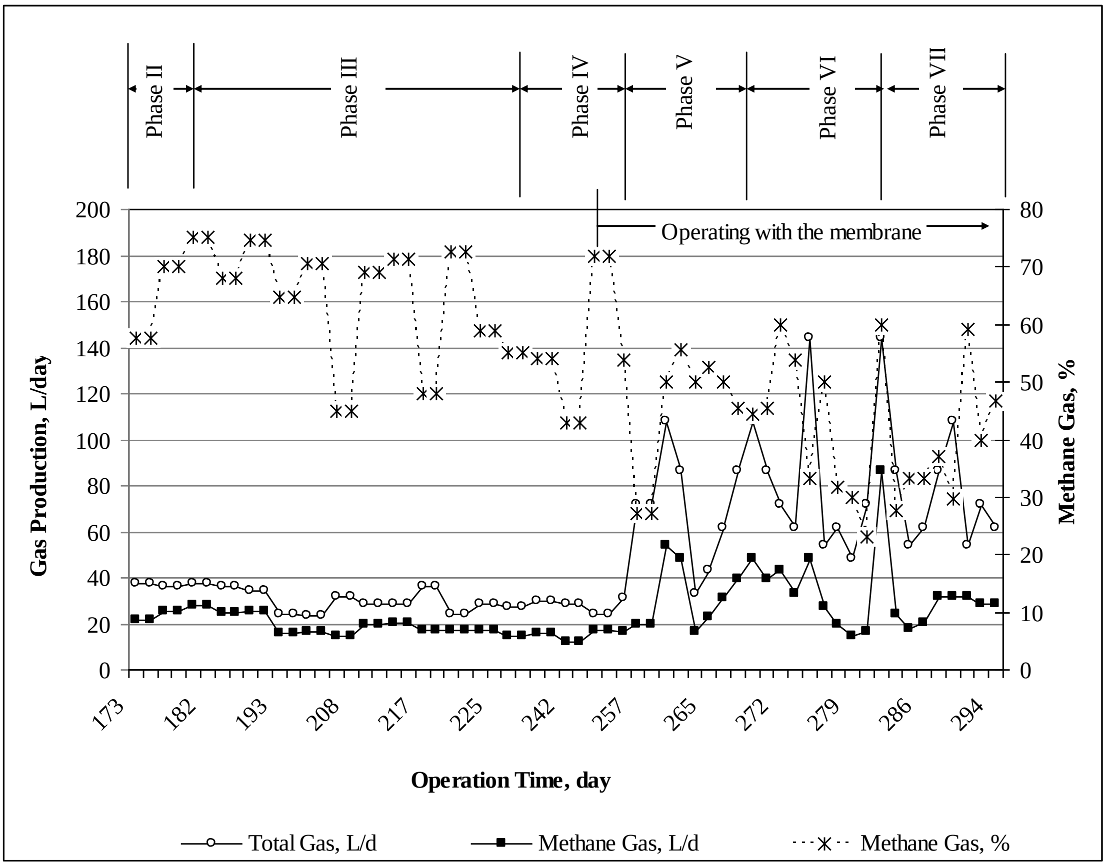

Figure 4.13 Total biogas and methane gas production

Average methane gas percentage of the total produced biogas during Phase II (2.5 kg COD/m^3.d OLR), Phase III (3.33 kg COD/m^3.d OLR), Phase IV (5 kg COD/m^3.d OLR), Phase V (7.5 kg COD/m^3.d OLR), Phase VI (15 kg COD/m^3.d OLR), and Phase VII (10 kg COD/m^3.d OLR) were observed as 66, 65, 56, 46, 43 and 41%, respectively. Although the amount of produced total gas did not decrease, methane gas percentage in the biogas decreased with increasing organic loading rate. Membrane operation did not give positive effect on the production of methane gas. During the all operating time, average total biogas production, methane gas production, and methane gas percentage in the biogas were 50 L/d, 25 L/d, and 50 %, respectively.

4.5 Biomass Properties during the Operation

Following the addition of the inoculation sludge, variations of total solids (TS) and the organic fraction of the solid material (TVS) in the reactor was periodically monitored by taken sludge samples from discharge valve at the bottom of reactor.

Due to there was no Solid/Liquid/Gas separation system in the reactor, the escape of solid material occurred. Therefore, as shown in Figure 4.14, reduction in the amount of solid material was observed. But, the increase in the content of organic material of solid material showed that an increase in the amount of viable microorganisms in the system. During 300-days period of operation the amount of total solid material decreased from 24% to 4%. However, the organic material content of solid material increased from 16% to around 82%.

Following commissioning the UF module a slightly increase in both solid material and the organic material content of the solid material were observed.

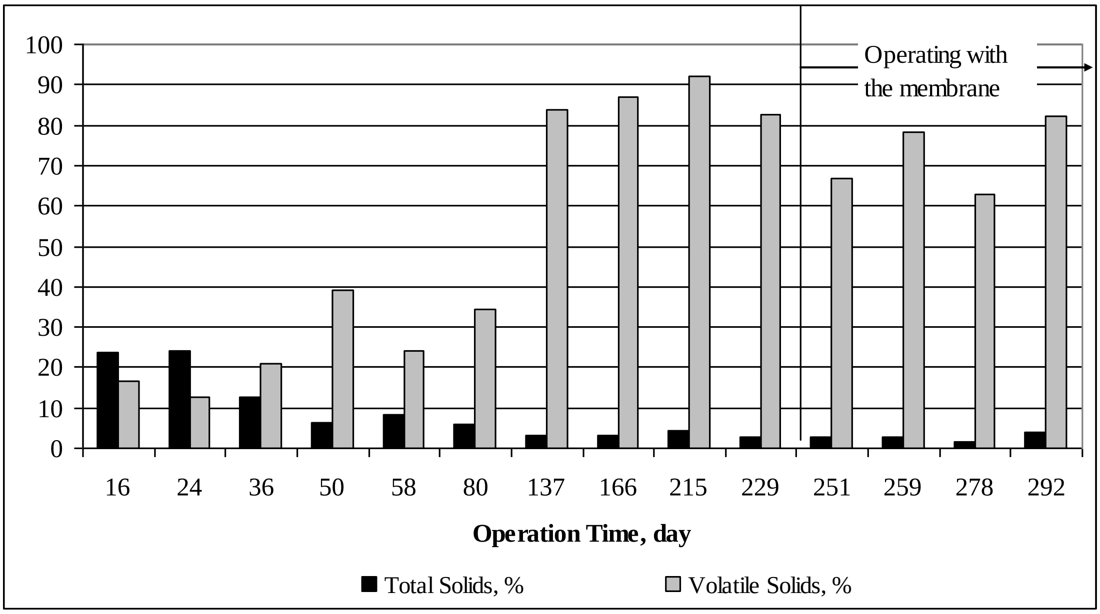

Figure 4.14 Total solid (TS) and organic material content of solid material (TVS) in the reactor

Also in order to determine the dewatering property of sludge in the reactor, at the end of the study, CST analyses were done. CST value of sludge sample was 897 s as average. CST for unconditioned domestic wastewater treatment plant sludge is about 200 s. A CST of 10 s or less is considered a good value for superior dewatering performance (Turovskiĭ & Mathai, 2006).

