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**Anaerobic Bio-Treatability of Wash Wastewater from  
Returned Beer Bottles**

By Pengjie Li

A Thesis  
in  
The Department  
of  
Building, Civil and Environmental Engineering

Presented in Partial Fulfillment of the Requirements  
for the Degree of Master of Applied Science  
at Concordia University  
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## **ABSTRACT**

### **Anaerobic Bio-Treatability of Wash Wastewater from Returned Beer Bottles**

Pengjie Li

With the gradually increasing levels of water pollution, more and more stringent regulations have been issued to restrict direct discharge, especially industrial wastewater discharge. This pushes more and more industries to seek suitable treatment techniques for their effluents. Anaerobic treatment technology is a feasible choice for treating high – strength industrial wastewater effluent. This study focuses on researching the bio-treatability of wastewater from washing returned beer bottles in anaerobic environment. A comparison of two bioreactors – ASBR (Anaerobic Sequencing Batch Reactor) and UASB (Upflow Anaerobic Sludge Blanket) reactors was preformed in the experiments. The experiments were performed at room temperature and 35°C under organic loading rates (OLR) from 2 kg/m<sup>3</sup>.d to 20 kg/m<sup>3</sup>.d. At the same time, the soluble COD reduction, methane production, volatile fatty acid (VFA) concentration in the effluent, and volatile suspended solid (VSS) in the effluent were measured at all organic loading levels. The results show that the performance in the ASBR was better than that in the UASB reactor without a recirculation system at the two temperatures under all organic loading levels. In the ASBR, the soluble COD obtained the reduction of 57% - 95% and 70%-93% under an OLR of 2 kg/m<sup>3</sup>.d-20 kg/m<sup>3</sup>.d at room temperature and 35°C, respectively. In the UASB reactor without a recirculation system, the soluble COD reduction was 49%-78% and 65%-80% under the same OLR with the ASBR at room temperature and 35°C, respectively. Methane production was measured in the ASBR at both temperatures.

Results were close to the theoretical data under an OLR of  $2 \text{ kg/m}^3\cdot\text{d}$ - $6 \text{ kg/m}^3\cdot\text{d}$ , lower than theoretical data under an OLR of  $8 \text{ kg/m}^3\cdot\text{d}$ - $20 \text{ kg/m}^3\cdot\text{d}$ . VFA concentrations in both reactor effluents increased with an increase in the OLR under all loading levels at the two temperatures. Both reactors could maintain the biomass inside the reactor so as to achieve low VSS levels in both reactor effluents throughout the whole experiment. In many full-scale or lab-scale experiments, the UASB reactor is operated with or without recirculation system, and the ratio of recirculation to feed is changed from 0 to 10. Based on the obtained results of soluble COD reduction in the UASB reactor without recirculation, under an OLR of  $6 \text{ kg/m}^3\cdot\text{d}$  to  $20 \text{ kg/m}^3\cdot\text{d}$  at room temperature and  $8 \text{ kg/m}^3\cdot\text{d}$  to  $20 \text{ kg/m}^3\cdot\text{d}$  at  $35^\circ\text{C}$ , the UASB reactor requires a recirculation system; the ratio of recirculation to feed was also modelled in this study.

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# ***CHAPTER 1***

## **INTRODUCTION**

### **1.1 Statement of Problem**

With rapid industrial and agricultural development and enhancement of the living standard, wastewater pollution has brought an enormous problem to our highly important water bodies, sometimes even destroys their ecosystem balance and causes eutrophication phenomena and the death of marine life.

Industrial wastewater is a type of wastewater which is difficult to treat because of its high organic concentration, large variability of physical, chemical, and biological characteristics among different industries. At present, the pollution due to the direct discharge of untreated industrial wastewater to surface water systems or municipal sewer systems has gradually increased. More and more countries have enacted stringent regulations to restrict direct discharge. The increasing trend of water pollution also leads to the research and development of industrial wastewater treatment techniques.

With effluent characteristics of large amounts of flow, high oxygen demand and biodegradability, brewery wastewater is an excellent wastewater to research treatment. At present, a large percentage of breweries still rely on municipal sewer discharge systems for wastewater disposal, and some plants have been building their own treatment systems for treating effluents. With the expected more stringent environmental regulations and increasing sewer discharge fees, some operations have been looking into more efficient ways of treating the wastewater (Lo *et al.*, 1999).

## **1.2 Treatment Technologies Alternatives**

The currently available alternatives of wastewater treatment technologies involve physical, chemical, and biological treatment technologies. Meanwhile, the biological treatment technology is divided into two fields – aerobic and anaerobic treatment. They all have advantages and disadvantages as well as applying conditions for treating wastewater. (See detailed information in “Literature Review”).

With excellent advantages, such as high removal efficiencies, low surplus sludge production, energy production through biogas (methane), low operating cost, and compact construction, anaerobic treatment has gained tremendous success over the past two decades (Frankin 2001) for treatment of wastewater.

At the same time, due to its more competitive, reliable, and durable ability, anaerobic technology is also considered as a good alternative for wastewater treatment, especially for high strength industrial effluents, i.e. with  $\text{COD} \geq 5000 \text{ mg/L}$  (Young and McCarty, 1969; Hobson *et al.*, 1974; Speece, 1983; Witt *et al.*, 1979). At present, there are at least 420 anaerobic full-scale treatment facilities operating internationally (Huss, 1981; Camilleri, 1988 a and b; Bonastre and Paris, 1989; Heijnen *et al.*, 1989; Craveiro, 1991; Lettinga and Hulshoff Pol, 1986; Young, 1991; Habets, 1993; Safety, 1994).

The key to successful application of anaerobic treatment is to un-couple the hydraulic retention time (of wastewater) and the solids retention time (of biomass) within the reactor (Frankin 2001). Short hydraulic retention time and high removal efficiency has successfully been gained in many full - scale reactors. The other advantage of anaerobic treatment is greatly reduced nutrient requirements which are an important

economic factor (Witt *et al.*, 1979), and after some time acclimation, even toxic effluents can also be biodegraded in an anaerobic environment. Nowadays, several types of anaerobic reactors have been researched, designed, and applied, such as the upflow anaerobic sludge blanket, anaerobic sequencing batch reactor, fixed film anaerobic filter, fluidized bed system, expanded granular sludge bed reactor, multiplate anaerobic reactor, etc.

The main drawbacks of anaerobic treatment are long start-up time and the sensitivity of anaerobic biomass relating to pH and temperature in the reactor. Just as Goodwin and Stuart (1994) said, "Methanogenic bacteria are inhibited at pH values below 6.6. The optimal range of pH values of anaerobic bacteria is 6.9 to 7.2. The optimal temperature of anaerobic bacteria is 35°C or 55°C".

However, the fact is that anaerobic treatment produces an effluent that is rarely, especially for high organic loadings, of sufficient quality to be discharged without further treatment (Huss, 1981; Odegaard, 1988). Therefore, the combination of anaerobic and aerobic treatment is being applied in many cases, and has obtained a good quality of effluent.

### **1.3 Objectives of the Research**

At present, almost all studies have been performed on the entire brewery wastewater, very little is known about the bio-treatability of the wash wastewater from returned beer bottles, which contains mostly beer. Therefore this research was conducted with a primary objective to study the bio-treatability of wastewater effluent from washing

returned beer bottles by using anaerobic treatment technology. The specific objectives were:

1. To investigate the bio-treatability of wastewater effluent from washing returned beer bottles by using anaerobic treatment technology.
2. To compare the treatment efficiencies for wastewater effluent from washing returned beer bottles between the upflow anaerobic sludge blanket (UASB) reactor and the anaerobic sequencing batch reactor (ASBR) at room temperature and 35°C.
3. To model the ratio of recirculation to feed in the UASB reactor at room temperature and 35°C.

## ***CHAPTER 2***

### **LITERATURE REVIEW**

#### **2.1 Water Source Pollution**

Water source pollution continuously exists and always concerns environmental engineers even though they had adopted a variety of wastewater treatment technologies. Water bodies, such as rivers, lakes, oceans, and groundwater systems, are important and active components of natural ecosystems. Among water bodies, there exist some continuous processes of materials and energies transformation or circulation to ensure a stable food-chain and balance of nature by interdependence and inter-competition. Therefore, when wastewater containing various contaminants and pollutants is discharged into a unit water body, it not only pollutes that unit but also contaminates the whole water source system. Sometimes it is difficult for environmental engineers to determine the specific source of pollutants.

Water is one of our important living sources. The major pollution problems are: (1) the decrease of dissolved oxygen (DO) in water that causes the death of marine life, (2) the increase of bacterial levels that causes human disease and transmission, (3) eutrophication (the excessive algae and plant growth), such as blue green algae, algal mats, which cause bad tastes, odors and aesthetics of water bodies and may destroy the balance of ecosystem, (4) the increase of toxic chemical levels, that is high levels of carcinogens in water supply, closing of fisheries due to unsafe toxic levels, and upset of ecosystems. Generally, the principal pollution sources of water can be divided into two

broad categories (Thomann *et al.*, 1987): point source pollutions and non-point source pollutions. The point source pollutions come in large amounts from a well-defined single point of discharge, whereas the non-point source pollution comes from large area discharges.

At present, with the economic growth, commercial, industrial, agricultural, and tourism developments, water quality in various water resources throughout the world has followed a continuously decreasing trend, which is expected to accelerate and continuously cover more areas (Anonymous, April 24, 2002). For instance, lakes, rivers and oceans are destroyed by discharging untreated wastewater, especially untreated industrial wastewater. Water source pollution has resulted in changes of the physical, chemical and biological characteristics of water resources; at the same time, it also impacts the desired use of water resources, pollutes and deteriorates our living water system as well as other resources.

Therefore, facing the critical problems of water source pollution, the main objectives of the field of water quality engineering are trying to enact strict regulations to control and reduce the pollution of water bodies, and research and develop effective management and treatment technologies to maintain the water quality to satisfy the desired use of water.

## **2.2 Industrial Wastewater Review**

Industrial wastewater pollution is a type of water source pollution. Because of a wide variety of industries and highly variable amounts of wastewater as well as their varying characteristics, industrial wastewater is difficult to treat. Usually they have a high



dissolved oxygen demand. The amount of industrial wastewater can vary from several hundred liters per day to tens of millions of liters per day (Wastewater – Department of Environmental Protection, July 30 2002). If they are not pretreated and directly discharged into surface water bodies or even into municipal sewer systems, it will cause loss of dissolved oxygen due to the presence of chemical oxygen demand (COD) and biochemical oxygen demand (BOD), and will lead to the presence of total coliform bacteria (TCB) (Anonymous, April 24, 2002), suspended solids (SS), and nutrients in the receiving system. Industrial wastewater also includes heavy metals, oils and greases, pesticides, and many toxic organic and inorganic compounds that will cause problems in the receiving system.

Because of this variability, industrial wastewater requires techniques for treatment that must be developed on case-by-case or industry-by-industry basis rather than by a uniform treatment standard. Anaerobic technologies have been developed and have been extensively used in industrial wastewater treatment over the past two decades. The earliest application of high rate anaerobic technology in industrial wastewater treatment was in the mid 70's, in which anaerobic technology was applied to treat wastewater from the sugar industry (Frankin, 2001). With the development of anaerobic technologies, more and more types of anaerobic bioreactors have been studied and applied. Some established databases (Table 2.1) show that the application of anaerobic technology is an increasing trend, and the applied types of anaerobic bioreactors also tend towards diversification. The data shown in Table 2.1 was from 65 different countries.

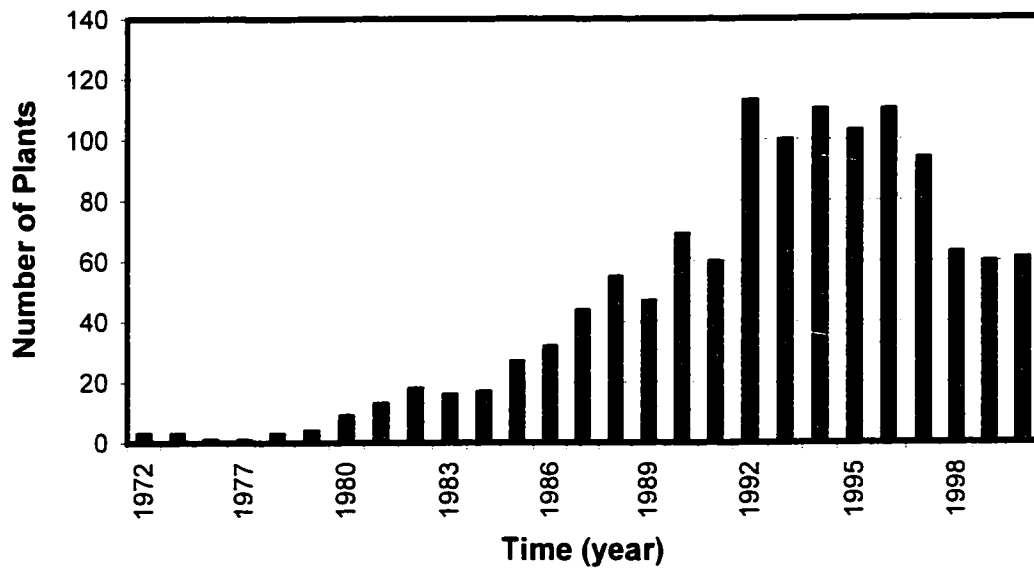
**Table 2.1** Full Scale Plants for Industrial Applications (Source: Frankin, 2001)

<b>Vendor</b>	<b>Number of plants</b>	<b>Type of anaerobic bioreactor</b>
ADI	98	Lagoon, Hybrid
Biothane	297	Contact, UASB, EGSB
Degremont	94	Contact, FB, Fixed Bed
Grontmij	38	UASB
Kurita	53	UASB, EGSB
Paques	370	IC, UASB
Proserpol (SGN)	48	Fixed Bed
Purac	67	Contact
VA TECH (CT Umwelt/ Sulzer)	62	Fixed Bed, Lagoon
Others	88	Mainly UASB
Total	1215	

**Note:** EGSB: Expanded Granular Sludge Blanket.

FB: Fluidized Bed Reactor.

In addition, some databases also show that the number of installed plants per year in the world presents an increasing trend.



**Figure 2.1** Number of Plants Installed per year in the World (Source: Frankin, 2001)

Figure 2.1 shows the number of installed plants per year that has reduced to around 60 at present. This is mainly caused by a reduced number built in Asia (Frankin, 2001). Table 2.1 and Figure 2.1 clearly show that anaerobic treatment technology is a feasible treatment technology for a wide variety of industrial wastewaters, and they have been accepted by the industrialized western world as well as less developing countries.

Because of the high concentrations of COD, BOD or TSS (total suspended solids) as well as toxicants in industrial wastewater, the effluent does not usually satisfy the discharge standard that is regulated by the government after anaerobic treatment. Generally, an anaerobic treatment unit followed by an aerobic treatment unit is common in the industrial field of wastewater treatment, and has obtained high removal efficiencies and cost- efficient benefits (Anonymous, *Enviroasia*, August 2, 2002)

## **2.3 Brewery Wastewater Characteristics**

Beer is a fermented beverage with a lower alcohol content than 10% (World Bank Group, 1998). Beer is brewed from malted barley, caramel malt, roasted malt, hops, selected yeast and pure soft water. Therefore there are a lot of nutrient components contained in beer that are beneficial to human health. The processing of beer needs to consume a large amount of water; at the same time, it also produces plenty of wastewater. A modern brewery can generate between 1 and 5 million liters of wastewater per day (Anonymous, 1997) or 3 to 5 cubic meters per cubic meter of sold beer (World Bank Group, 1998). The brewery wastewater comes from the brewing and the packaging sections of brewery (de *Vegt et al.*, 1992; Le Clair, 1984; Mahmud, 1979). Wastewater generated in the brewing section is from the cleaning of the brew kettle, the fermentation tank, and brewing residue; whereas, wastewater generated in the packaging section is from the bottle washing operation, losses occurred from the filling of the bottles, and the cleaning of the equipment and returned beer bottles (de *Vegt et al.*, 1992; Huang *et al.*, 1986; Le Clair, 1984; Mahmud, 1979). The average characteristics of untreated effluent discharge of breweries are listed in Table 2.2.