4.6 Solid Fractions of the Anaerobic Reactor and Membrane Effluent

The total solid (TS), total volatile solid (TVS), suspended solid (SS) and volatile suspended solid parameters were monitored in order to control system efficiency at the applications of 15,000 mg/L and 20,000 mg/L influent COD. These parameters were measured periodically after commissioning the UF both anaerobic reactor effluent and permeate. Figure 4.15 shows the values of total solid concentrations of anaerobic reactor effluent and permeate, and TS removal efficiencies of the UF membrane system. Figure 4.16 shows the values of total volatile solid and removal efficiencies. Figure 4.17 shows the values of suspended solid and removal efficiencies. Figure 4.18 shows the values of volatile suspended solid and removal efficiencies.

Average total and volatile solid concentrations of anaerobic reactor effluent is 7,000 mg/L and 2,660 mg/L, respectively. UF did not remove total and volatile solids efficiently and maximum 25% TS and 38% TVS removal were obtained with UF membrane system while the average removal efficiencies was 15% TS and 31% TVS (Figure 4.15 and 4.16).

Ultrafiltration membrane system can produce high quality water, free of suspended solids, colloidal material and bacteria (Taylor & Wiesner, 1999). As it is expected, high suspended solid and volatile solid removal efficiencies were obtained with UF membrane system, in this study. As seen from Figure 4.17 and 4.18, during the operation of UF membrane system average 97% SS and 93% VSS removal was achieved.

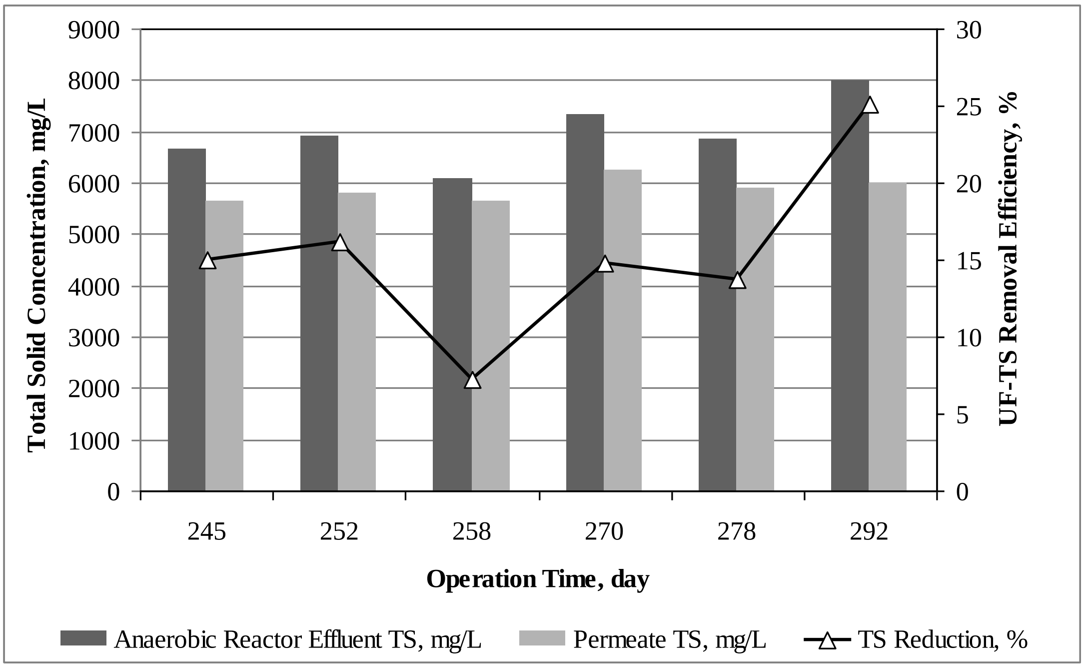

Figure 4.15 Total solid concentrations of anaerobic reactor effluent and permeate, and TS removal efficiencies of UF membrane system.

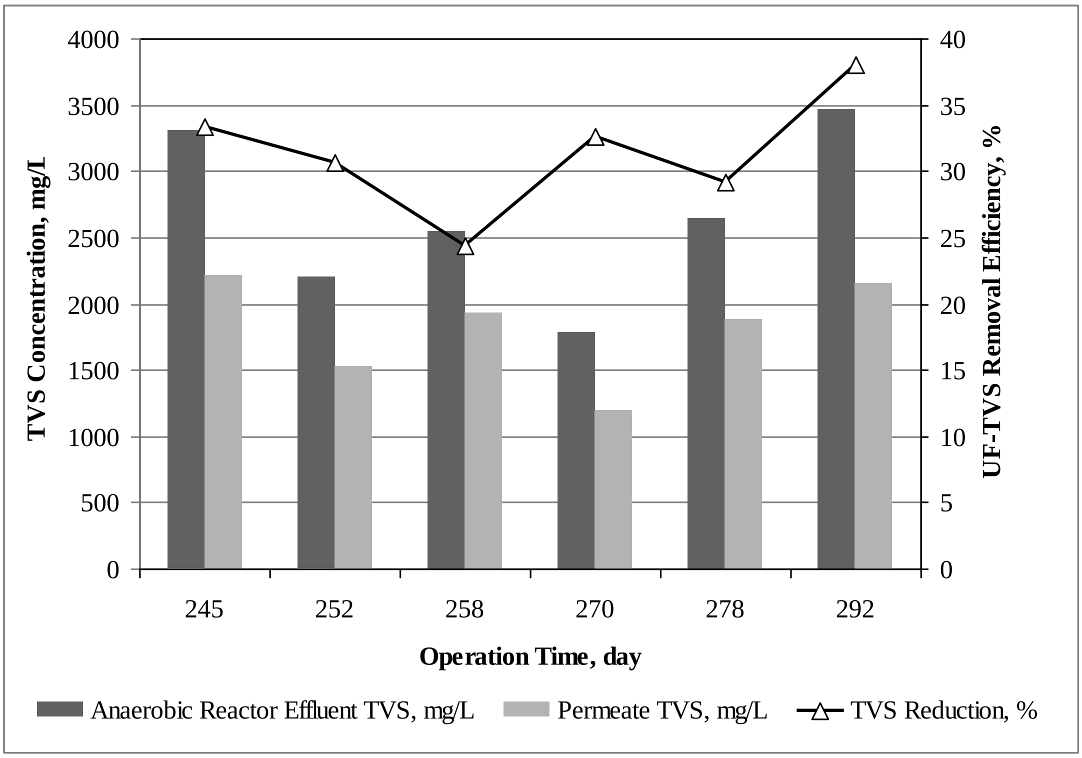

Figure 4.16 Total volatile solid concentrations of anaerobic reactor effluent and permeate, and TVS removal efficiencies of UF membrane system.

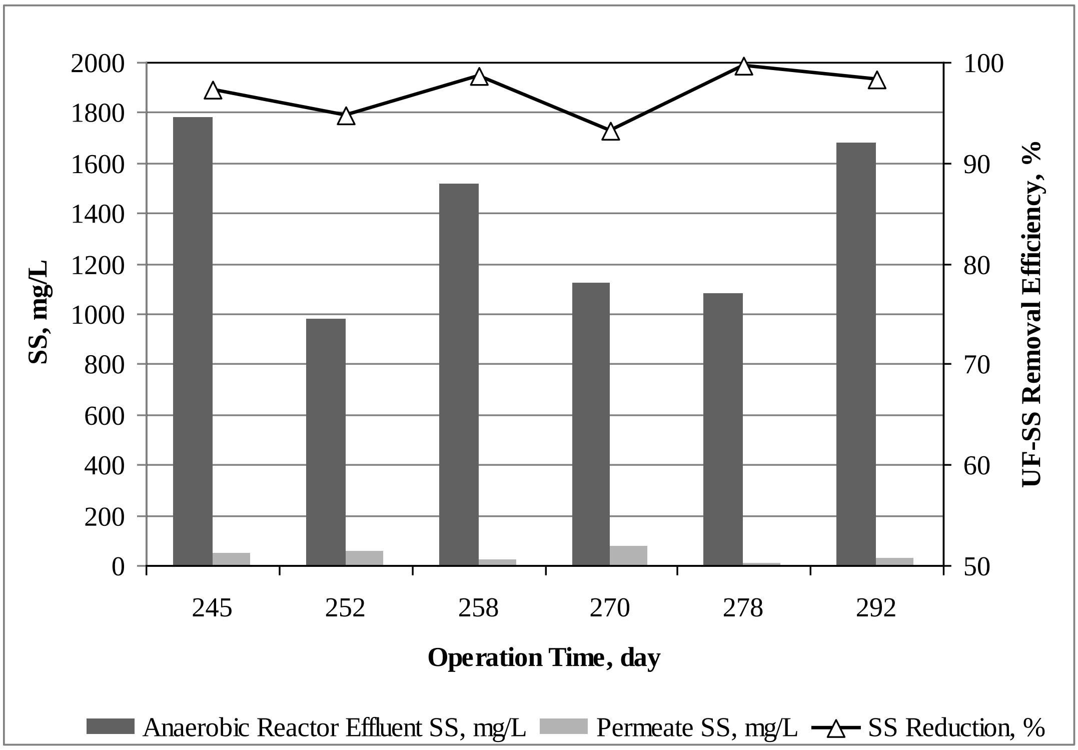

Figure 4.17 Total suspended solid concentrations of anaerobic reactor effluent and permeate, and SS removal efficiencies of UF membrane system.

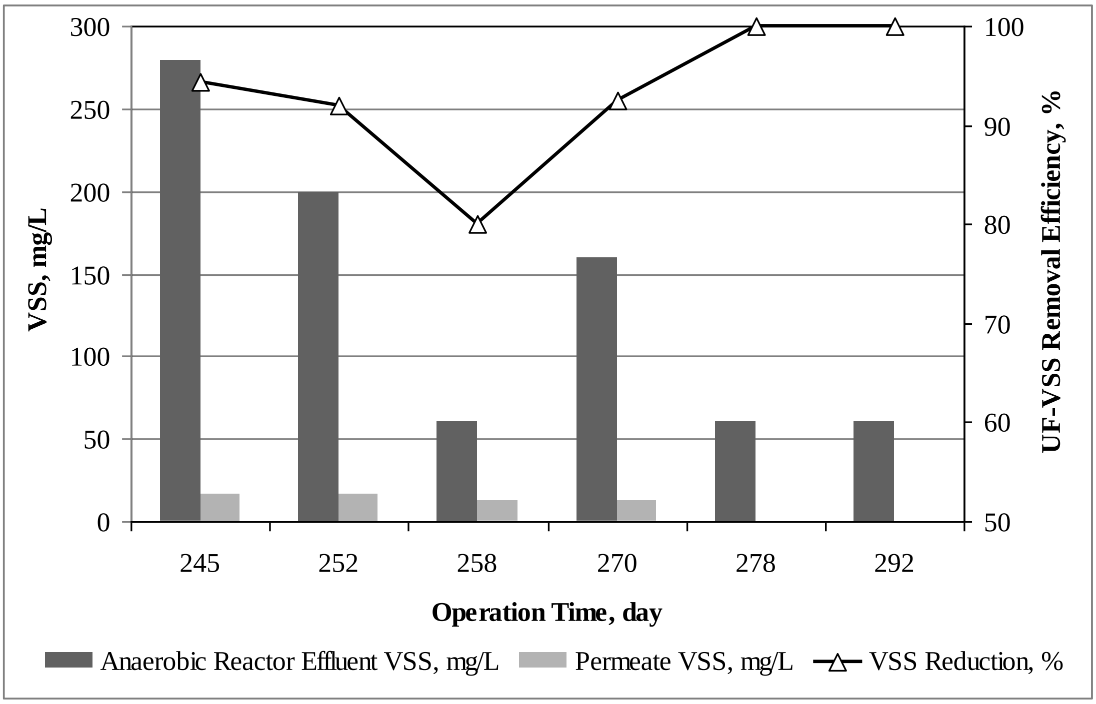

Figure 4.18 Volatile suspended solid concentrations of anaerobic reactor effluent and permeate, and VSS removal efficiencies of UF membrane system.

CHAPTER FIVE
KINETIC MODELS APPLIED TO EXPERIMENTAL RESULTS

5.1 General

A mathematical model describing the process in whole or in part is used to optimize the process design and the process controls, to develop automatic process controls, to assist in understanding the underlying biological and transport mechanisms (Buyukkamaci, 2001). Using models helps us to better understand the complex processes. They allow us to systematically analyze these systems and identify important variables and parameters. Biological kinetic equations express microbial growth and substrate utilization rates in terms of biological kinetic coefficients, food-to-biomass ratio, and the mean cell residence time. The cell yield coefficient, Y, is one of the most important parameters used in biological kinetic models. It represents the mass of biomass produced per substrate removed. The endogenous decay rate, k_d, represents the rate of biomass loss due to endogenous respiration. The maximum specific growth rate (μ_m) is the maximum growth rate achievable when the concentration of the growth limiting nutrient is not limiting.

There are numerous mathematical models, including Monod, First-order, Second-order, Grau et al., Stover-Kincannon, Contois, Chen&Hashimoto, Barthakur, and etc. have been introduced in anaerobic processes to determine the importance of relationships between the design data and experimental results (Turkdogan et al., 2010).

5.2 Kinetic Models Applied to Experimental Studies

In this study, Monod model, Second-order model, Sundstorm et al. model, and Grau et al. model was applied to the experimental results.

5.2.1 Monod Model

Many of biokinetic models on anaerobic biodegradation are based on Monod model. *The Monod rate equation applies to a single strain of bacteria growing on a single 'rate-limiting' substrate and relates the rate of uptake of that substrate to its concentration in the growth medium. It assumes that all other substrates and nutrients are present in excess, and it further assumes that the products of the reaction do not accumulate sufficiently to inhibit the fermentation. It describes a form of 'saturation kinetics' in which the rate of reaction, initially proportional to the concentration of substrate, gradually approaches a maximum value which cannot be exceed no matter how high a concentration of substrate is applied* (McCarty, 1991, p. 18). Monod kinetics is formulated by the following equations:

$$L_r = \frac{1}{X}\,\frac{dS}{dt} = \frac{k_{max}\,S}{K_s + S} \qquad \text{(Eq. 5.1.a)}$$

$$L_r = \frac{Q\,(S_o - S)}{V\,X_r} \qquad \text{(Eq.5.1.b)}$$

$$\frac{1}{\theta_c} = Y\,L_r - b \qquad \text{(Eq.5.1.c)}$$

$$\theta_c = \frac{V\,X_r}{Q\,X_e} \qquad \text{(Eq.5.1.d)}$$

in which:

dS/dt = substrate utilization rate, mg/L.d

k_{max} = maximum specific substrate utilization rate, g COD/g VSS.d

S = effluent substrate concentration, mg COD/L

θ_c = mean cell residence time, d

Y = cell yield coefficient, mg VSS/ mg COD removed

K_s = half saturation concentration, mg/L

L_r = specific substrate utilization rate, mg/mg.d

b = specific microorganism decay rate, d^{-1}

X = biomass concentration, mg/L

X_e = effluent microbial concentration, mg/L

X_r = concentration of microorganisms in the reactor, mg/L

Data used in this model for the anaerobic model reactor are given in Table 5.1, and the graph of determining of the maximum specific substrate utilization rate (k), half saturation concentration (K_s), and cell yield coefficient (Y) are given in Figure 5.1.a and 5.1.b.