**Table 2.2** Average Characteristics of Brewery Wastewater

Characteristics	Amount	Reference
Water – to – Beer ratio	4 – 8 m <sup>3</sup> water consumption / m <sup>3</sup> beer produced	World Bank Group, 1998
Wastewater – to – Beer ratio	3 – 5 m <sup>3</sup> wastewater produced / m <sup>3</sup> sold beer	World Bank Group, 1998
Chemical Oxygen Demand	2,000 – 3,000 mg/L	Technical Papers, April 27, 2002; Craveiro, 1986; Fand, 1990; Le Clair, 1984; Oliva, 1990.
Biochemical Oxygen Demand	1,200 – 1,800 mg/L	Technical Papers, April 27, 2002
BOD / COD	0.65	Technical Papers, April 27, 2002
Suspended Solid	400 – 700 mg/L	Technical Papers, April 27, 2002
Total Nitrogen	80 – 120 mg/L	Technical Papers, April 27, 2002
Total Phosphorous	30 – 60 mg/L	Technical Papers, April 27, 2002
Heavy Metal Concentration	Very Low	Anonymous, <i>Carlton &amp; United Breweries</i> , April 10, 2002
pH	2 – 12	Technical Papers, April 27, 2002; Craveiro, 1986; Oliva, 1990; Ware, 1989.
Temperature	19 – 35 oC	Technical Papers, April 27, 2002; Le Clair, 1984; Oliva, 1990.

There is a big difference in the quantities of effluents from each individual process. It results in a significant fluctuation of pH, COD, BOD, and SS because of discontinuous discharges from the different departments of the brewery. For instance, bottle washing produces a large volume of effluent but contains lower levels of the total organic matter discharged from brewery (World Bank Group, 1998). The effluent from fermentation and filtering are higher in organic matter content but low in volume.

approximately 3% of total volume of wastewater but 97% of the BOD (World Bank Group, 1998). The pH value of the combined effluent has an average value of 7 but can fluctuate from 2 – 12. The average temperature of brewery wastewater effluent is 30°C. but the lower temperature is also often observed in cold regions or in the winter season.

Brewery wastewater has high biodegradability since it has a high ratio of BOD/COD that can be easily biodegraded. Usually nitrogen and phosphorus are sufficient, but adding nitrogen and phosphorus is still useful as shown in some cases in order to ensure a good biosolid quality (Anonymous, *Scientecmatrix*, April 8, 2002b). The effluent direct discharge standards from breweries into the surface water systems are shown in Table 2.3.

**Table 2.3** Effluent Discharge Standards from Breweries (Source: World Bank Group, 1998)

<b>Parameter</b>	<b>Maximum Value</b>
pH	6 -9
BOD (mg/L)	50
COD (mg/L)	250
TSS (mg/L)	50
Oil and Grease (mg/L)	10
Nitrogen (mg/L)	10
Phosphorus (mg/L)	5
Temperature Increase	≤ 3°C

Table 2.3 shows the effluent discharge standards from breweries that are the standard for directly discharging into surface waters. Whereas the standards for effluent discharge into the municipal sewer systems are that the COD must be less than 1000 mg/L, the BOD must be less than 200 mg/L, the TSS must be less than 300 mg/L (Municipal Services-Model Sewer Discharge Bylaw, May 8, 2001; Halifax Regional Municipality By-Low-W-101, June 20, 2001)

The comparison of Table 2.2 and Table 2.3 illustrates that the standard of the brewery effluent is higher than the standard of permitted discharge guidelines. If the brewery effluent is discharged into municipal sewer systems or the surface water bodies directly, breweries will be penalized. Therefore, in order to avoid the penalty and protect the environment, before discharging their effluent to the municipal sewer systems or surface water bodies, the effluent must be pretreated to meet the regulations enacted by the government.

Another new challenge for environmental engineers is that the water resources are becoming scarce worldwide. The reuse of wastewater is a good choice. For example, brewery industries produce significant amounts of wastewater. At the same time, the brewery wastewater is also highly biodegradable. If advanced treatment technologies are applied to brewery wastewater, such as anaerobic treatment, aerobic treatment, etc, zero discharge of the effluent will be feasible. The reuse of wastewater, in turn, can also greatly reduce the requirement for clean water so as to reduce the operating charge, which is beneficial to industries.

## **2.4 Wastewater Treatment Technologies**

To review the wastewater treatment technologies, they are roughly divided into three categories - physical, chemical and biological treatments. Every technology has its own advantages and disadvantages as well as their applied requirements. Technical choices depend on the raw wastewater characteristics and the requirements for effluent quality.

### **2.4.1 Physical and Chemical Wastewater Treatment Technologies**

Physical treatment technologies, such as sedimentation, sand bed or granular bed filtration, flotation, grit removal, sorption, etc, mainly apply physical processes to remove suspended solids from wastewater. Chemical treatment technologies mainly rely on chemical reactions between the additional chemical and inorganic contaminants to precipitate contaminants from wastewater. The common chemical treatment methods include coagulation and flocculation, ion exchange, disinfection, neutralization, etc.

Physical and chemical treatment technologies are always applied as an affiliated treatment technology, and cannot be applied independently to treat wastewater. They must be combined with another treatment technology, such as biological treatment, to gain the required effluent quality.

### **2.4.2 Biological Wastewater Treatment Technologies**

With their excellent advantages, biological wastewater treatment technology has been extensively applied in wastewater treatment and has gained great success and high



removal efficiencies for organic concentration in many cases. Biological treatment processes mainly use bacteria to degrade organic concentration in wastewater to satisfy the discharge standards. Biological treatment technology has several advantages over physical and chemical technologies (Lecture 7 – Lecture Outline, June 1, 2002):

- Effective wastewater treatment capacity: high surface area to volume ratio.
- Robustness.
- Treated effluent can satisfy discharge standards to municipal sewer systems or surface water bodies.

In order to treat wastewater with a variety of characteristics, more and more biological treatment techniques have been researched and developed. The biological treatment is usually composed of aerobic treatment and/or anaerobic treatment. The following sub-section will introduce the principles and reactor types for aerobic and anaerobic wastewater treatment as well as their comparison.

#### **2.4.2.1 Aerobic Wastewater Treatment Technology**

The earliest development of the activated sludge process was in 1882 in Europe and the principle of sludge recycle came into existence around the year 1912 (Verstraete *et al.*, 1986). The “activated sludge process” was created when Arden and Lockett (1914) described “the sludge as being activated”. Therefore, the use of aerobic biological treatment can be traced back to the late nineteenth century, and by the 1930s, it became a standard method of wastewater treatment (Rittmann, 1987).

#### **2.4.2.1.1 Aerobic Wastewater Treatment Principles**

Aerobic treatment is the natural biological degradation and purification process in which aerobic bacteria that thrive in oxygen-rich environments to break down complex organic matter in wastewater into simple and stable carbon dioxide, water, nitrate, sulphate, phosphate and biomass (Anonymous, *Scientecmatrix*, April 8, 2002a; Sreekrishnan *et al.*, April 2002; Taylor *et al.*, 1996). In the aerobic process, the aerobic bacteria use complex organics as their carbon and energy source and degrade them. The process can be completed by the following three steps:

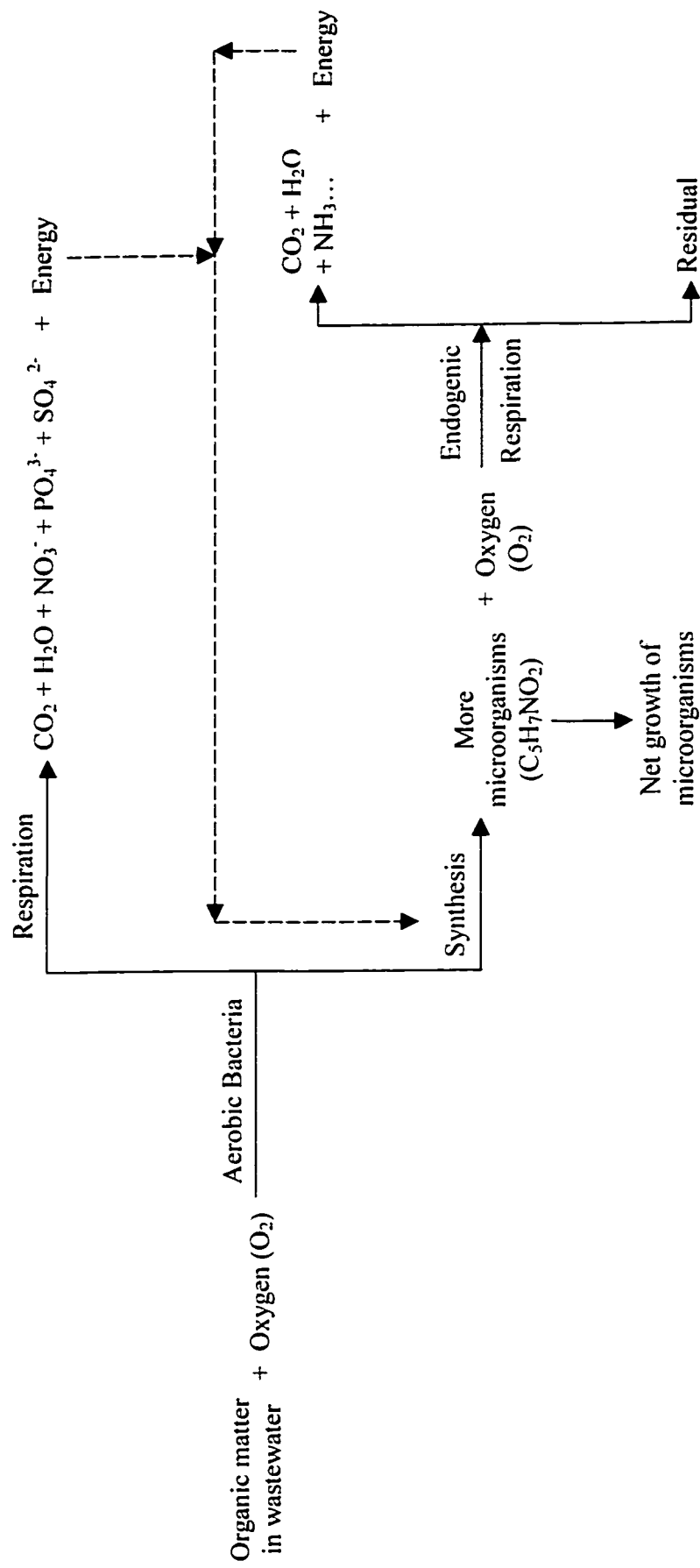
##### **1. Primary removal and adsorption:**

In many activated sludge systems, only a few minutes (3 to 5 minutes) contacting of the wastewater with activated sludge is required for a high removal rate of organic matter in wastewater. This step is called “the primary rapid removal” that mainly uses the large surface area of activated sludge (2,000 to 100,000 m<sup>3</sup>/m<sup>3</sup> mixed liquor) (Haerbin Building Engineering Institute, 1981) to adsorb and remove suspended solids and colloids from the wastewater. Sometimes when the primary removal rate is greater than the largest growth rate of sludge, the organic matter is stored on the surface of microorganism cells. After several hours of aeration, the organic matter can be absorbed and metabolized by the microorganism. So within the primary period, the amount of organic matter removed by the sludge is limited and depends on the characteristics of the wastewater and the contacting time of the wastewater with activated sludge (Haerbin Building Engineering Institute, 1981). For example, if there are plenty of

suspended solids and colloids in the wastewater, then the primary removal rate is high. In contrast, when there are large amounts of soluble organic matter in the wastewater, the primary removal rate is low. Another example is if the recycling activated sludge is not aerated enough during the aeration period, organic matter that is stored in activated sludge will be metabolized insufficiently. The sludge does not regenerate and cannot recover its activity properly. So the primary removal rate is certainly decreased. However, if the recycled activated sludge is aerated for a long time, the sludge is in long-time endogenic respiration, it will oxidize by itself and lose activity that also decreases the primary removal rate of wastewater.

## **2. Metabolism**

Within this step, aerobic bacteria use various types of organic matter in the wastewater as energy and carbon sources. First, under oxygen-rich conditions some complex organics are oxidized and decomposed to stable inorganic matter, such as carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ). Energy is released to synthesize new bacteria. Figure 2.2 shows the pathway of metabolism of aerobic bacteria.



**Figure 2.2 Aerobic Pathways**

Figure 2.2 illustrates the processes of aerobic microorganism metabolism. The processes mainly consist of oxidation and decomposition of organic matter in wastewater, synthesis of microorganisms (growth of activated sludge), and the consumption of oxygen. When oxygen is supplied sufficiently, the process of growth of activated sludge and the process of removal of organic matter are in parallel, namely, the growing period of activated sludge is also the rapid removal period for organic matter (Haerbin Building Engineering Institute, 1981; Anonymous, *Scientecmatrix*, April 8, 2002a).

Figure 2.2 also illustrates that some microorganisms are oxidized and decomposed during the process of synthesis of new cells and release energy. This procedure is called endogenic respiration. When organic matter is abundant, new cells are synthesized in large quantities, endogenic respiration is not remarkable; but when organic matter is exhausted by aerobic microorganisms, endogenic respiration will become the main process for supplying energy. The process also needs to consume oxygen. The produced new cells that are not consumed by the process of endogenic respiration are regarded as net growth of microorganisms (surplus sludge). In aerobic treatment processes, either oxidation or synthesis can remove organic matter from wastewater, and only the synthesized new cells are easy to separate from wastewater (Haerbin Building Engineering Institute, 1981).

### **3. Settling**

During the aeration period, air diffusers agitate and mix wastewater with bacteria, so the solids and bacteria cannot separate and settle from the wastewater. A settler

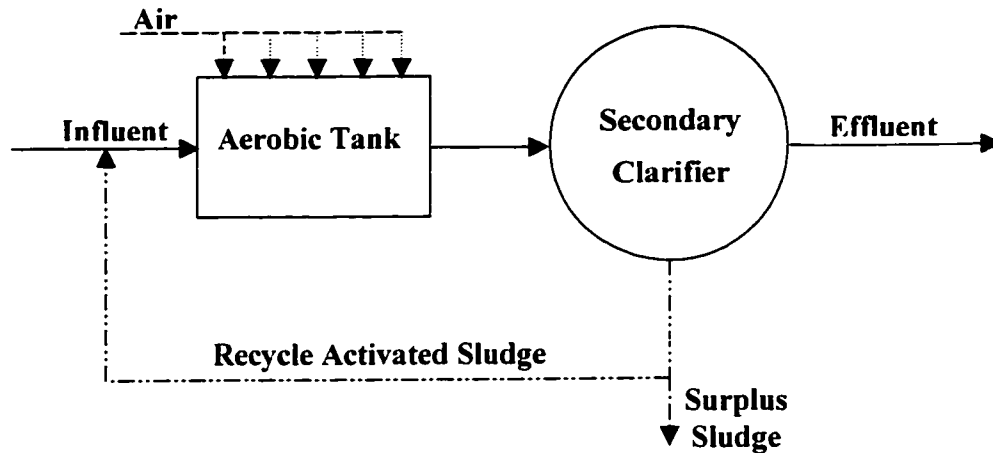
should be placed after the aerobic tank for separating the solids so as to obtain a high quality effluent.

#### **2.4.2.1.2 Reactor Types for Aerobic Wastewater Treatment**

Aerobic treatment technology is a more efficient and quick wastewater treatment method. At present, the main operating types of aerobic treatment units (ATUs) include: suspended - growth tank, attached - growth reactor, and sequencing batch reactor. The primary settler may be placed before these reactors in order to remove large solids and protect the ATUs.

##### **1. Suspended – Growth**

Suspended-growth systems, such as aerated lagoons, high contact reactors, etc. mainly use activated sludge that is suspended in the tank to purify the wastewater. This method is an effective treatment method for municipal and industrial wastewater. The suspended-growth system is divided into two tanks. The first tank is called the aerobic tank in which the bacteria are free-floating (David *et al.*, 2001) and air is compressed through the liquid. In this tank, the complex organic matter is broken down to simple and stable inorganic matter; and at the same time, energy is released which is used by bacteria for growth. The second tank usually is called the secondary clarifier, and can separate bacteria and solids out of wastewater by gravity. The two tanks are connected by pipe at the bottom or by pump (David *et al.*, 2001). The settled bacteria from the clarifier are recycled back into the aerobic tank and mixed with influent that is critical for high quality effluent. The treated effluent from the clarifier is discharged to the next system.