Table5.1 Data used in Monod model

θc (d)	1/ θc (d^{-1})	Q (L/d)	So (mg COD/L)	S (mg COD/L)
32,63	0,031	3,33	15000	6750
39,51	0,025	5	15000	3000
29,33	0,034	5	15000	3500
19,9	0,05	10	15000	5625
10,25	0,098	10	15000	7500
38,73	0,026	5	20000	5000
Xr (mgVSS/L)	**Lr (mg COD /mg VSS.d)**	**1/ Lr (mg VSS / mg COD.d)**	**1/S (L/mg COD)**	
19360	0,142	7,04	$1{,}48 x 10^{-4}$	
19360	0,309	3,227	$3{,}33 x 10^{-4}$	
22290	0,258	3,877	$2{,}85 x 10^{-4}$	
22290	0,421	2,378	$1{,}77 x 10^{-4}$	
11070	0,678	1,476	$1{,}33 x 10^{-4}$	
32536	0,231	4,338	$2 x 10^{-4}$	

Although the correlation coefficient of Figure 5.1 (a) is high (R^2 = 0.8731), it is very low for Figure 5.1 (b) (R^2 = 0.3211). So, it can be said that Monod model is not suitable for these results. However, kinetic constants of Monod model were calculated. Cell yield coefficient (Y) and microorganism decay rate (b) was found as 0.1372 mg VSS/ mg COD removed and 0.0027 d^{-1}, respectively, from Figure 5.1 (a). From Figure 5.1 (b), K_s/k and 1/k was found as 7,968.7 and 1.25, respectively. Therefore, maximum specific substrate utilization rate (k) is 0.80 g COD/g VSS.d and half saturation concentration (K_s) is 6,375 mg COD/L, for the anaerobic model reactor.

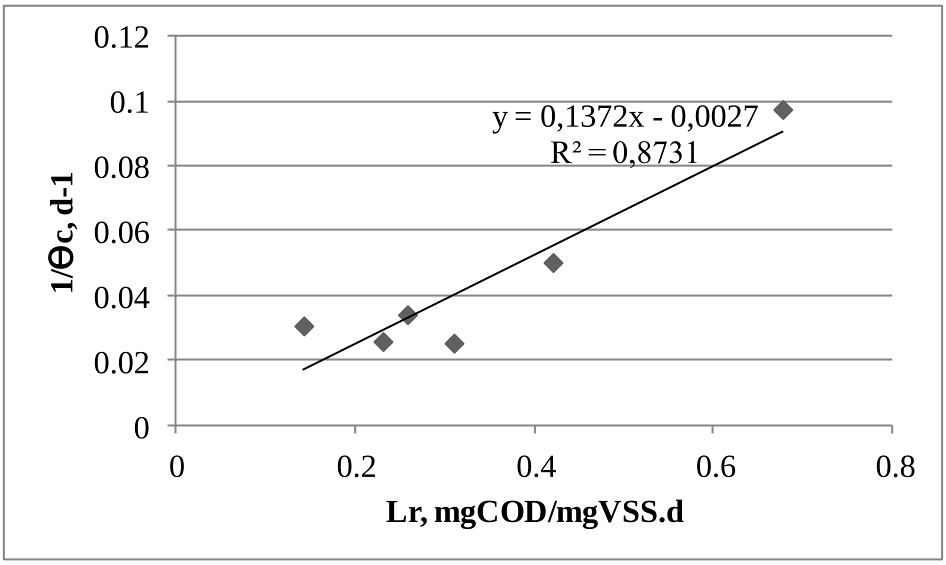

Figure 5.1 (a) Monod model application

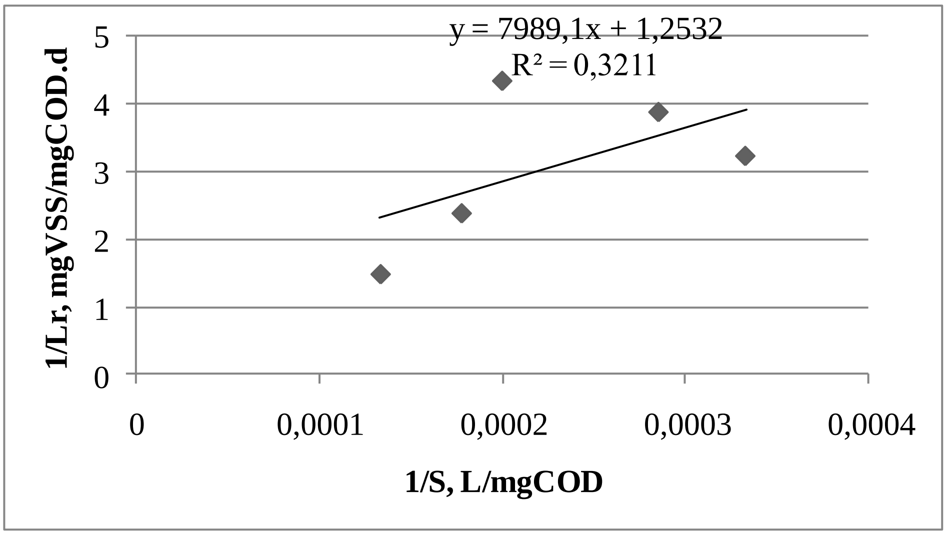

Figure 5.1 (b) Monod model application

5.2.2 Second-order Kinetic Model

General equation of second-order kinetic model is given below (Ubay & Öztürk, 1991, p. 171):

$$\frac{-dS}{dt} = k_{n(S)}\, X\, (S/S_o)^n \qquad \text{(Eq. 5.2.a)}$$

If Eq. 5.2.a. is integrated, Eq. 5.2.b will be obtained,

$$S = \frac{S_o^2}{S_o + k_{2(S)}\, X\, \theta} \qquad \text{(Eq.5.2.b)}$$

If Eq. 5.2.b is linearilized, Eq. 5.2.c will be obtained,

$$\frac{S_o\, \theta}{S_o - S} = \theta + \frac{S_o}{k_{2(S)}\, X_o} \qquad \text{(Eq.5.2.c)}$$

If the second term of the right part of this equation is accepted as a constant, Eq. 5.2.d will be obtained,

$$\frac{S_o\,\theta}{S_o - S} = a + b\,\theta \qquad \text{(Eq.5.2.d)}$$

Where, $a = S_o / (k_{2(S)}\,X)$ and b is a constant greater than unity. $(S_o - S) / S_o$ expresses the substrate removal efficiency and it is symbolized as E. Therefore, Eq. 5.2.e can be written as follows:

$$\frac{\theta}{E} = a + b\,\theta \qquad \text{(Eq.5.2.e)}$$

Where,

S and S_o = effluent and influent substrate concentration (mg COD/L)

X = the average biomass concentration in the reactor (mg VSS/L)

θ = hydraulic retention time (d)

$k_{2(S)}$ = second-order substrate removal rate constant (d^{-1})

Data used for second-order kinetic model is given in Table 5.2 and (a) and (b) were obtained using Figure 5.2.