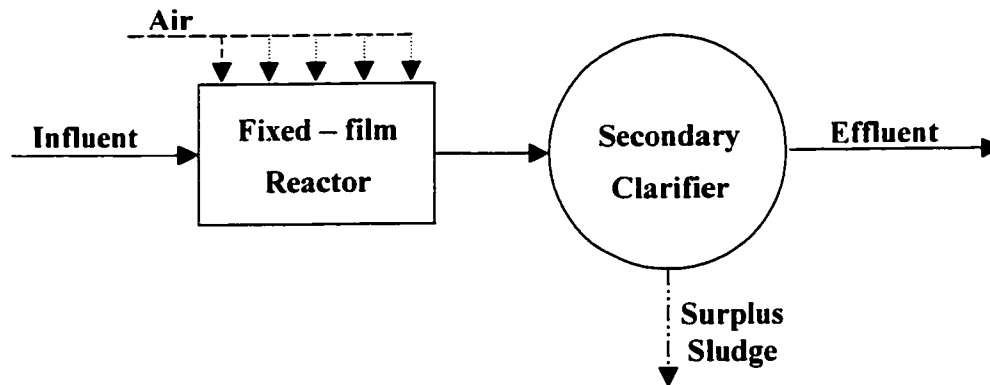
**Figure 2.3** Suspended – Growth ATU Schematic Diagram

Figure 2.3 illustrates the working process of the suspended – growth ATU. Even though the process is simple, the system is likely to have problems with bulking sludge when wastewater is overloaded into the system. The bulking sludge is difficult to settle or sink to the bottom of clarifier, and sometimes can clog the outlet (David *et al.*, 2001).

## **2. Fixed - Film Reactor**

The principle used in the fixed - film reactor is that wastewater is spread onto a specific medium surface to form a biofilm. When the biofilm becomes mature, aerobic bacteria living in the biofilm ingest organic matter from wastewater, and biodegrade them. Thereby wastewater is treated. During the process of biodegradation, air is provided to the fixed biofilm to create an oxygen – rich environment. The biofilm can grow on any surface of medium, such as fabric, plastic, styrofoam, and gravel (David *et al.*, 2001), and continuously sloughs off and

regenerates. The sloughed off biofilm is discharged with the treated wastewater. A secondary clarifier should thus follow the fixed - film reactor.



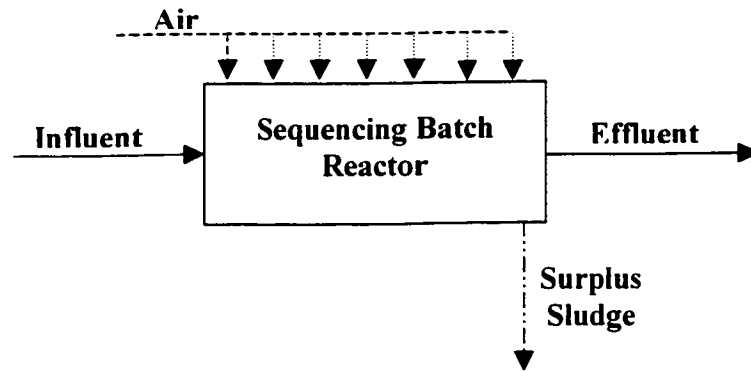
**Figure 2.4** Fixed – Film Reactor ATU Schematic Diagram

Figure 2.4 illustrates the schematic diagram of the fixed – film reactor process. Since the bacteria are fixed on the biofilm, there is no need for recycling, which saves operating costs; but this method is expensive because the design is required to push the biomass sloughing off and regeneration continuously. The effluent from fixed-film reactor is of consistently high quality. Bulking sludge is uncommon (David *et al.*, 2001). The disadvantages are that the wastewater that is injected into the fixed – film reactor is easy to clog the biofilm. Therefore the influent must be pretreated before entering the fixed – film reactor in order to remove suspended solids, grease, etc.



### 3. Sequencing Batch Reactor (SBR)

The sequencing batch reactor is a form in which aeration, reaction, settling, decant functions are combined in a single reactor. This type of reactor does not need a separate clarifier. In an SBR, wastewater treatment is completed within a unit, which is different from the above-mentioned two types of reactors. The influent progresses through a sequencing process, rather than a sequence of separated tanks.



**Figure 2.5** Sequencing Batch Reactor ATU Schematic Diagram

Figure 2.5 illustrates the processes within an SBR. Feeding, aeration, and effluent decant are periodically operated. Since it is simple, flexible, and reliable to operate and land requirements are small, the SBR is applied extensively. But since the SBR system needs to be controlled carefully, it requires skilled operators and has more potential for mechanical and electrical failure.

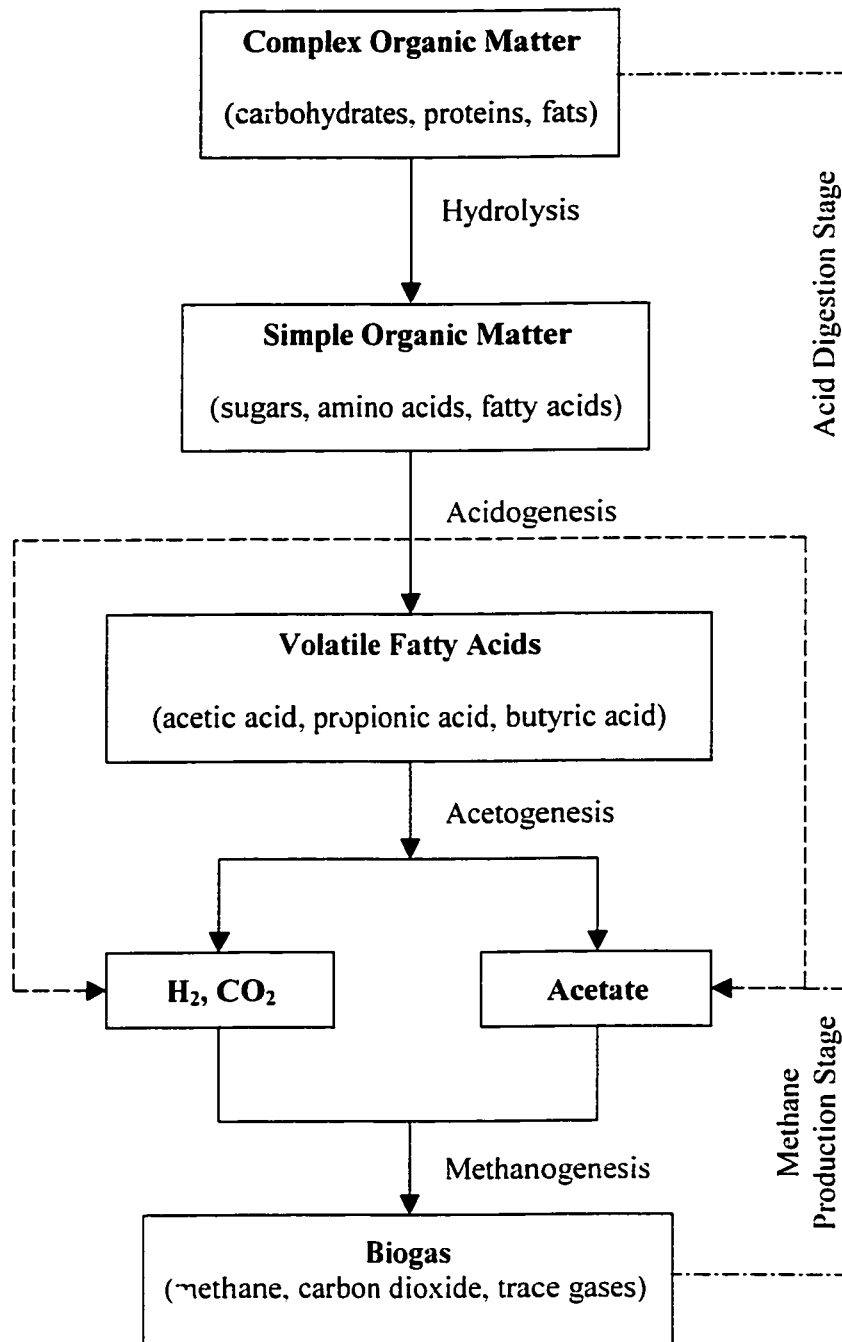
#### 2.4.2.2 Anaerobic Wastewater Treatment Technology

Around 1881, anaerobic treatment was reported to be a useful method for reducing the concentration of organic material. In the early seventies, North American

who interested in anaerobic biotechnology began to rise and has continued to grow considerably (Chynoweth *et al.*, 1980; Sheridan, 1982). Some digestors were used to produce methane for home heating and cooking in developing countries (Environment Canada, 1988). The following sub-sections will introduce the principles of anaerobic wastewater treatment as well as anaerobic bioreactors.

#### **2.4.2.2.1 Anaerobic Wastewater Treatment Principles**

Anaerobic digestion has proven to be an excellent way to treat solid, liquid, or semisolid organic wastes, offering significant advantages over more conventional aerobic, especially from an energetic and environmental viewpoint (Marin *et al.*, 1999). The anaerobic process is a natural gasification process, which uses anaerobic bacteria consortia under an oxygen deficient environment to biodegrade and convert complex organic matter in wastewater. Biogas and lower amounts of biomass are produced. Biogas consists of methane ( $\text{CH}_4$ ) (50% - 80%), carbon dioxide ( $\text{CO}_2$ ) (20% - 50%), and other trace gases such as hydrogen ( $\text{H}_2$ ), carbon monoxide ( $\text{CO}$ ), nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), and hydrogen sulfide ( $\text{H}_2\text{S}$ ). (EREC, April 21, 2002).



**Figure 2.6** Anaerobic Pathways

Figure 2.6 illustrates four continuous biodegradation processes for anaerobic treatment. They are called hydrolysis, fermentation or acidogenesis, acetogenesis, and methanogenesis processes. Different processes use different types of bacteria consortia. In the hydrolysis process, complex organic matter is hydrolyzed to simple organic matter by water splitting force. In the acidogenesis process, acidogenic bacteria ferment simple organic compounds to short organic acids (volatile fatty acids),  $H_2$ , and  $CO_2$ . In the acetogenesis process, volatile fatty acids (VFA) are converted to acetate,  $H_2$ , and  $CO_2$  by acetogenic bacteria. Finally methanogens convert the acetate and  $H_2 / CO_2$  gas to methane ( $CH_4$ ). Usually, the first three steps are put together and called acid digestion stage. The fourth step is called methane production stage.

### **1. Acid digestion stage**

In the acid digestion stage, acidogenic and acetogenic bacteria have high capacities to tolerate the large variations of pH, temperature, and organic acids. They have short generation times of several minutes to several hours. Most of them are heterotrophic bacteria. During this stage, since organic acids are formed and accumulated, the pH values may decrease less than 5. After that, due to the decomposition of the organic acids and production of  $H_2$ ,  $CO_2$ , and acetate, the pH values begin to increase to 6.6 to 6.8.

### **2. Methane production stage**

In the methane production stage, two groups of bacteria are involved in methanogenesis process – the hydrogenophilic ( $H_2$  – utilizing bacteria) and the

aceticlastic methanogens. For instance, in an anaerobic digester, these organisms are respectively responsible for 30% and 70% of the methane production (Buffiere *et al.*, 1995). They have the following characteristics:

- (1) Weak capacity for tolerating pH variations. The range must be kept in between 6.6 and 7.8. The optimum range is 6.9 to 7.2 (Haerbin Building Engineering Institute, 1981; Ong *et al.*, 2002; Rebac *et al.*, 1999; Sung *et al.*, 1995; Goodwin *et al.*, 1994; Goodwin *et al.*, 2001; Lo *et al.*, 1999; EL-Mamouni *et al.*, 1992).
- (2) Weak capacity for adjusting temperature. The optimal temperature ranges of anaerobic treatment are mesophilic (30 to 35°C) and thermophilic (50 to 60°C) (Haerbin Building Engineering Institute, 1981). If methanogenic bacteria are acclimated under one temperature condition, and the temperature is increased or decreased by 2°C, the anaerobic process may be destroyed, especially for the thermophilic range (Haerbin Building Engineering Institute, 1981). Therefore the methane production process needs to maintain a constant temperature.
- (3) Longer generation times. Usually, one regeneration time requires 4 to 5 days (Haerbin Building Engineering Institute, 1981).
- (4) Stronger specificity. Each type of methanogenic bacteria can only metabolize one type of substrate. For obtaining a high biodegradability of specific substrate, the methanogenic bacteria must be acclimated to the specific substrate.

(5) Methanogenic bacteria can oxidize molecular hydrogen and use CO<sub>2</sub> as acceptor to generate CH<sub>4</sub> and H<sub>2</sub>O.



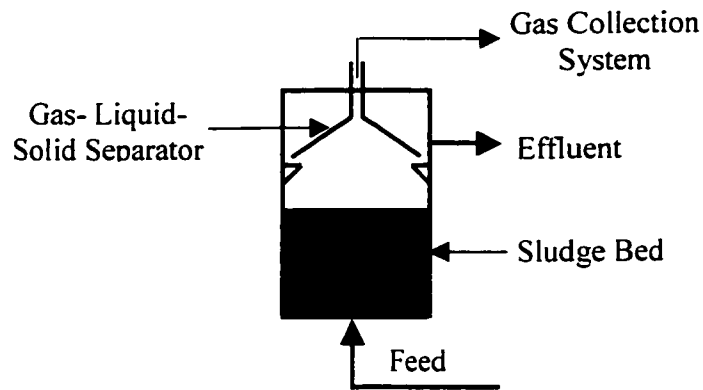
The methanogenic bacteria do not have high requirements for nutrients. Usually, CO<sub>2</sub> and NH<sub>3</sub> can act as its carbon and nitrogen sources. The methane production stage is the main controlling stage that controls the removal efficiency of organics.

Although produced methane is useful energy since it is a combustible gas, it is also dangerous to human beings. The anaerobic treatment system must be sealed. Therefore the capital cost of anaerobic treatment unit is more expensive than aerobic treatment unit.

#### **2.4.2.2.2 Reactor Types for Anaerobic Wastewater Treatment**

Since anaerobic technology has proven to be a useful tool for treating high-strength wastewater and become popular, variety types of anaerobic reactors have been produced and developed. The commonly used anaerobic reactors are described as follows.

## 1. Upflow Anaerobic Sludge Blanket (UASB) Reactor



**Figure 2.7** Upflow Anaerobic Sludge Blanket Reactor

The upflow anaerobic sludge blanket (UASB) process and its derivatives have demonstrated excellent performance and stability in numerous full-scale operations worldwide (Lettinga *et al.*, 1980; Lettinga, 1995; Angenent, *et al.*, 2001). The UASB reactor uses a continuous feeding mode in which wastewater is continuously pumped into the distribution system that is located on the bottom of reactor, and then is distributed through the sludge bed that is previously inoculated into the reactor. The anaerobic bacteria, which live in the sludge bed, contacts the wastewater and anaerobically degrades the organic matter in the wastewater, and rapidly converts it into biogas through a series of intermediates. The biogas is rich in methane.

An upward circulation of wastewater and gasborne sludge is formed within the reactor during the operation period. The dense, granular sludge can detach from the attached gas bubbles and sink back to the bottom establishing a return downward circulation. Therefore the return downward flow of degassed sludge ensures effective

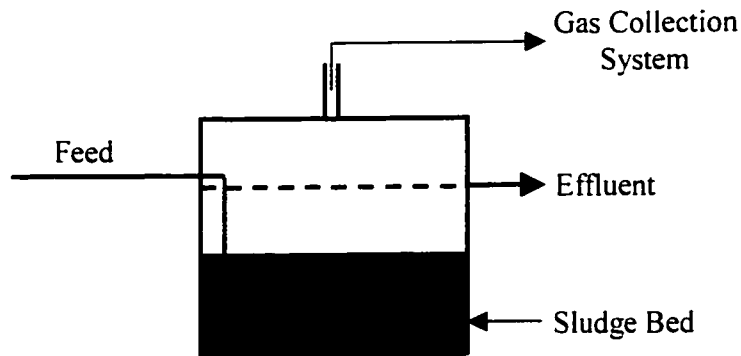
contact with the upward flow of wastewater and creates a continuous convection without the need for any energy consumption by mechanical or hydraulic agitation within the reactor. As a result, these processes can be operated at high organic loading rates (Lettinga, 1995). Moreover, washout of biomass with the effluent due to excessive bed expansion or poor granulation (Guiot, *et al.*, 1995) can occur.

In addition, at the top of the UASB reactor, a gas – liquid – solid separator is set to prevent wash out of biomass with the effluent. Because significant biomass loss will significantly decrease the performance of the reactor, a gas – liquid – solid separator is an important section in the design of the UASB reactor, which can efficiently separate solids from the effluent to ensure a high quality of effluent.

The design of the UASB reactor allows a high biomass concentration in the reactor to ensure a high conversion rate at high loading to be achieved routinely. Reports show that the UASB reactor can treat loading rates of 5 to 35 kg COD /m<sup>3</sup>-day with 50 to 90% efficiencies.