Table 5.2 Data used in second-order kinetic model

θ (HRT) (d)	**S_o (mgCOD/L)**	**S (mgCOD/L)**	**X_r (mgVSS/L)**	**E (%)**	**θ/E**	**$k_{2(S)}$ (d^{-1})**
3	15000	6750	19360	55	5.45	0.77
2	15000	3000	19360	80	2.5	0.77
2	15000	3500	22290	76.7	2.61	0.67
1	15000	5625	22290	62.5	1.6	0.67
1	15000	7500	11070	50	2	1.34
2	20000	5000	32536	75	2.67	0.61

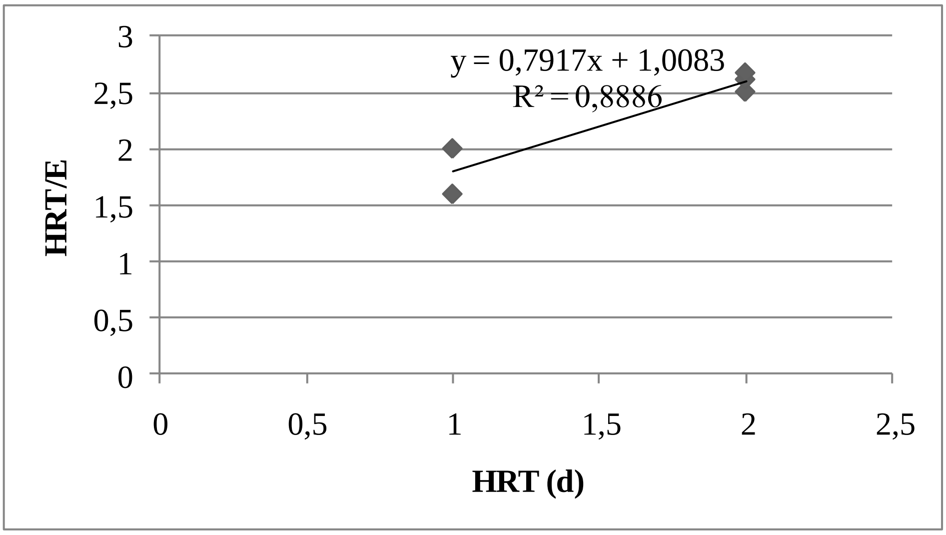

Figure 5.2 Second-order kinetic model application

From Figure 5.2, (a) and (b) values can be found as 1.0083 and 0.7917, respectively with the correlation coefficient of R^2 = 0.89. Second-order substrate removal rate constants ($k_{2(S)}$), which were calculated from (a) values, are given in Table 5.5.

$$S = S_o \left(1 - \frac{\theta}{1.0083\,\theta + 0.7917}\right)$$

5.2.3 Sundstorm et al. Model

"This model is known as Lineweaver-Burk model and based on the Monod model. General expression for Sundstorm et al. model is given by the following equation" (Nandy & Kaul, 1991, p. 700);

$$L = \frac{L_{max}\, S}{K_s + S} \qquad \text{(Eq. 5.3)}$$

Where,

L = substrate loading rate (kg COD/m^3.d)

L_{max} = maximum substrate loading rate (kg COD/m^3.d)

K_s = half saturation constant (Monod model) (mg COD/L)

Data used for Sundstorm et al. model is given in Table 5.3. Maximum substrate loading rate (L_{max}) and half saturation constant (K_s) parameters were calculated from Figure 5.3.

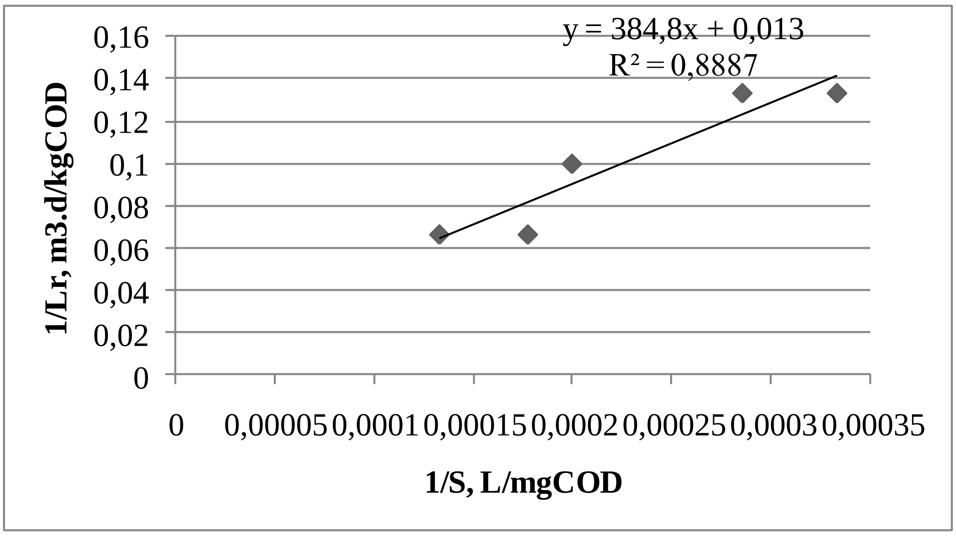

Figure 5.3 Sundstrom et al. model application

Table 5.3 Data used in Sundstrom et al. model

θ (HRT) (d)	**L (OLR) ($kgCOD/m^3.d$)**	**S_e (mgCOD/L)**	**1/S (L/mgCOD)**	**1/L ($m^3.d/kgCOD$)**
3	5	6750	1.48×10^{-4}	0.2
2	7.5	3000	3.33×10^{-4}	0.133
2	7.5	3500	2.86×10^{-4}	0.133
1	15	5625	1.78×10^{-4}	0.067
1	15	7500	1.33×10^{-4}	0.067
2	10	5000	2.00×10^{-4}	0.1

From Figure 5.3, $1/L_{max}$ = 0.013 and K_s/L_{max} = 384.8 are obtained with the correlation of R^2 = 0.88. So, L_{max} and K_s can be found as 76.92 $kgCOD/m^3.d$ and 29600 mg COD/L, respectively, for the anaerobic model reactor. Although a relatively high correlation coefficient, due to determined too high L_{max} and K_s values, this model is not appropriate.