## 2. Anaerobic Sequencing Batch Reactor (ASBR)



**Figure 2.8** Anaerobic Sequencing Batch Reactor (ASBR)

The anaerobic sequencing batch reactor is an anaerobic version of the conventional SBR technology (Lemna Technology, St. Paul, Minnesota, 1999; Mulligan, *et al.*, 2001). Sung and Dagure (1992 and 1995) at Iowa State University have been conducting the studies of anaerobic sequencing batch reactor (Habben, 1991; Pidaparti, 1992; Kaiser, 1991). The operating mode of the ASBR is different from the UASB reactor. It is a sequencing batch-operating mode in which the wastewater is fed at the beginning of the sequence, and discharges effluent at the end. The amount of effluent is the same as the influent within the sequence. ASBR completes all processes within a single reactor, namely, four steps of fill, react, settle, decant are completed during a three to six hour cycle within a single reactor.

In the ASBR, it is common to refer to "feast" and "famine" conditions. Right after filling, the anaerobic bacteria that respond for conversion of organic matter to biogas are in a feasting condition with lots of their food (organic matter) available. Under the feasting environment, biogas is produced at a very high rate; and at the same time, the

concentration of organic matter in the wastewater decreases rapidly. Near the end of the sequence, the bacteria have consumed all food and enter the famine condition. At this time, biogas is produced slowly that provides ideal conditions for settling and decanting. This is the key feature of ASBR which enables the system to retain very high concentrations of biomass.

Since the settling process is finished in the reactor, ASBRs do not need a separate clarifier. But generally, a holding tank, which receives the wastewater prior to discharge into the ASBR, is needed to ensure that the ASBR tolerates shock flow.

The operation of the ASBR requires timers and controllers for proper controlling. ASBR reactors need mixing mechanisms to mix the wastewater and biomass so that there is no short-circuiting or dead zones existing inside the reactor. ASBRs are suitable for treatment of a variety of high strength industrial wastewaters. Some reports show that the treated levels by an ASBR can achieve 15 to 30 kg/m<sup>3</sup>.day with 75 to 94% COD removal efficiencies (Mulligan *et al.*, 2001).

### **3. Expanded Granular Sludge Blanket (EGSB) Reactor**

The EGSB reactor has been developed based on the sludge granulation concept of UASB reactor. The improvement of EGSB over UASB is that the EGSB process provides high upflow velocities (greater than 4 m/h, whereas that of UASB is 1m/h) (Rebac *et al.*, 1998) to expand the biobed that provides better condition of contacting between biomass and wastewater and eliminates the dead zones (Mulligan *et al.*, 2001; van der Last *et al.*, 1992). Thereby a high removal rate of organic matter is achieved routinely. The EGSB reactor is designed to have a large ratio of height to

diameter and to use the recycle system of the effluent in which the wastewater is pumped into the reactor at high upflow velocity through a distribution system that is located at the bottom of the reactor, and then is pushed up and through the biobed. The anaerobic bacteria in the biobed will degrade and convert organic matter in the wastewater to methane through anaerobic pathways. The large ratio of height to diameter ensures a longer contact pathway and high quality effluent. The recycle system can dilute the inhibitory contaminants in the wastewater. Therefore, the EGSB reactors have some advantages due to the above principle, such as simplicity, flexibility, and high efficiency (Anonymous, *Biothane UASB*, April 23, 2002). At the same time, the high volumetric loading rates result in a low requirement for land, with a slender and vertical construction. The EGSB reactor also has a high hydraulic balancing capacity because of its high recycle ratio.

According to literature, the high loading wastewater (15,000 to 35,000 mg/L) (Anonymous, *Biothane UASB*, April 23, 2002) can be treated very well in the EGSB reactor, even in low temperature environments. There are approximately 10 installations in the U.S. The highest capacity (26 kg COD /m<sup>3</sup>-day) was installed in 1996 at the Redhood Brewery (Mulligan *et al.*, 2001).

#### **4. Multiplate Reactor**

The multiplate reactor is a new technique developed by SNC Research Corporation for treating high concentration industrial wastewater. It was developed based on the UASB conception. The first full-scale unit (450 m<sup>3</sup>) was constructed in 1991 at a dairy plant in the province of Quebec (Mulligan *et al.*, 1996). The reactor consists of

plates, a shell, parallel feed entrances, lateral gas exits, and effluent exit (Mulligan *et al.*, 2001). The influent is pumped into the reactor from the bottom and side inlets, passing through the sludge bed that was inoculated before. Anaerobic bacteria in the sludge bed degrade and convert organic matter to biogas that is released by gas exits, which are located at the side and top of the reactor. Biogas, passing through the biomass, stirs up biomass and cleans up connecting conduits, thus preventing the formation of dead pockets.

Since plates are set in the multiplate reactor, the reactor is divided into several chambers. High concentrations of organics can be treated in the reactor due to the high concentrations of sludge and ability to remove gas at several places. Therefore after treatment by the multiplate reactor, the effluent can achieve a very high quality. Based on design of multiplate reactor, it can handle organic loadings from 2 to 30 kg COD /m<sup>3</sup>-day with more than 90% removal efficiency.

## **5. Continuously Stirred Reactor (CSR)**

The continuously stirred reactor is a conventional anaerobic contact process that is applicable for treating wastewater containing 2 to 5 kg COD /m<sup>3</sup>-day (Anonymous. *Biothane UASB*, April 23, 2002). It is especially suited for treatment of wastewaters that contains fats, oils, grease, etc.

The continuously stirred reactor has a specially designed mixer inside to ensure good contact of the wastewater with the biomass. A clarifier, such as flotation separators, thickeners, and settlers, must follow the CSR in order to settle solids from the

effluent. This type reactor is cost – effective for low flows with the removal efficiencies of about 90% of COD and BOD.

## **6. Fixed film Reactor**

The fixed film reactor is different from the suspended film reactor that was mentioned above. There is a medium inside the reactor. The material of the medium can used rocks or plastic support media. Anaerobic bacteria grow on the surface of the medium, which allows SRT (sludge retention time) up to 100 days to be achieved (Mulligan *et al.*, 2001). This type of reactor is very stable and can tolerate variations in flow and concentration of influent, and there is not significant biomass washout. The operating mode can be upward or downward flow.

Organic loadings of 5 to 30 kg COD /m<sup>3</sup>-day and media with specific surface areas of 100 m<sup>2</sup>/m<sup>3</sup> are usually employed (Mulligan, *et al.*, 2001). COD concentrations of 1000 to 30,000 mg/L with soluble and insoluble COD ratios greater than one and with suspended solids levels lower than 500 mg/L (Mulligan, *et al.*, 2001) can work best using fixed film reactor under an anaerobic environment.

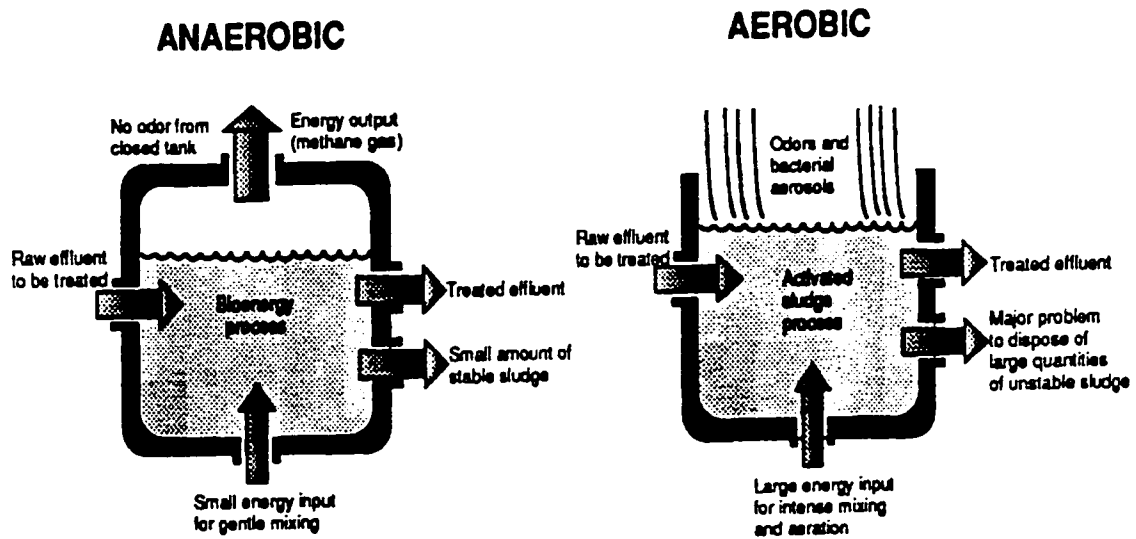
## **7. Fluidized Bed Reactor (FB)**

The fluidized or expanded bed is a new anaerobic technology developed in which particles are used such as sand, high density plastic beads, styrene and polyvinylbenzene beads, crushed rock or granular activated carbon (1.35 g/cm<sup>3</sup>) with diameters of 0.1 to 0.7 mm are suspended by the liquid velocity (Iza, 1991). The FB technology offers many advantages, such as a high concentration of biomass attached

onto the high density carrier which is easily kept in the biomass inside the reactor. At the same time, a large surface area for biodegradation of organic matter is also provided by the small size particles (Bull, *et al.*, 1984) that increase the chance for mass transfer of organic matter. A high velocity of fluid flow allows dilution of the wastewater with the effluent that can greatly decrease the effect of overloads and toxicants (Marin, *et al.*, 1999). High velocity also reduces the possibility of plugging (Mulligan *et al.*, 2001). Fluidized bed reactors have been operated with different substrates (Iza 1991). The best range that the FB reactor can treat very well is 30 to 60 kg COD/m<sup>3</sup>-day.

#### **2.4.2.3 Comparison of Aerobic and Anaerobic Technologies**

The two main types of biological treatment – aerobic and anaerobic treatment have been described in detail. Their treatment mechanisms are different. A comparison between anaerobic and aerobic processes is illustrated in Figure 2.9. A comparison of both treatment techniques is also presented in Table 2.4.



**Figure 2.9** Comparison between Anaerobic and Aerobic Processes (Source: Ditchfield, 1986)

**Table 2.4** Comparisons of Anaerobic and Aerobic Technologies (Source: Enviroasia Ltd., June 2, 2002; Haerbin Building Engineering Institute, 1981; Speece, 1996; Eckenfelder *et al.*, 1988.)

Parameter		Aerobic technology	Anaerobic technology
Condition Requirement	Oxygen	Require oxygen – rich environment	No need for oxygen
	pH	6.5 – 9.0	6.6 – 7.8
	Temperature	Treatment efficiency is best at temperature of 20 – 30 °C. Can treat rather cold wastewater. No elevated temperatures needed.	Treatment efficiency is best at temperature of 30 – 35°C or 50 – 60°C. Can treat warm wastewater. It has requirement for elevating temperature of treated wastewater.
	Organic loads	Best for lower concentrations of organic matter in the wastewater.	Best for medium and high concentrations of organic matter in the wastewater
	Toxicant	Toxic components are often acceptable. It does not require long – term acclimation.	Toxic components must be acclimated for long term. After that, toxic components can be degraded using anaerobic technologies.
	Nutrients	High nutrient requirement. Theoretically, COD: N: P = 100: 5: 1	Lower nutrient requirement. Theoretically, COD: N: P = 350: 7:1 for high loading. COD: N: P = 1000: 7: 1 for low loading.



Process	High quality effluent can be obtained through proper design.	High quality effluent can be obtained only following an additional aerobic post-treatment (polishing).
	N- and P- are removed simultaneously.	No significant N- and P- removal.
	Clogging danger when using carrier medium	No clogging danger from sludge production
	Large land requirement	Less land needed. The reactor can be housed.
	Possible odor problems, or high volumes of waste air to be treatment	No odor problems and waste air in case of systems using closed tanks
By - products	High excess sludge produced that is difficult to dewater	Very small surplus sludge growth that is relatively easy to dewater
		Valuable biogas – methane produced that is useful for additional energy.
Costs	Relatively low investment cost	Relatively higher investment costs
	High maintenance costs	Low maintenance costs
	High operating fees for: Aeration (power), nutrients (N, P), excess sludge disposal. Small plant is feasible.	Low operating fees. Requires low power consumption, no or little nutrient requirements, little surplus sludge disposal, small plant is less economical.

Figure 2.9 and Table 2.4 illustrate the differences between aerobic and anaerobic technologies. Anaerobic technology can transform waste (organic contaminants) to useful energy (methane), at the same time, there is less sludge produced that is relatively easy to dewater than activated sludge from aerobic treatment units. These advantages greatly push the application of anaerobic technology in wastewater treatment, especially in high-strength industrial wastewater treatment. Since a large amount of surplus sludge is produced within aerobic process and high requirements for aerobic, aerobic technology is not suitable for treating high loads of wastewater, especially high loads in industrial wastewater.

However, there are also drawbacks in anaerobic technology. The major one is that it requires more stringent process control but only reduces the organic pollution by 85 to 90%, which means a second step is usually needed to guarantee high quality effluents (Anonymous, *Scientecmatrix*, April 8, 2002a). In addition, the anaerobic technology is not effective for removing nitrogen and phosphorus. This is another reason to apply an aerobic treatment unit, which can remove the residual nutrients, after the anaerobic treatment unit.

To sum it up, the best choice for treating high loads in industrial wastewater is an anaerobic treatment unit for pretreatment. and then an aerobic treatment unit to obtain a high quality effluent to satisfy the requirements of discharge standards.

## **2.5 Rationale for the Study**

The characteristics of brewery wastewater were shown in section 2.3 to have a high soluble organic concentration and biodegradability with significant pH fluctuations.

Due to the increase in surcharge levied by the government, breweries are searching for methods to reduce effluent pollutant concentrations. At present, biological treatment technologies have been successfully used to treat brewery wastewater and have obtained high effluent quality. Table 2.5 lists some full-scale brewery wastewater treatment plants worldwide.

**Table 2.5** Full-Scale Brewery Wastewater Treatment Plant (Source: Anonymous, *Enviroasia*, August 2, 2002)

<b>Name of Brewery</b>	<b>Treatment Technique</b>	<b>Capacity kg COD/day</b>	<b>Location</b>
Carlsberg Brewery Wastewater Treatment Plant	UASB + aerobic	3,300	Malaysia
San Miguel Shunde Brewery Wastewater Treatment Plant	UASB + aerobic	9,900	China
Kingsway Brewery Wastewater Treatment Plant	UASB + aerobic	27,060	China
Vietnam Brewery Wastewater Treatment Plant	UASB	14,000	Vietnam
Kaiser Brewery Wastewater Treatment Plant	UASB + aerobic	16,500	Brazil
Khon Kaen Brewery Wastewater Treatment Plant	UASB + aerobic	16,800	Thailand

Table 2.5 sufficiently shows that the UASB + aerobic technique has already been extensively applied in brewery wastewater treatment worldwide. At the same time, other sources also present some application examples of biological treatment processes at full- or lab-scale. Table 2.6 summarizes the application of biological treatment technologies in the brewery industry.

**Table 2.6 Summary of Brewery Wastewater Treatment Processes**

Reactor Configuration	OLR (kg COD/m <sup>3</sup> .d)	HRT	Operating Temp. (°C)	% Removal	Reference
<b>Anaerobic Treatment</b>					
Full-Scale Completely Mixed Reactor	0.31	6 days	20	80-85	Wat. Eng. & Manag., 1993
Lab Scale AFBR <sup>a</sup>	33 -36	2-2.5h	25	85	Liang, <i>et al.</i> , 1993
Lab Scale Fixed-Film	2.15-2.69	8-10h	35	70-82	Lo, <i>et al.</i> , 1988
Lab Scale AFBR	30	3h	25	72	Oliva, <i>et al.</i> , 1990
Lab Scale UASB <sup>a</sup>	12.2	4h	25	89	Yan, <i>et al.</i> , 1996
Full Scale UASB <sup>a</sup>	6.9-7.6	6.1-6.5h	30	80-90	Sax, <i>et al.</i> , 1985
Lab Scale CUMAR	28.5	4.2 days	35	97	Ince, <i>et al.</i> , 1993
<b>Aerobic Treatment</b>					
Full Scale Deep Shaft	14	5h	34	94	Le Clair, 1984
Lab Scale Soft Packing	6-13	1.9h	>10	74	Huang, 1986
Lab Scale Jet Loop <sup>a</sup>	50	3.7-4h	35-39	97	Bloor, <i>et al.</i> , 1995

**Note:** <sup>a</sup> Feed and % removal expressed as soluble COD.

AFBR: Anaerobic Fluidized Bed Reactor.