5.2.4 Grau et al. Model

Grau et al. (1975) model is that the predicted effluent substrate concentration (S) is a function of influent substrate concentration (S_o) (Pavlostathis&Giraldo-Gomez, 1991, p. 38). This model has been used for suspended growth systems. Equations used at this model are given below:

$$\mu = \frac{\mu_{max} S}{S_o} - b \qquad \text{(Eq. 5.4.a)}$$

$$\frac{-dS}{dt} = \frac{\mu_{max} X S}{S_o} \qquad \text{(Eq. 5.4.b)}$$

$$S = \frac{S_o (1 + b\,\theta_c)}{\mu\,\theta_c} \qquad \text{(Eq. 5.4.c)}$$

Where,

μ_{max} = the maximum specific microorganism growth rate (d^{-1})

dS/dt = substrate removal rate (mg COD/L d)

X = microorganism concentration (VSS) in the reactor (g/L)

θ_c = mean cell residence time (d)

μ = specific microorganism growth rate (d^{-1})

Data used in Grau et al. model is given in Table 5.4. When $1/\theta_c$ values are plotted versus S/So values, this equation will give maximum specific growth rate (μ_{max}) and microorganism decay rate (b). These values were found from Figure 5.4.

Table 5.4 Data used in Grau et al. model

θ (HRT) (d)	**S_o (mgCOD/L)**	**S (mgCOD/L)**	**S/S_o**	**θ_c**	**$1/\theta_c$**
3	15000	6750	0.45	32.63	0.031
2	15000	3000	0.2	39.51	0.025
2	15000	3500	0.23	29.33	0.034
1	15000	5625	0.38	19.9	0.050
1	15000	7500	0.5	10.25	0.098
2	20000	5000	0.25	38.73	0.026

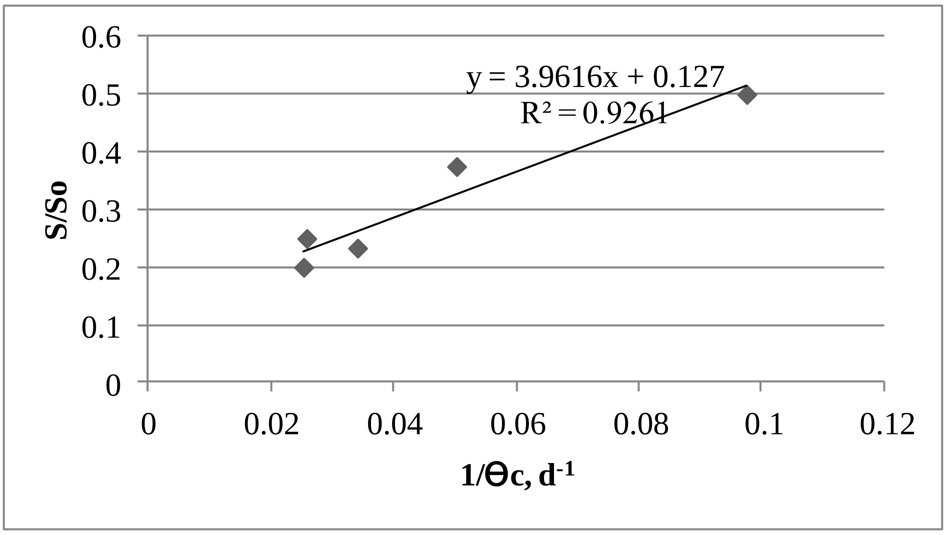

Figure 5.4 Grau et al. model application

From Figure 5.4, specific growth rate (μ_m) and microorganism decay rate (b) were found as 0.25 d^{-1} and 0.03 d^{-1}, respectively. Sumihar et al. (2002) found similar results for various substrates utilized in anaerobic treatment processes. The authors reported that specific growth rate varied between 0.0013-3.121 d^{-1} and microorganism decay rate varied between 0.005-0.253 d^{-1}.

5.2.5 Stover-Kincannon Model for Biogas Production

Methane production is an important parameter for anaerobic treatment systems; therefore, the methane production kinetics should also be determined. Methane production kinetic models were applied to anaerobic model reactor.

Methane production per removed COD per day versus organic loading rate is given in Figure 5.5.

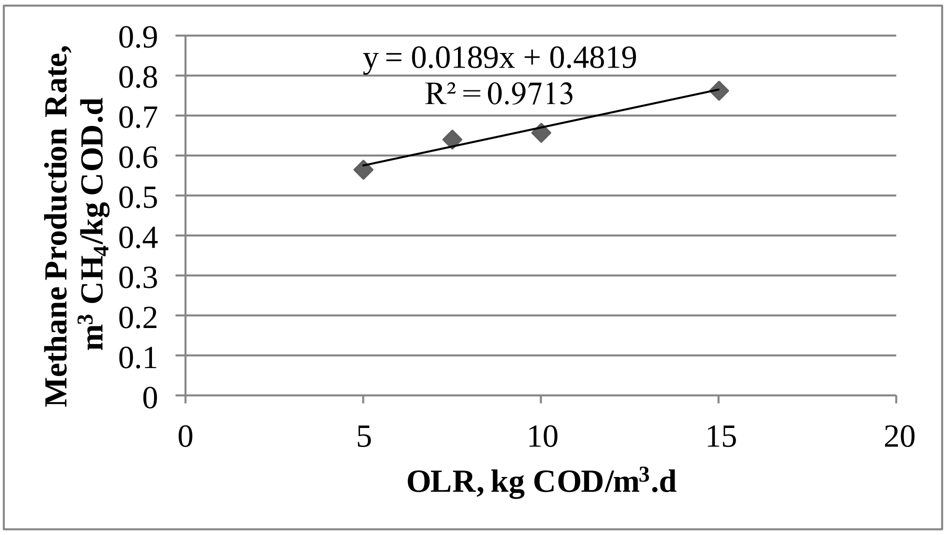

Figure 5.5 Methane production rate versus total loading rate

The specific methane production rate versus the organic loading rate is plotted in Figure 5.6, which confirms that the methane production rate was a function of the organic loading rate and that it could be described similarly to organic substrate removal kinetics (Buyukkamaci, 2001).

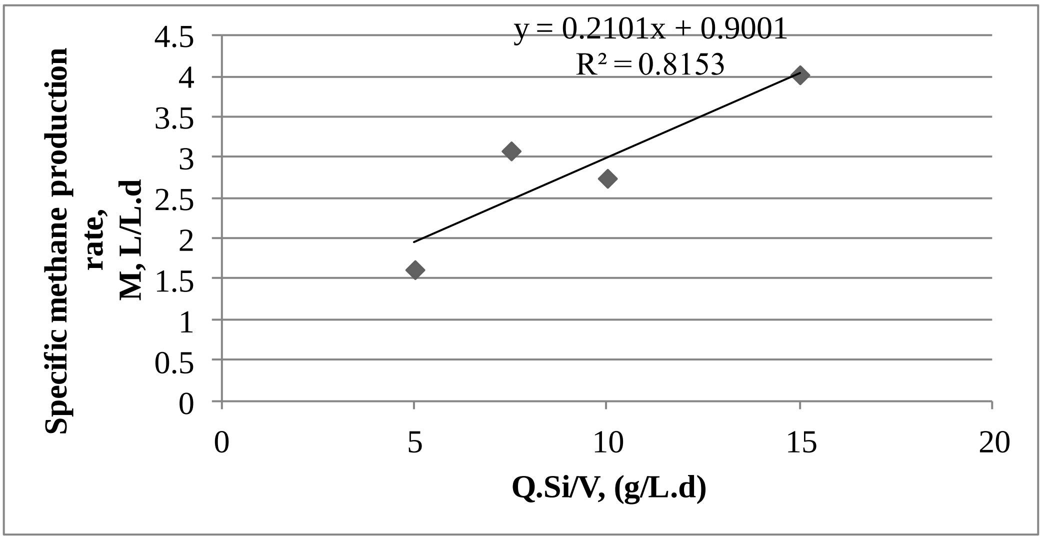

Figure 5.6 Specific methane production rate versus organic loading rate

The methane production rate can be expressed as follows:

$$M = \frac{M_{max}\,(QS_i/V)}{M_B + (QS_i/V)} \qquad \text{(Eq. 5.5.a)}$$

Where,

M = specific methane production rate (L/L d)

M_{max} = maximum specific methane production rate (L/L d)

M_B = constant

QS_i/V = organic loading rate (g/L d)

The inverse of the methane production rate is plotted against the inverse of the OLR; a straight line portion of intercept and slope of line gives $1/M_{max}$ and M_B/M_{max}, respectively. This graph is given in Figure 5.7 and data used for this model is given in Table 5.5. In this table G is specific biogas production rate and it is given with Eq. 5.5.b below.