Tables 2.5 and 2.6 sufficiently show the rationality of the application of biological treatment techniques in brewery wastewater, especially anaerobic treatment techniques. In addition, almost all studies have been performed on the entire brewery wastewater. very little is known about the bio-treatability of the wash wastewater from returned beer bottles, which contains mostly beer.

This study mainly focuses on the study for bio-treatability of wash wastewater from returned beer bottles through the comparison of two types of anaerobic bioreactors. If the wash wastewater, which is a major proportion in volume of the brewery wastewater, with high organic content can be treated, then the amount of wastewater discharged from the brewery can be reduced significantly.

## ***CHAPTER 3***

### **MATERIALS AND METHODS**

#### **3.1 Materials**

##### **3.1.1 Seed Sludge**

The sludge was collected from the SNC anaerobic reactor at a cheese factory in Chambord, Quebec, and had been stored in a fridge at 4°C under anaerobic conditions before seeding the test reactor. Since there was not enough activity, before starting the formal experiments, the sludge was acclimated 3 months with the substrate at room temperature.

##### **3.1.2 Substrate**

In this study, the substrates used were beer and glucose (glucose was only used in the preliminary test stage). The brand of beer used was Russe Boreale with the alcohol concentration of 5%, and glucose used was pure glucose powder purchased from Fisher Scientific Company. The soluble COD concentration of the original beer is  $1.1 \times 10^5$  mg/L, and the pH value of original beer is around 4.5. Since beer is soluble, through testing, the total COD concentration of original beer ( $=1.15 \times 10^5$  mg/L) is almost the same as its soluble COD concentration, therefore the soluble COD reduction is only measured in the study.

### 3.1.3 Feed Solution

The COD concentration in the feed solution of beer is made by adding beer to distilled water (made in the laboratory), whereas, the feed solution of glucose is made by adding glucose powder to distilled water. The amount of beer or glucose for each COD concentration is listed in Table 3.1

**Table 3.1** COD Concentration and the Added Amount of Beer and Glucose

<b>COD Concentration (mg/L)</b>	<b>Amount of Beer Added (mL/L distilled water)</b>	<b>Amount of Glucose Added (g/L distilled water)</b>
1000	9.1	0.9091
2000	18.2	1.8182
3000	27.3	2.7273
4000	36.4	3.6364
5000	45.5	4.5455
7000	63.7	6.3637
10,000	91	9.0910

*Note:* Table 3.1 can be applied throughout the study.

### 3.1.4 Nutrients

The nutrients used in this study were  $(\text{NH}_4)_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  purchased from Fisher Scientific Company.  $(\text{NH}_4)_2\text{CO}_3$  was used as a source of nitrogen, and  $(\text{NH}_4)_2\text{HPO}_4$  was used as a source of nitrogen and phosphorus.

### 3.1.5 Yeast Extract

In this study, some test stages used yeast extract. It is powder and was purchased from Fisher Scientific Company.

### 3.1.6 Trace Metals

In this study, some test stages involved also used trace metals that were required by biomass. All trace metals used in this study were purchased from Fisher Scientific Company and are listed in Table 3.2.

**Table 3.2:** Trace Metals Used in Substrate Choice Stage

Element	Chemical
Al	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$
Ca	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
Co	$\text{CoCl}_2$ (97%)
Cu	$\text{CuCl}_2$ (99%)
Fe	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
Mg	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Mn	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$
Mo	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
Ni	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
Zn	$\text{ZnCl}_2$



### **3.1.7 NaHCO<sub>3</sub>**

The pH value is an important factor in anaerobic wastewater treatment that was mentioned in the literature review. In this study, NaHCO<sub>3</sub> was used to adjust pH inside reactor, influent, and effluent. NaHCO<sub>3</sub> (technical grade) was purchased from Fisher Scientific Company. Certain amounts of NaHCO<sub>3</sub> were weighted by a balance (Denver Instrument M-220 Analytical Balance) and were directly added into feed solution during the period of the experiments.

### **3.1.8 KOH**

The pure KOH powder was used in this study to make a KOH solution with a concentration of 500 g/L to absorb CO<sub>2</sub> from produced biogas. It was purchased from Fisher Scientific Company.

## **3.2 Analytical Methods**

### **3.2.1 COD Analysis**

The COD values of samples from influent and effluent were determined by using a Perkin Elmer Lambda 40 UV/VIS spectrometer. The method adopted is a colorimetric method. Oxygen consumed is measured against standards at 600 nm with a spectrometer. A boiling mixture of chromic and sulfuric acids can oxidize most types of organic matter. The principle is that a sample is refluxed in a strongly acid solution with a known excess

of potassium dichromate ( $K_2Cr_2O_7$ ). During this reaction, six valence chromium ( $Cr^{6+}$ ) is reduced to three valence chromium ( $Cr^{3+}$ ). The density of the green color of the chromium ion ( $Cr^{3+}$ ) is measured. The measurement is done against a standard calibration.

Before testing, the standard KHP (potassium hydrogen phthalate) solution of 1.500 mg/L COD must be prepared. The method for making the KHP standard solution was:

1. Lightly crush the powder chemical of KHP.
2. Take a certain amount of KHP and dry in oven (LINDBERG/BUE Gravimetric Oven) at 120° Celsius to constant weight.
3. Dissolve 1275 mg of KHP in distilled water (made in laboratory) and dilute to 1000 mL. This solution has a theoretical COD of 1500 mgO<sub>2</sub>/L.

In the COD testing procedure, the standard COD reagent twist – cap vials with 10 mL volume purchased from Bioscience Inc. were used. The COD reagent is approved by the EPA as a micro – COD test. The total volume of the COD reagent in the vial was 5 mL. The standard range of COD was 20 – 900 mg/L. The stages of COD testing were divided into 11 steps.

1. Preheat a COD heater block to 150° Celsius.
2. Prepare two blank vials (COD = 0 mg/L) and one standard vial (COD = 300 mg/L).

Two blank vials were used to zero the system. The standard vial was used to plot the

standard curve of absorbance versus known COD concentration. The process method of blank vials was:

- a. Remove the cap from a COD twist – cap vial.
- b. Using a pipette measures distilled water of 2.5mL and carefully add it down the side of the vial so that it forms a layer on the top of the reagents
- c. Replace the twist cap and be sure it is tight.

Similarly, the process method of 300 mg/L COD standard vial was

- d. Repeat step a.
- e. Using a pipette measures 1.5mL of KHP solution and 1.0mL of distilled water, respectively, and put them into a vial carefully in order to form a layer on the top of the reagents.
- f. Repeat step c.

**Note:** Two blank vials (COD = 0 mg/L) and one standard vial (COD = 300 mg/L) must be prepared every time for standardizing the UV/VIS spectrometer.

3. Process sample vials: (each sample is prepared in triplicate)
  - g. Repeat step a.
  - h. Carefully add 2.5 mL of diluted sample down the side of a vial so as to form a layer on top of the reagent.
  - i. Repeat step c.

4. Take all vials processed above and thoroughly mix the contents sealed in vials by Vortex Mixer.
5. Place all vials in a COD heater block to heat for 2 hour under  $150^{\circ} \pm 2^{\circ}$  Celsius.
6. Remove the vials from the heater block and allow cooling at room temperature for 1 hour.
7. Allow any suspended precipitate to settle and wipe the outside of each vial clean.
8. Use “Standard Range reagent (20 – 900 mg/L COD)” method, and set the wavelength of the spectrometer to 600 nm, and then use procedural blank vials to zero the absorbance reading.
9. Read the absorbance of each standard and sample sequentially on the UV/VIS spectrometer.
10. Plot a graphic calibration curve of the absorbance of standards to their known concentration.
11. Compare absorbance of samples with the graphic calibration curve to determine COD concentration of samples.

### **3.2.2 Volatile Fatty Acids**

Volatile fatty acid (VFA) concentration in the effluent was determined by a Beckman – Coulter system gold HPLC (high pressure liquid chromatography)

equipment. In the HPLC equipment, the column used was a YMC 8476 HPLC Column; the solvent was 50 mM ammonium phosphate solution with pH value of 2.4; the flow-rate was set as 1 mL/min; the total run time for test each sample was 20 min; operation temperature was 30°C; the injected volume of each sample was 10 µL; detective channel was the wavelength of 210 nm. Each sample was tested in duplicate. The steps of determination are listed below.

1. Prepare standard mixture solution. Add 1g pure acetic acid, propionic acid, and butyric acid, respectively, to HPLC water of 1L to make the mixture solution regarded as a 1% concentration.
2. Filter the standard mixture solution and effluent sample by Whatman syringe filter of 0.45 µm pore size, and put them into special vials.
3. Put the special vials into the tray of HPLC equipment, and then use HPLC software to analyze the concentration of acetic acid, propionic acid, and butyric acid of samples.

### **3.2.3 MLVSS in Reactor and VSS in Effluent**

The sludge concentration is expressed as MLVSS in reactor or VSS in the effluent. The processes of testing MLVSS and VSS are the same. Each sample was tested in triplicate. The detailed procedure of testing MLVSS is:

1. Pre-dry a gooch crucible with Whatman GF/C filter paper in a Fisher Scientific Isotemp<sup>®</sup> muffle furnace at 550° +/- 2° Celsius for 1 hour and allow it to cool in

desiccator (Sanpla Dry Keeper, Automatic Dehumidifying Desiccator) for 30 min. it was weighed immediately using a balance (Denver Instrument M-220 Analytical Balance) and called “weight 1”.

2. A small syringe was used to take a 0.5 mL well-mixed sample from the 2 L reactor. and transfer it into a pre-weighed gooch crucible to filter them by a vacuum pump filtration system.
3. The gooch crucible was dried with the residue to dryness in an oven (LINDBERG/BUE Gravimetric Oven) at  $105^{\circ} \pm 2^{\circ}$  Celsius for 1 hour and allowed it to cool in the desiccator for 10min. It was weighed immediately and called “weight 2”.
4. The gooch crucible was ignited with the residue in a muffle furnace at  $550^{\circ} \pm 2^{\circ}$  Celsius for 2 hour, allowed it to cool in the desiccator for 30 min and then weighed it by a balance immediately and called “weight 3”.
5. The MLVSS in reactor =  $(\text{weight 3} - \text{weight 2}) / 0.5 \text{ mL}$ .

The testing procedure of VSS in effluent was the same as that of the MLVSS in reactor, only in step 2 and 5 of testing MLVSS, the volume was changed from 0.5 mL to 10 mL.

### **3.2.4 pH Value**

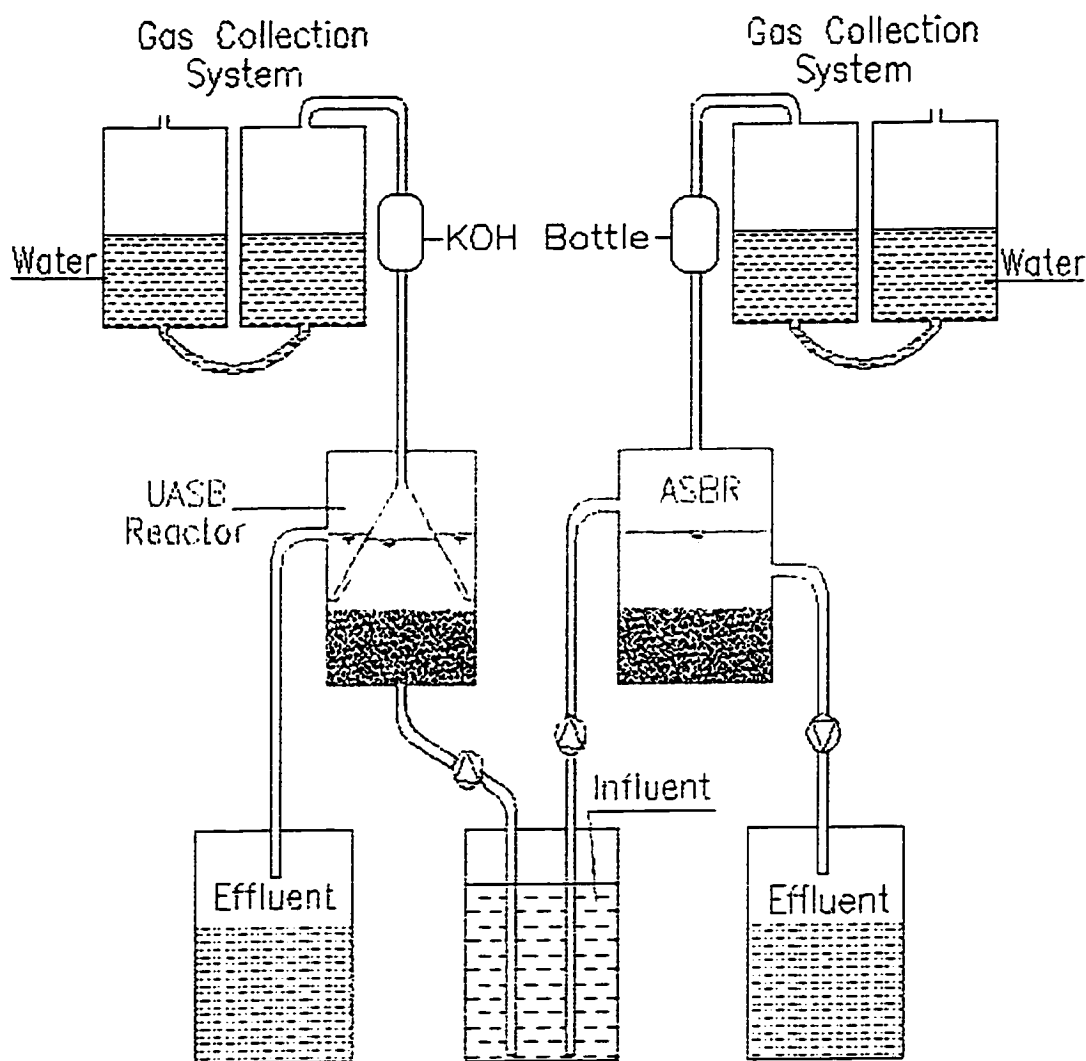
A portable pH meter with probe (Fisher Scientific Accumet Research pH Meter/Probe) was used to monitor the pH values in the influent and effluent. It was also used to monitor the pH values of mixed liquor in the reactor.

### **3.2.5 Temperature and Dissolved Oxygen**

A general temperature meter was used for monitoring room temperature. The dissolved oxygen (DO) and temperature in liquid were monitored by an AQUA CHECK\* Conductivity, DO, pH and Temperature Meter (Model 51600).

## **3.3 Apparatus**

The UASB reactor and the ASBR system are illustrated in Figure 3.1. They have an identical cylindrical shape with a height of 20.8 cm and diameter of 14.6 cm. Both reactors are plastic bottles with a 3L total volume and were purchased from Fisher Scientific Company. The reactors were sealed by a screw cap located on the top. The working volume of each reactor was 1200 mL/day. The influent was pumped into two reactors from a 3 L influent container by Masterflex peristaltic pumps (with variable speed controller). All connectors in the systems of two reactors were purchased from Fisher Scientific Company.



**Figure 3.1** Setup of ASBR and UASB Reactor Systems

In the UASB reactor, the feed was pumped into the reactor continuously by a peristaltic pump from the inlet that was located on the center of bottom of the UASB reactor. The feed rate was 1200 mL/day. One outlet of the effluent was set on the height of 2L volume level of reactor from the bottom; the effluent port connected with an effluent container by a plastic tube for discharging effluent. At about 1/2 of the reactor



height, a rim with approximately 1.2 cm height was fixed inside the reactor to prevent gas escape between the reactor wall and the gas collector. A funnel was placed up – side down above the rim and cover some section of the rim in order to ensure the gas collected properly. The funnel was connected with the gas collection system of the UASB reactor.

In the ASBR system, one feed port was located above the 2 L volume level from bottom and a plastic tube with diameter of 3 mm was connected with feed port inside the reactor to the bottom of the reactor in order to ensure the feed was well - mixed with biomass. One outlet of effluent was located on the 1.7 L volume level from the bottom of the reactor. The working volume of each sequence was 300 mL. Two peristaltic pumps were used in the ASBR system. Within a sequence, the feed solution of 300 mL was pumped into the reactor at the beginning of the sequence, and the effluent of 300 mL was pumped out from the reactor to an effluent container at the end of the sequence. The operation of the ASBR was controlled by Cole-Parmer Timer (with controller. Model No. 029-3). A stirrer (CORNING Stirrer) was used for mixing the influent with the biomass intermittently. The stirrer was operated at 1 min per hour. The stirrer was set up to 4.5. Three timers were used in the ASBR system. One timer was connected with the feed pump to control feeding, one timer was connected with the effluent pump to control effluent discharge, and the last one was connected with the stirrer to control the operation of the stirrer.

### 3.4 Biogas Collection

Biogas produced from the ASBR and UASB reactors was collected by the gas collection system that is connected with the reactor. The gas collection systems in the UASB and ASBR systems are the same. The sketch diagram of gas collection system is shown in Figure 3.1. The bottles used in the gas collection system were plastic bottles with 2L volume and purchased from Fisher Scientific Company. All connectors in the gas system were purchased from Fisher Scientific Company. The design of the gas collection system allowed measurement of the produced gas by volume. In the design, the reactor was first connected with a bottle in which KOH solution of 500 g/L concentration was filled inside in order to absorb  $\text{CO}_2$  properly from produced gas (the concentration of KOH solution refer to the standard method for absorbing  $\text{CO}_2$  from produced biogas, APHA, *2720B Sludge digester gas*, 1989), and then it connected with the gas collection system. The others trace gases produced, such as  $\text{H}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{N}_2$ ,  $\text{O}_2$ , etc, were ignored in the measurement in this study. Therefore the total volume measured in the gas collection system was considered as the volume of methane production.

### 3.5 Reactor Operation

The study was performed in two groups. The first group was performed at room temperature and lasted 25 days; the initial COD loading rate was  $2 \text{ kg/m}^3\cdot\text{d}$ ; the highest COD loading rate was  $20,000 \text{ kg/m}^3\cdot\text{d}$ ; the hydraulic retention time was 12 hour. Since

this study compares the performance efficiency of the two different reactors, the operational parameters of both systems were kept as equal as possible. The working procedure in both systems has been introduced in section 3.3 in detail. In both reactors, the COD loading rate was gradually increased by increasing the amount of beer in the feed solution. At the same time, the amount of nutrients increased proportionally with COD load. In the first group, the inoculated amount of sludge in both reactors at the beginning was 17 g/L MLVSS. The operational parameters in both reactors are shown in Tables 3.3 and 3.4.

**Table 3.3** Operational Parameters in both Reactors at Room Temperature

<b>Operational Parameters</b>		<b>UASB Reactor</b>	<b>ASBR</b>
Total Volume of Reactor (mL)		2000	2000
Working Volume per day (mL)		1200	1200
Upflow Feed Rate (mL/d)		1200	-
COD Concentration in Influent (mg/L)		1000 – 10,000	1000 – 10,000
COD Loading Rate (kg/m <sup>3</sup> .d)		2 - 20	2 - 20
Hydraulic Retention Time (hrs)		12	12
Nutrients	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (g/g COD/L)	0.312	0.312
	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> (g/g COD/L)	0.0426	0.0426

**Table 3.4** Sequencing Characteristics of the ASBR

<b>Sequencing Characteristics</b>	<b>Value</b>
Number of Sequences per day	4
Length of Sequence (h)	6
Volume of Feed per Sequence (mL)	300
Volume Decanted per Sequence (mL)	300
Length of Feed Time (min)	5
Length of Reaction Time (min)	291
Length of Settling Time (min)	60
Length of Decanting Time (min)	4

In this test group, the pH in both reactors was maintained in the optimal range (6.9 to 7.2) by adjusting the amount of  $\text{NaHCO}_3$ . The amount of  $\text{NaHCO}_3$  added will be described in section 5.1.2. At the same time, during the period, the soluble COD reduction, VFA concentration in the effluent, VSS in the effluent, methane production, pH and temperature were measured by standard methods mentioned in this chapter, respectively. The performance parameters and the frequency of analyses are shown in Table 3.5.

**Table 3.5** Performance Parameters and Their Frequency of Analyses

<b>Parameters</b>	<b>Frequency</b>
Soluble COD Reduction	1/4 days
Methane Production	1/4 days
Acetic Acid Concentration in Effluent	1/4 days
Propionic Acid Concentration in Effluent	1/4 days
VSS in Effluent	1/4 days
pH in Influent	1/ day
pH in Effluent	1/0.5 day
Temperature	1/0.5 day
MLVSS in Both Reactors	At end of test

The second test group was performed at 35°C and lasted 29 days; the initial COD loading rate was 2 kg/m<sup>3</sup>.d; the highest COD loading rate was 20,000 kg/m<sup>3</sup>.d; the hydraulic retention time was 12 hour. Since this group was also the comparison of the ASBR and UASB reactors, the operational parameters of both reactors were kept as equal as possible. The only difference between the first group and second group tests was that the temperature was changed from room temperature to 35°C. All other performance parameters in the second group were the same as in the first group. Therefore Tables 3.3, 3.4, and 3.5 can also be applied to the second test group. In the second group, soluble COD reduction, VFA concentration in the effluent, VSS in the effluent, methane production, and pH were measured by the same method as the first group, respectively.

## **CHAPTER 4**

### **PRELIMINARY TESTS AND RESULTS**

At the beginning of the experiments, the activity of sludge and bio-treatability of the wash wastewater from returned beer bottles were not known; therefore before starting the formal experiments, they were tested. The testing stage was done by two steps and was respectively called substrate choice and optimal condition.

#### **4.1 Substrate Choice**

Since many papers did their anaerobic experiments with glucose (Ong *et al.*, 2002; El-Mamouni *et al.*, 1992; Angenent *et al.*, 1995) and had proven that glucose was easily biodegraded under anaerobic conditions, at the beginning of this study, glucose was used with nutrients and trace metals as the ideal condition #1, and three different conditions of beer were applied for comparing with condition #1 in order to find optimal conditions of beer for formal experiments in the future. A total of 4 conditions were used:

1. Glucose with nutrients, yeast, and trace metals called “condition #1”.
2. Beer with nutrients, yeast, and trace metals called “condition #2”.
3. Beer with nutrients called “condition #3”.
4. Beer called “condition #4”.

The same concentration of COD was used in the 4 conditions throughout this step study. The actual amounts of nutrients, yeast, and trace metals used in each condition are shown in Table 4.1.

**Table 4.1:** Contents of Nutrients, Yeast, and Trace Metal Solution

Parameter		Condition 1	Condition 2	Condition 3	Condition 4
Nutrients	Nitrogen (g/g COD/L)	0.312	0.312	0.312	0
	Phosphorus (g/g COD/L)	0.0426	0.0426	0.0426	0
Yeast (g/g COD/L)		0.02	0.02	0	0
Trace Metal solution (mL/g COD /L)		10	10	0	0

*Note:* The compositions of trace metals in solution are shown in Table 4.2

**Table 4.2:** Quantities of Trace Metals in Solution

Element	Chemical	Quantities (mg/L)
Al	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	1.9
Ca	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	693.8
Co	$\text{CoCl}_2$ (97%)	4.1
Cu	$\text{CuCl}_2$ (99%)	0.61
Fe	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	482.1
Mg	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2563.5
Mn	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	3.1
Mo	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	0.2
Ni	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	2.0
Zn	$\text{ZnCl}_2$	6.3

Firstly, the sludge was acclimated under 4 different conditions of solution using a COD concentration of 1000 mg/L for 10 days, and fresh solution was changed every day, respectively. The sludge was acclimated at room temperature during the first 4 days, and was transferred to the incubator to continuously acclimate at 35°C during the latter 6 days. The wet weight of sludge seeded in each condition system was 75.1g. The total volume of each system was 200 ml. The pH values in the 4 systems were adjusted every day by adding NaHCO<sub>3</sub>, and these systems were kept in the range of 6.6 to 8.0.

After 10 days of acclimation under anaerobic conditions, the COD reductions of 1000 mg/L in the 4 systems were tested at 35°C under a hydraulic retention time (HRT) of 24 hour. The results are shown in Table 4.3.

**Table 4.3:** Reduction of 1000 mg/L COD over 24 hour at 35°C

<b>Parameter</b>	<b>Condition 1</b>	<b>Condition 2</b>	<b>Condition 3</b>	<b>Condition 4</b>
COD reduction (%)	75.5	75.4	75.8	75.6
MLVSS (g/L)	20.6	21.0	23.1	23.0

**Note:** 1. Since the bottles were smaller, when the systems were run, the systems cannot be mixed very well.

2. MLVSS: Mixed Liquor Volatile Suspended Solids

The results in Table 4.3 illustrate that even if the sludge has been stored in the fridge, it still has good characteristics for COD reduction under anaerobic conditions. It



also indicates that even though the systems were not mixed completely in the 250 mL plastic cylindrical bottles (the height of the bottle is 11.8 cm and the diameter of the bottle is 5.2 cm) by a shaker (INNOVA™ 2000 PLATFORM Shaker) with the rate of shaking of 120 rpm, it can also get about 75% reduction of 1000 mg/L COD loading under 35°C over one day retention time in 4 systems.

Following the above results, the 4 systems were changed to 500 ml flasks in order to maintain good mixing in each system by a shaker (the rate of shaking was 120 rpm). Then 4 solutions of 5,000 mg/L COD were used to feed the systems for one week, respectively. After one week, the reduction of 5,000 mg/L COD at 35°C with 24 h retention times was tested, and the results are listed in Table 4.4. After that, the same procedure and conditions that were used in the 5,000 mg/L COD loading level were also used for the reduction of 10,000 mg/L COD. The results are also shown in Table 4.4.

**Table 4.4:** Reduction of 5,000 mg/L COD and 10,000 mg/L COD at 35°C (24 hour retention times)

System	5,000 mg/L COD			10,000 mg/L COD		
	COD	pH		COD	pH	
	reduction	Initial <sup>a</sup>	Final <sup>b</sup>	reduction	Initial <sup>a</sup>	Final <sup>b</sup>
Condition 1	91.5	7.02	7.55	49.7	7.03	5.52
Condition 2	84.2	7.00	7.96	90.7	7.07	8.16
Condition 3	84.3	7.08	7.94	86.3	7.04	8.06
Condition 4	74.9	7.05	6.38	53	7.06	5.4

*Note:* a represents the pH values taken at the beginning of testing.

b represents the pH values taken at the end of testing

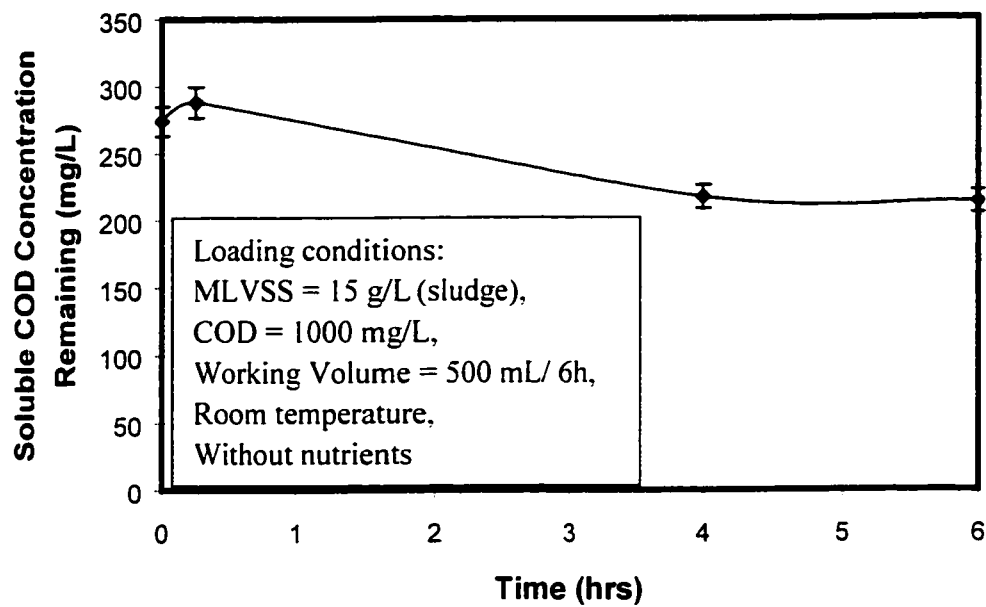
As methanogenic bacteria are inhibited at pH values below 6.6 and the optimal ranges are 6.9 to 7.2, Table 4.4 illustrates the COD reduction in condition #4 system under the loading of 5,000 mg/L COD concentration was lower than that in other three systems because the pH in condition #4 system was lower than 6.6, which inhibited the activity of methanogens and decreased COD removal efficiency. Similarly, the COD reduction in condition #1 and #4 systems under the loading of 10,000 mg/L COD were low because the pH values in both systems were lower than 6.6.

As illustrated in Tables 4.3 and 4.4, COD reduction can be achieved in the 4 systems, and the condition #4 is the least expensive for operation. Therefore condition #4 – beer without nutrients and trace metals was chosen as the first choice in the next study.

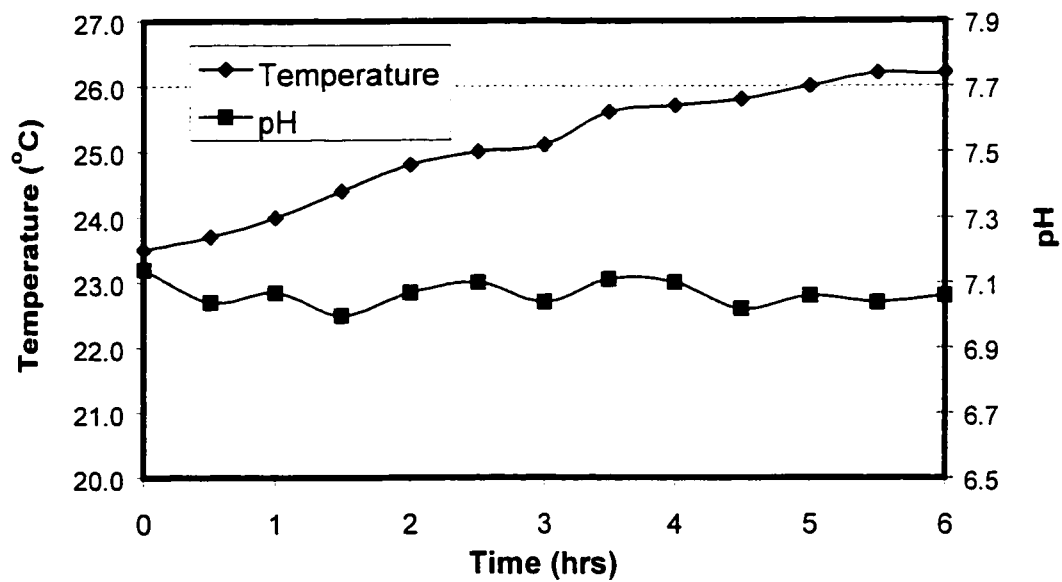
## 4.2 Optimal Conditions

The following study was to seek the optimal conditions for future experiments using an anaerobic batch reactor (ABR). This reactor is a plastic container with a square cross-sectional shape and a volume of 2.8 L. It was purchased from a store. It has a tight cap to seal the system. The total volume of mixed liquor inside the reactor was 2 L.

According to the above results and discussion in section 4.1, the sludge must be acclimated before using. Therefore about 2.5L sludge was taken out from fridge that was mentioned above, and acclimated only using beer at room temperature. The COD concentration of the beer was added to the 2.5L sludge was about 1000 mg/L. After 15 days of continuous acclimation, 15 g/L MLVSS of sludge was taken and inoculated into the 2L ABR for testing COD reduction. In this stage, the soluble COD remaining in the supernatant was tested over 6 h retention times in order to determine the performance in ASBR in future. The ABR adopted intermittent mixing mode, namely, stirring 1 min per 1 hour, the intensity of stirring was 4.5. First, the working volume of one batch of 6 hour was adopted 500 mL. The soluble COD reduction is shown in Figure 4.1. The variations of pH values and temperature during the cycle of 6 hour are shown in Figure 4.2.