Table 5.5 Data used for Stover-Kincannon model for methane production

V/QS_i (Ld/g)	**1/M (Ld/L)**	**1/G (Ld/L)**	**V/QS_i (Ld/g)**	**1/M (Ld/L)**	**1/G (Ld/L)**
0.3	0.46	0.027	0.13	0.26	0.03
0.3	0.46	0.027	0.13	0.6	0.016
0.3	0.36	0.027	0.13	0.32	0.009
0.3	0.41	0.028	0.13	0.21	0.016
0.3	0.49	0.035	0.07	0.3	0.019
0.3	0.58	0.028	0.07	0.37	0.021
0.3	0.57	0.042	0.07	0.69	0.007
0.3	0.59	0.037	0.07	0.12	0.012
0.2	0.67	0.034	0.1	0.42	0.016
0.2	0.63	0.042	0.1	0.49	0.012
0.2	0.59	0.032	0.1	0.3	0.019
0.2	0.6	0.014	0.1	0.3	0.016
0.13	0.51	0.009	0.1	0.35	0.013

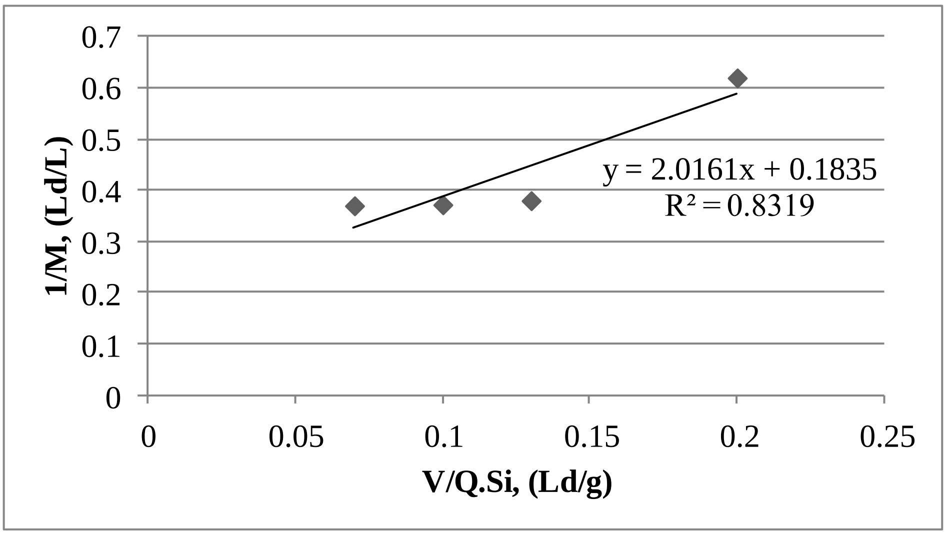

Figure 5.7 Determination of methane production kinetic constants

From Figure 5.7, M_B and M_{max} can be estimated as 10.99 g/L d and 5.45 L/L d, respectively. The regression line has an R^2 value of 0.83. Introduction of these values to Equation 5.5.a, produces:

$$M = \frac{5.45\,(QS_i/V)}{10.99 + (QS_i/V)}$$

Similarly, total gas production can be formulated as a function of organic loading rate. Equation 5.5.b gives the relationship between gas production and OLR.

$$G = \frac{G_{max}\,(QS_i/V)}{G_B + (QS_i/V)} \qquad \text{(Eq. 5.5b)}$$

Where,

G = specific biogas production rate (L/L d)

G_{max} = maximum specific biogas production rate (L/L d)

G_B = constant

QS_i/V = organic loading rate (g/L d)

The inverse of the gas production rate is plotted against the inverse of the OLR; a straight line portion of intercept and slope of line gives $1/G_{max}$ and G_B/G_{max}, respectively. This graph is given in Figure 5.8 and data used for this model is given in Table 5.5.

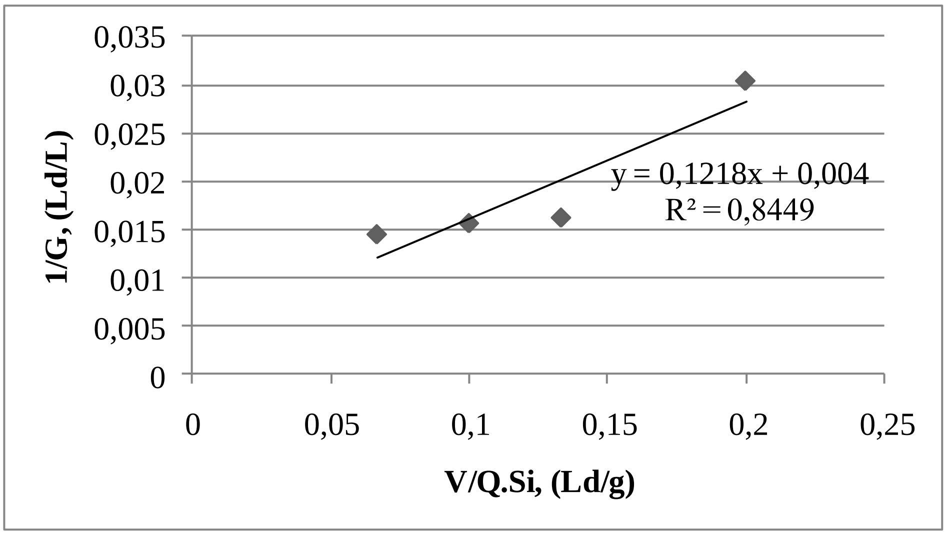

Figure 5.8 Determination of biogas production kinetic constants

From Figure 5.8, G_{max} and G_B can be estimated as 250 L/L d and 30.45 g/L d, respectively with correlation coefficient (R^2 = 0.85). Therefore, Equation 5.5.b comes to this form:

$$G = \frac{250\,(QS_i/V)}{30.45 + (QS_i/V)}$$

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

At this study, performances of an anaerobic side-stream membrane bioreactor performance for high strength wastewaters were evaluated. For this purpose, various organic loading rates, hydraulic retention time, and influent COD concentrations were applied. The study was created by two main sections:

1. Experimental studies conducted with synthetic wastewater.
2. Determination of the kinetic coefficients of the system.

In accordance with this study, the following conclusions were obtained:

6.1.1 Experimental Studies Conducted with Synthetic Wastewater

The anaerobic reactor was operated for 7 different operational conditions with synthetic wastewater which was prepared from diluted molasses. The operational conditions with ranging from 2000 to 20,000 mg/L COD concentration and ranging from 1 to 5 days hydraulic retention time was applied. Due to delays of purchasing the UF membrane filtration system, four different operational conditions were applied during the study. The system performance was evaluated at three hydraulic retention time (3, 2, and 1 day) and two influent COD concentrations (15,000-20,000 mg/L). In these conditions the following results were obtained:

- During the start-up period, there were small pH fluctuations and it generally remained between 6 and 7. The average pH levels of the anaerobic reactor effluent were 6.6. The minimum value of the pH was 5.17 while the maximum was 7.93. The pH level in the reactor did not reach values to inhibit the activity of microorganisms.