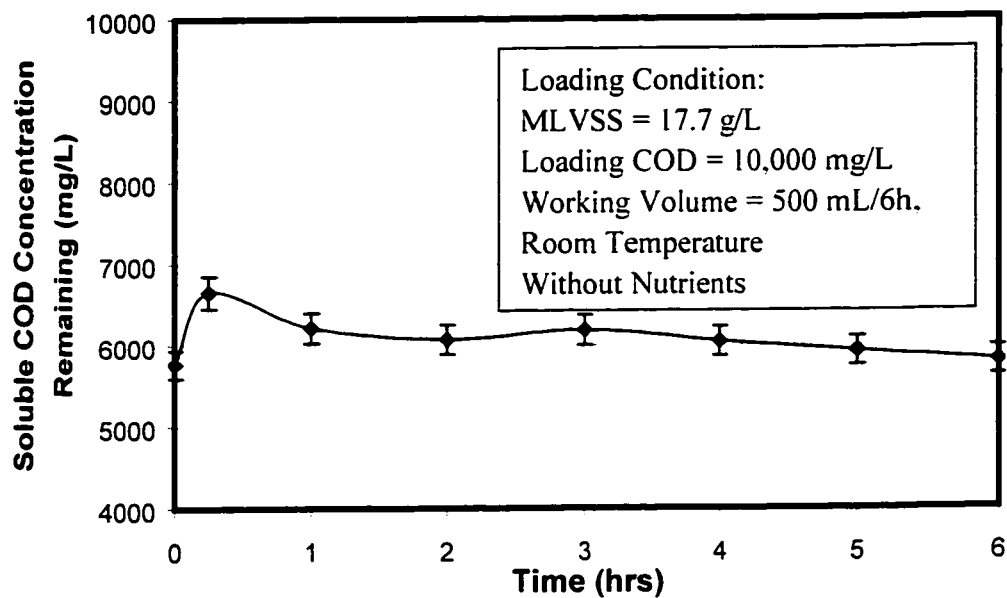
**Figure 4.1** Soluble COD Concentration Remaining in the Supernatant of the ABR during a Typical Six – Hour Cycle



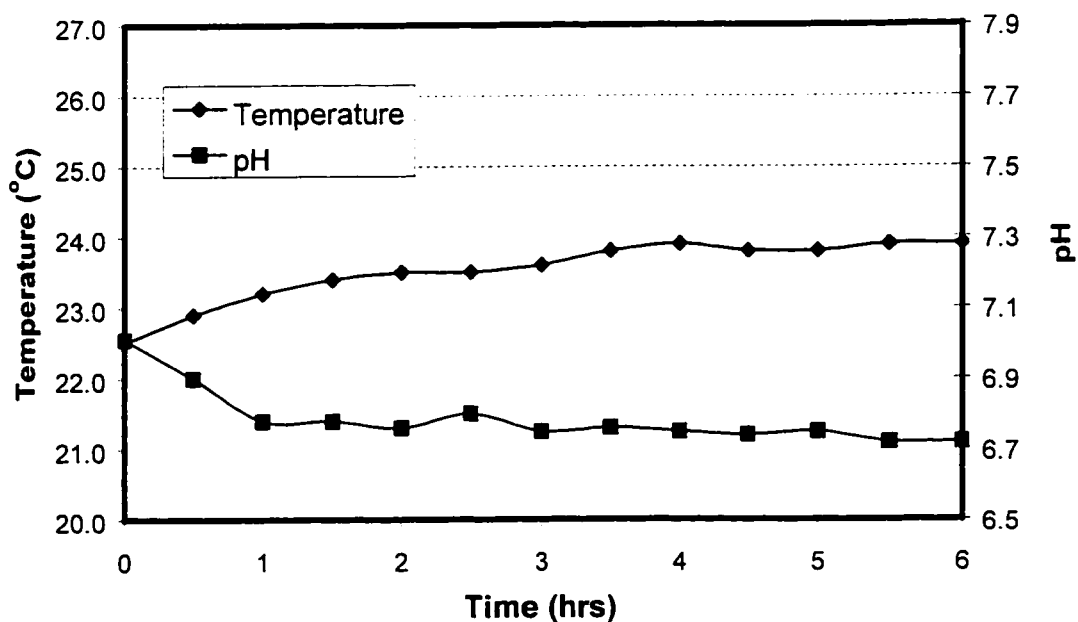
**Figure 4.2** Variations of pH and Temperature in the Supernatant of the ABR during a Typical Six – Hour Cycle

Figure 4.1 illustrates the variation of soluble COD concentration in ABR over a 6 hour cycle. It is significant to note that the soluble COD is high during the beginning of the cycle, but drops off rapidly and decreases significantly in four hours. The reduction of 1000 mg/L COD loading is 78.7% at room temperature over 6 hour. The dissolved oxygen (DO) concentration inside reactor was monitored by a DO meter during the testing period in order to confirm the anaerobic condition inside, the values of dissolved oxygen inside reactor were in the range of 0 to 0.1 mg/L which is an anaerobic environment.

The COD concentration of the feed solution was changed from 1000 mg/L to 10,000 mg/L, and was used to acclimate the sludge in anaerobic batch reactor during the next 7 days at room temperature. After 7 days, the COD reduction was tested at room temperature over 6 hour. At the same time, the pH values and temperature were monitored. Those results are shown in Figures 4.3 and 4.4.



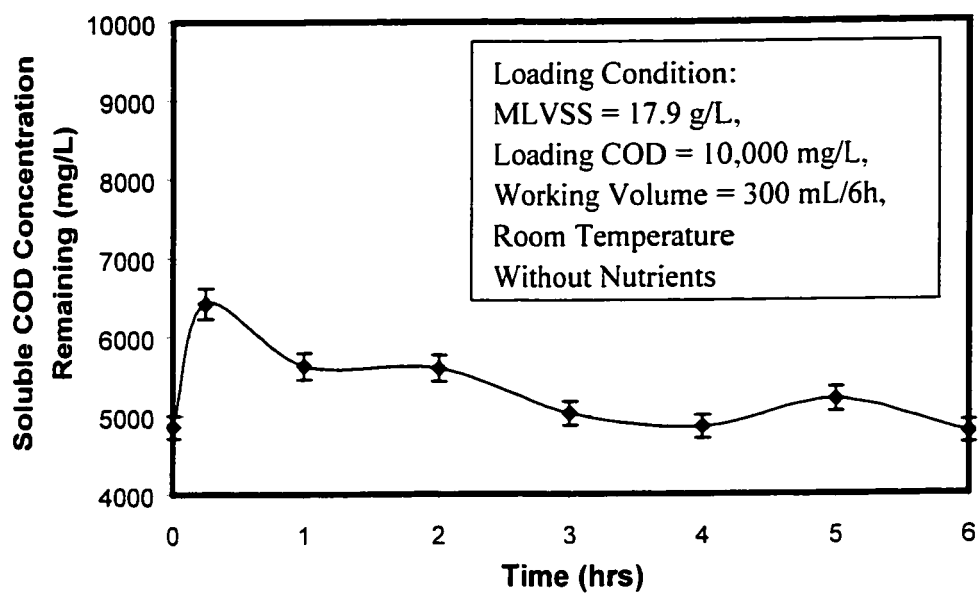
**Figure 4.3** Soluble COD Concentration Remaining in the Supernatant of the ABR during a Typical Six – Hour Cycle



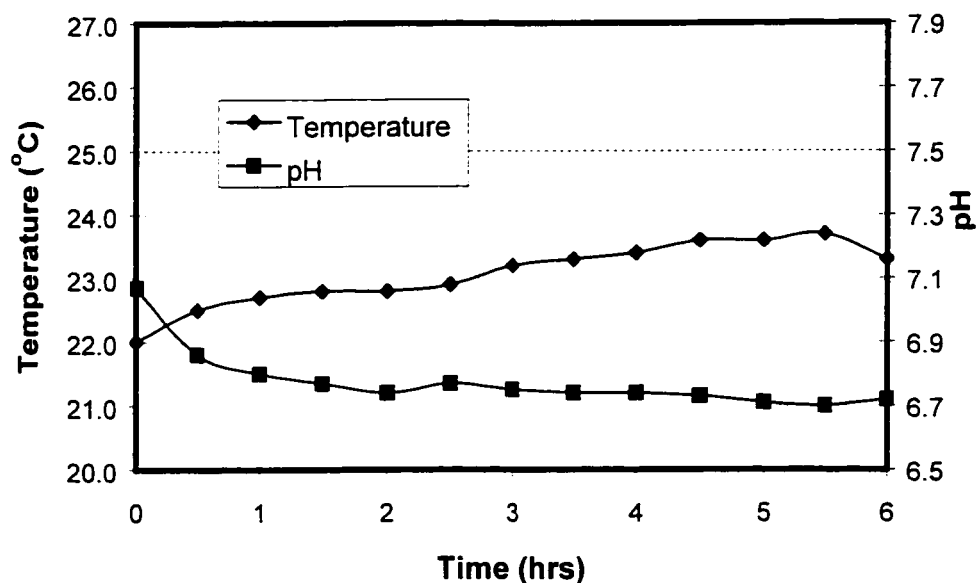
**Figure 4.4** Variations of pH and Temperature in the Supernatant of the ABR during a Typical Six – Hour Cycle

Figure 4.3 illustrates that the variation of soluble COD concentration remaining in the supernatant of the ABR for a loading condition of 10,000 mg/L COD at room temperature over 6 h. It is clear that the soluble COD is high at the beginning of the loading and drops off fast. The COD concentration remaining after 6 h is higher than initial value (time = 0 h), which means 6 h is not enough for one batch reaction under this condition. The reduction of COD in this cycle at room temperature was 42% over 6 h. The results also illustrate there is lower biodegradation ability of the sludge for high organic loadings for the beer solution without nutrients.

According to the above results, a working volume of one batch was decreased from 500 mL to 300 mL, while keeping the same procedure for continuously testing the COD reduction of 10,000 mg/L of beer solution. The results are shown in Figure 4.5. At the same time, the pH values and temperature were monitored, and the results are shown in Figure 4.6.



**Figure 4.5** Soluble COD concentration remaining in the Supernatant of the ABR during a Typical Six – Hour Cycle



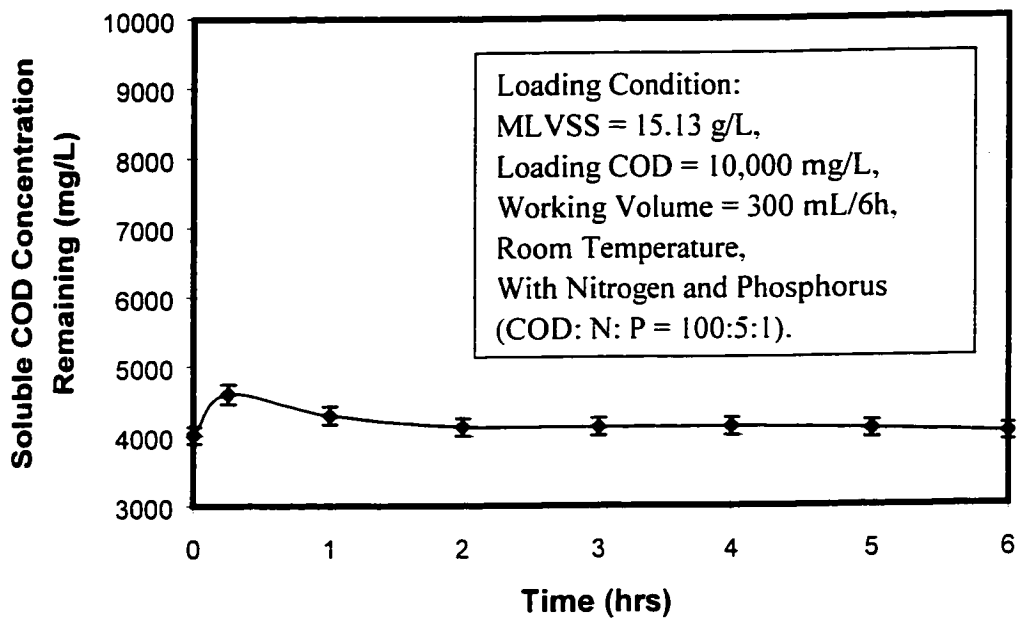
**Figure 4.6** Variations of pH and Temperature in the Supernatant of the ABR during a Typical Six – Hour Cycle



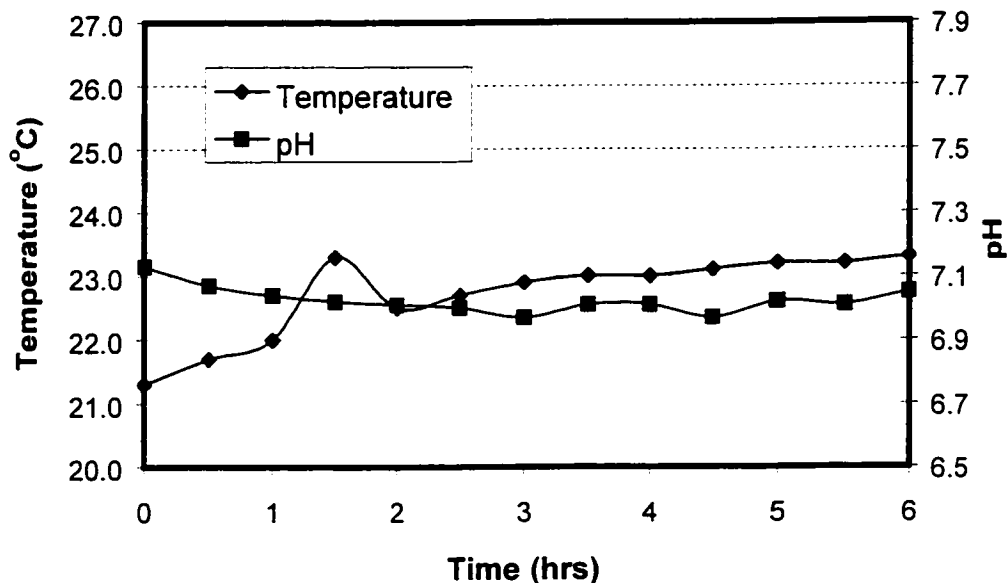
Figure 4.5 illustrates that the COD concentration can be reduced to the initial level after 6 hour. but high COD removal cannot be obtained under a high organic loading condition of beer solution at room temperature even if the working volume is decreased. The reduction of COD in this cycle at room temperature was 52%.

The above results indicate that the organics in the beer cannot be removed efficiently without supplying additional nutrients or trace metals, even though there are nutrients or trace metals already exist in beer. Therefore in the next experiment, some nutrients were added into the feed solution, such as nitrogen and phosphorus, to replenish the lack of nutrients in the beer. Theoretically, the minimum ratio of COD: N: P for a high organic loading is equal to 350:7:1; whereas for a low organic loading, it is 1000:7:1 (Speece, 1996). Therefore, in the next study, the ratio of COD: N: P of 100: 5: 1 would be used, which was same as condition #3 mentioned in section 4.1.

The concentrations of nutrients used in this step were:  $(\text{NH}_4)_2\text{CO}_3$ , 0.312 g/L;  $(\text{NH}_4)_2\text{HPO}_4$ , 0.0426 g/L. The organic loading level of 10,000 mg/L COD with nutrients was used to test the reduction of COD. The testing procedure was the same with before and results are shown in Figures 4.7 and 4.8.