- A little bit higher pH values of membrane effluent (permeate) were measured than anaerobic reactor effluent. The average pH levels of permeates were 7.25. The minimum value of the pH was 6.13 while the maximum was 8.48.

- The values of alkalinity of the anaerobic raector were measured between 940 and 4,430 mg/L as $CaCO_3$. The level of alkalinity in the reactor decreased just one time under 1000 mg/L, which is the critical value.

- During the operation the average VFA concentration in the anaerobic reactor was around 1300 mg/L. VFA concentrations increased with the 20,000 mg/L influent COD concentrations applications.

- VFA/Alkalinity ratio varied between 0.1 and 1.45. The ratio of VFA to alkalinity was generally above 0.4. Despite this undesirable situation, the level of alkalinity in the reactor decreased just one time under 1000 mg/L and although some pH values were under 6.5, the pH levels remained 6.74 as the average value. These results showed that acidity did not become a problem in the reactor.

- The permeate alkalinities were generally a little bit less than the anaerobic reactor effluent alkalinities. The values of alkalinity were measured between 2,700 and 4,000 mg/L as $CaCO_3$.

- Electrical conductivity parameter is generally used to estimate salinity level. Significant salinity removal with UF cannot be achieved. The values of EC were measured between 4.01 and 8.7 mS/cm.

- Without operating UF module, maximum COD removal efficiency of 88.24 % was achieved at OLR of 3.33 kg COD/m^3.d and HRT of 3 day. Comparing to 4 days of HRT application, 13.24% higher removal efficiency was achieved at 3 days of HRT. Decreasing HRT and increasing organic loading rate caused significant organic material removal until 15,000 mg/L of influent COD concentration application.

- After commissioning of the membrane, HRT was reduced from 3 day to 1 day while COD concentration kept constant at 15,000 mg/L and at these conditions maximum organic loading rate of 15 kg COD/m^3.d was applied to the system. Organic material removal efficiency adversely affected from the decreasing HRT to 1 day and increasing of organic loading rate to 15 kg COD/m^3.d and 23.21% lower COD removal efficiency was obtained comparing to HRT of 3 day application.

- After UF applications, maximum 81.25% COD removal efficiency was achieved at 10 kg COD/m^3.d OLR and HRT of 2 day with a COD concentration of 20,000 mg/L. Experimental studies results showed that UF membrane application after anaerobic reactor did not give significant effect on COD removal efficiency.

- However, while the anaerobic reactor was operating without UF module, maximum COD removal efficiency (88.24%) was obtained from the COD concentration of the influent (10,000 mg/L) was half of the COD concentration of the influent (20,000 mg/L) with a maximum COD removal efficiency (81.25%) was obtained after putting into operation UF module. It should not be ignored.

- Maximum 75% COD removal efficiency was obtained with UF membrane system and average COD removal efficiency was about 45%.

- If the overall system performances are assessed, minimum COD removal efficiencies were obtained at lowest HRT applications. 85.94 %, 72.99%, and 79.53% average COD removal efficiencies were obtained in 7.5 kg COD/m^3.d (COD_i = 15,000 mg/L, HRT = 2 day), 15 kg COD/m^3.d (COD_i = 15,000 mg/L, HRT = 1 day) and 10 kg COD/m^3.d (COD_i = 20,000 mg/L, HRT = 2 day) of organic loading rates, respectively. A maximum efficiency of 95 % at OLR of 7.5 kg COD/m^3.d and HRT of 2 day was achieved. The changes in HRT relatively influence the COD removal in the MBR. Decreasing of the efficiency of the system was observed while the organic loading values are increasing.

- Average methane gas percentage of the total produced biogas during Phase II (2.5 kg COD/m^3.d OLR), Phase III (3.33 kg COD/m^3.d OLR), Phase IV (5 kg COD/m^3.d OLR), Phase V (7.5 kg COD/m^3.d OLR), Phase VI (15 kg COD/m^3.d OLR), and Phase VII (10 kg COD/m^3.d OLR) were observed as 66, 65, 56, 46, 43 and 41%, respectively.

- During the all operating time, average total biogas production, methane gas production, and methane gas percentage in the biogas were 50 L/d, 25 L/d, and 50 %, respectively.

6.1.2 Determination of The Kinetic Coefficients of The System

In this study, Monod model, Second-order model, Sundstorm et al. model, Grau et al. model, and Stover-Kincannon model was applied to the experimental results. The obtained results are summarized below.

- As a result of application of Monod model with the correlation coefficient is high (R^2 =.0.8731), cell yield coefficient (Y) 0.1372 mg VSS/ mg COD removed and microorganism decay rate (b) 0.0027 d^{-1}; maximum specific substrate utilization rate (k) 0.80 g COD/g VSS.d and half saturation concentration (Ks) 6,375 mg COD/L with the correlation is very low (R^2 = 0.3211) were calculated.

- As a result of application of Second-order kinetic model, the equation which is used to estimate the effluent substrate concentration depending on influent substrate concentration and hydraulic retention time was obtained:

$$S = S_o \left(1 - \frac{\theta}{1.0083\,\theta + 0.7917}\right)$$

- As a result of application of Sundstorm et al. model with the correlation of $R^2 = 0.88$, maximum substrate loading rate (L_{max}) and half saturation constant (K_s) were calculated as 76.92 kgCOD/m^3.d and 29600 mg COD/L, respectively. Although a relatively high correlation coefficient, due to determined too high L_{max} and K_s values, this model is not appropriate.

- From Grau et al. model specific growth rate (μ_m) and microorganism decay rate (b) were calculated as 0.25 d^{-1} and 0.03 d^{-1}, respectively.

- As a result of application of Stover-Kincannon model constant (M_B), maximum specific methane production rate M_{max}, maximum specific biogas production rate (G_{max}) and constant (G_B) was estimated as 10.99 g/L d, 5.45 L/L d, 250 L/L d and 30.45 g/L d, respectively. The following equations were obtained below:

$$M = \frac{5.45\ (QS_i/V)}{10.99 + (QS_i/V)}$$

$$G = \frac{250\ (QS_i/V)}{30.45 + (QS_i/V)}$$

6.2 Recommendations

- There are limited studies on AnMBR systems in our country. So, this study will be useful and provide guidance for spread of anaerobic membrane bioreactors. The obtained results can be used for full-scale plant operations.

- Microorganism washout decreases the efficiency of the AnMBR systems. To overcome this problem, submerged AnMBR can be preferred.

- In the scope of the thesis, cost analyses were not carried out. Cost analyze of the system should be performed to evaluate AnMBR is economical or not, for further studies.

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