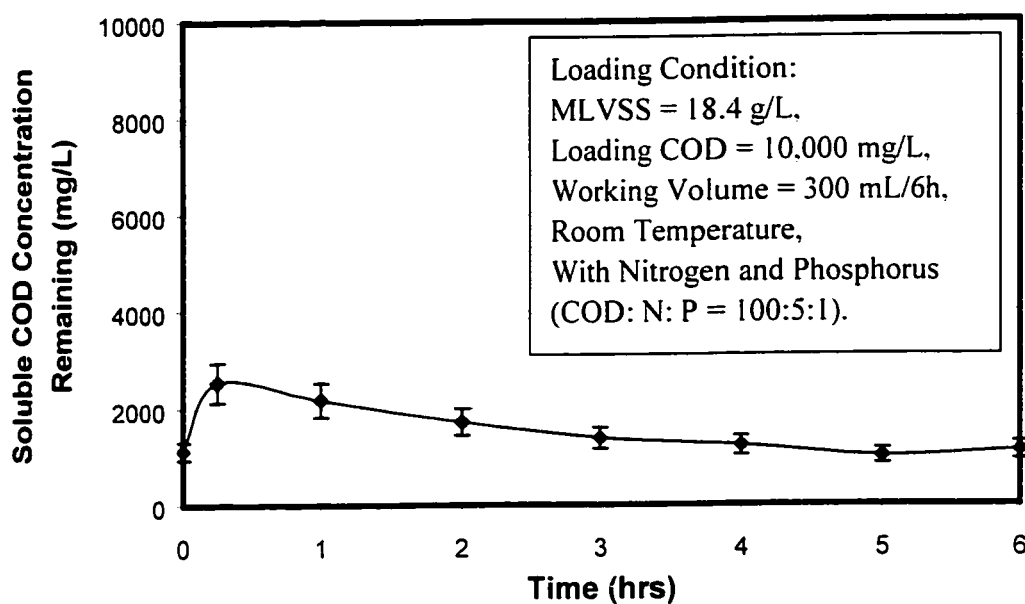


**Figure 4.7** Soluble COD Concentration Remaining in the Supernatant of the ABR during a Typical Six – Hour Cycle

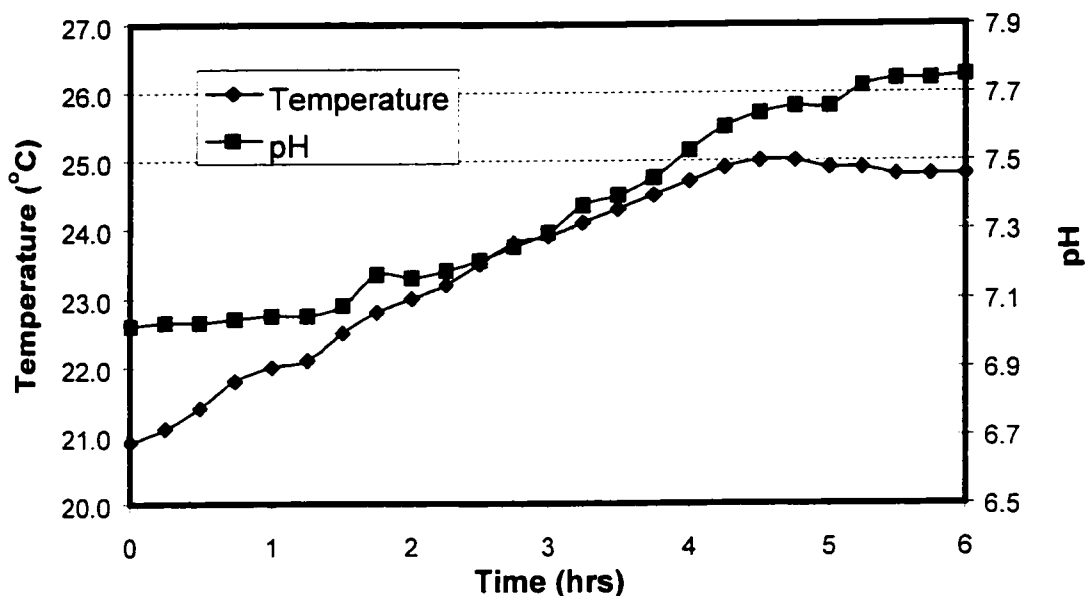


**Figure 4.8** Variations of pH and Temperature in the Supernatant of the ABR during a Typical Six – Hour Cycle

Figure 4.7 illustrates the COD reduction over 6h for a 10,000 mg/L COD loading of beer solution with nutrients and a sludge concentration of 15.13 g/L MLVSS at room temperature. In this step, the COD could be reduced to the initial level after 6 h. Comparison of the COD reduction in Figures 4.7 and 4.5 significantly indicates that the importance of nutrients on the biodegradation under anaerobic condition. But the total soluble COD reduction was only 59.8%, which was still not the desired COD removal efficiency. Therefore, the inoculated amount of sludge was increased and COD reduction was tested again. The results are shown in Figure 4.9. At the same time, the pH and temperature were also monitored over 6 h and the results are shown in Figure 4.10.



**Figure 4.9** Soluble COD Concentration Remaining in the Supernatant of the ABR during a Typical Six – Hour Cycle



**Figure 4.10** Variations of pH and Temperature in the Supernatant of the ABR during a Typical Six – Hour Cycle

Figure 4.9 illustrates that the COD reduction for 10,000 mg/L COD loading of beer solution with nutrients over 6 hour at room temperature. It is significant to note that the COD reduction of 88% was obtained. Comparison of Figure 4.9 and Figure 4.7 shows that the COD reduction in Figure 4.9 is higher than that in Figure 4.7, which proves the importance of the amount of the sludge in anaerobic treatment in the reduction of COD.

In addition, according to the results in Figure 4.9, the higher COD reduction at the loading of 10,000 mg/L COD was obtained under a sludge concentration of MLVSS = 18.4 g/L, but the volume of that amount sludge was close to 2/3 of the total volume of 2L, which was observed too much and may cause a large amount of sludge washout with the

effluent in subsequent experiments. At the same time, since the organic loading rate was gradually increased from 1000 mg/L COD to 10,000 mg/L COD in the next experiment, and the sludge amount would also increase with time during the testing period, the inoculated amount of sludge in the reactors of subsequent experiments, the ASBR and UASB reactors, would be chosen lower than the 18.4 g/L MLVSS.

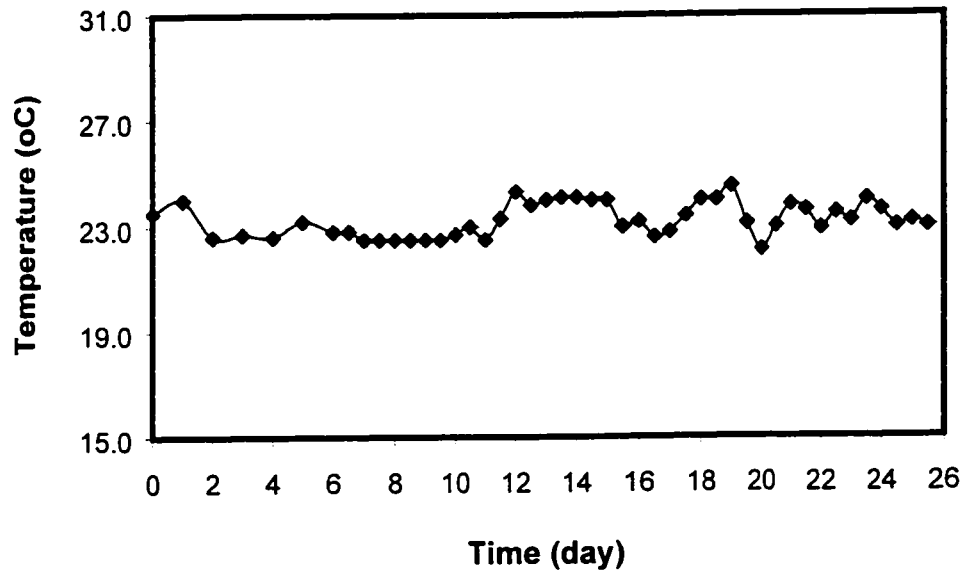
## ***CHAPTER 5***

### **RESULTS AND DISCUSSION**

This study focuses on the anaerobic bio-treatability of wash wastewater from returned beer bottles at two temperatures – room temperature and 35°C. The wastewater from washing returned beer bottles is called beer wastewater in the following sections. All experiments were performed at different organic loading rates basis. The following results from both bioreactors will be presented – COD reduction, methane production, the concentration of volatile fatty acids (VFA) in the effluent, and the concentration of volatile suspended solid (VSS) in the effluent. At the same time, the pH values and temperatures for both bioreactors were monitored during the testing period.

#### **5.1 Anaerobic Bio-treatability of Beer Wastewater at Room Temperature**

The first group experiment had been running at room temperature for 25 days. During this period, the variation of temperature is shown in Figure 5.1.

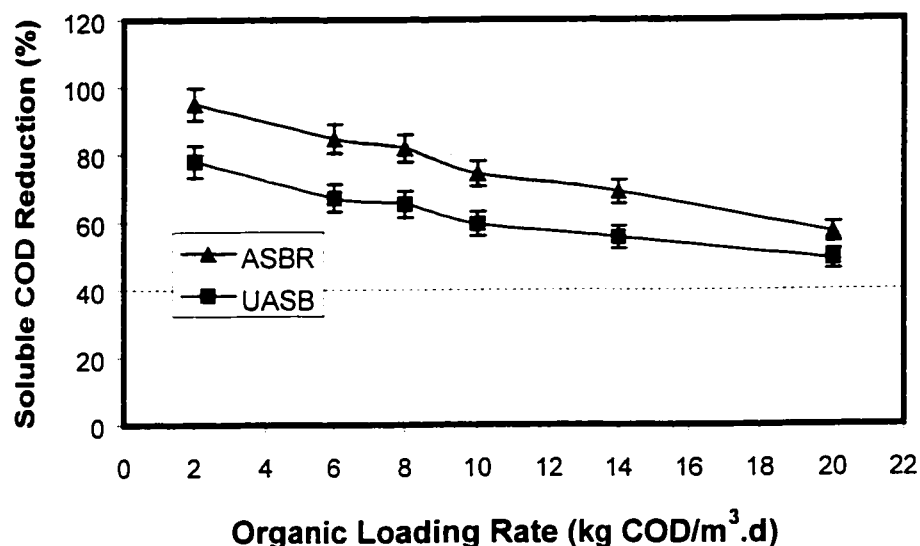


**Figure 5.1** Variation of Temperature during the First Group Experiment

Figure 5.1 shows that the variation of room temperature within this test group was smooth and small and in the range of 22.1°C to 24.1°C, this variation would not significantly affect the results of the experiment.

### 5.1.1 COD Reduction

The organic removal in both reactors, the ASBR and UASB reactors, was based on the soluble COD removal within the first group of experiments; the maximum COD loading rate in both reactors was 20 kg/m<sup>3</sup>.d; whereas, the minimum COD loading rate was 2 kg/m<sup>3</sup>.d; and the influent that was fed into both reactors came from one container for which all feed conditions were maintained consistent in two reactors. The soluble COD removal efficiencies at all loading rates are graphically shown in Figure 5.2.



**Figure 5.2** Soluble COD Removal Efficiency as a Function of OLR in the ASBR and UASB Reactors at Room Temperature

As illustrated in Figure 5.2, at room temperature, soluble COD removals in ASBR were in excess of 90% at low – strength organic loading rates ( $OLR < 4 \text{ kg/m}^3\text{.d}$ ), were between 90% - 80% at moderate strength organic loading rates ( $4 \text{ kg/m}^3\text{.d} < OLR < 8 \text{ kg/m}^3\text{.d}$ ), were lower than 80% at high – strength organic loading rates ( $OLR > 8 \text{ kg/m}^3\text{.d}$ ). Based on the above results, the ASBR performed somewhat more poorly at high – strength organic loading rates at room temperature, that means the ability of sludge for removing COD was poor even if it was acclimated for 3 months before inoculating into both reactors. However, the sludge still could high effectively treat low and moderate strength beer wastewater ( $OLR \leq 8 \text{ kg/m}^3\text{.d}$ ) in the ASBR after 3 months acclimation, and the effluent also could be directly discharged into the surface water



bodies for low-strength loadings ( $OLR \leq 3 \text{ kg/m}^3\cdot\text{d}$ ) and into the municipal sewer systems for moderate strength loadings ( $3 \text{ kg/m}^3\cdot\text{d} < OLR \leq 8 \text{ kg/m}^3\cdot\text{d}$ ), which satisfied the discharge standards. The effluent standard of the brewery for direct discharge to the surface water bodies is  $COD \leq 250 \text{ mg/L}$  (World Bank Group, 1998), and the effluent standard for direct discharge to a sanitary sewer or combined sewer systems is  $COD \leq 1000 \text{ mg/L}$  (Municipal Services – Model Sewer Discharge Bylaw, May 8, 2001).

On the other hand, during the literature review, some papers showed that the UASB reactors were operated with a recirculation system (Angenent *et al.*, 1995, El-Mamouni, *et al.*, 1992, Hickey *et al.*, 1991), and others without a recirculation system (Goodwin *et al.*, 1994, Goodwin *et al.*, 2001). The recirculation system within the UASB operating system not only dilutes high – strength organic loading and inhibitory toxicants in order to achieve high removal rates of organic concentrations but also increases the upflow velocity of the UASB reactor so as to adequately mix the biomass with the feed wastewater to achieve highly efficient contacting and removal of organics.

In addition, there is no definite conclusion on how many times the recycle flow should be used in the UASB reactor. Different rates of recirculation have been used in various papers (Angenent *et al.*, 1995, El-Mamouni, *et al.*, 1992, Hickey *et al.*, 1991, Goodwin *et al.*, 1994, Goodwin *et al.*, 2001) according to different operating conditions, biodegradation characteristics of biomass, and bio-treatabilities of the substrates. The range of the flow rate of recirculation was from 0 to 10 times the influent. Therefore,

based on the objectives of this study, which were to compare the treatment efficiencies of both reactors for beer wastewater, and at the same time, model the ratio of recirculation to feed in the UASB reactor system, the UASB reactor system was operated without a recirculation system.

Figure 5.2 also illustrates that the results of soluble COD removal efficiency in the UASB reactor without a recirculation system; it was lower at room temperature even for low – strength organic loading rate, and it was lower than that of the ASBR. The soluble COD reduction in the UASB reactor was between 70% - 80% at low – strength organic loadings ( $OLR < 6 \text{ kg/m}^3\cdot\text{d}$ ), was between 60% - 70% at moderate strength organic loadings ( $6 \text{ kg/m}^3\cdot\text{d} < OLR < 10 \text{ kg/m}^3\cdot\text{d}$ ), was lower than 60% at high – strength organic loadings ( $OLR > 10 \text{ kg/m}^3\cdot\text{d}$ ). However, the effluent from the UASB under low – strength loadings ( $OLR < 6 \text{ kg/m}^3\cdot\text{d}$ ) at room temperature also satisfied the discharge standard and can directly discharge into the municipal sewer systems. When the organic loading rate was higher than  $6 \text{ kg/m}^3\cdot\text{d}$  at room temperature, according to the experimental results, the UASB reactor should be run with a recirculation system.

Figure 5.2 also illustrates that soluble COD removal efficiencies in the UASB reactor decreased about 15% compared with that in the ASBR under the same organic loading rate at room temperature. If the soluble COD reduction in UASB reactor is expected to reach that level in the ASBR or more, the UASB system will require a recirculation system.

Following the above discussion of the performance of the UASB reactor system, when the organic loading rate is less than 6 kg/m<sup>3</sup>.d at room temperature, the concentration of COD in effluent from the UASB reactor is less than 1000 mg/L, which satisfies the municipal discharge standard. Therefore, based on the “ Mass Balance” principle, at the point of mixing recycle flow with feed flow, the mass should be balanced. The ratio of recirculation flow rate to feed flow rate can be calculated. The following presents the calculations.

In the UASB reactor, if one assumes that the concentration of COD in the feed is  $C_1$  kg/m<sup>3</sup>, the flow rate of the feed is  $Q_1$  m<sup>3</sup>/d; the concentration of COD in the effluent is  $C_2$  kg/m<sup>3</sup>, the mixture COD concentration of feed and recirculation is  $C_3$  kg/m<sup>3</sup>, the ratio of recirculation to feed is  $X$ , then:

The flow rate of the recirculation  $Q_2$  (m<sup>3</sup>/d) is:

$$Q_2 = X \times Q_1 \quad (5.0)$$

The flow rate of the mixture  $Q_3$  (m<sup>3</sup>/d) is:

$$Q_3 = Q_1 + Q_2 \quad (5.1)$$

Based on the “Mass Balance” principle, at the mixing point of recirculation and feed, the mass should be balanced and the equation is given:

$$Q_1 \times C_1 + Q_2 \times C_2 = Q_3 \times C_3 \quad (5.2)$$

Substituting Eq. 5.0 and 5.1 into Eq. 5.2, the solution is:

$$Q_1 \times C_1 + X \times Q_1 \times C_2 = (Q_1 + X \times Q_1) \times C_3 \quad (5.3)$$

Rewriting Eq. 5.3 gives:

$$C_1 + X \times C_2 = (1 + X) \times C_3$$

$$X = \frac{C_1 - C_3}{C_3 - C_2} \quad (5.4)$$

In this study, at room temperature, if the effluent from the UASB reactor satisfies the municipal discharge standard, namely  $C_2 \leq 1000 \text{ mg/L}$  ( $= 1 \text{ kg/m}^3$ ), the concentration of COD in influent  $C_3$  must be less than  $3000 \text{ mg/L}$  ( $= 3 \text{ kg/m}^3$ ). So the ratio ( $X_1$ ) of recirculation to feed is given by Eq. 5.4:

$$X_1 > \frac{C_1 - 3}{3 - 1} = \frac{C_1 - 3}{2} \quad (5.5)$$

According to Eq. 5.5, the ratio of recirculation to feed can be calculated and the results are listed in Table 5.1.

**Table 5.1** Ratio of Recirculation to Feed at Room Temperature (effluent directly discharges to the municipal sewer systems)

<b>COD Concentration in Feed (kg/m<sup>3</sup>)</b>	<b>Ratio of Recirculation to Feed</b>
<b>4.0</b>	<b>0.5</b>
<b>5.0</b>	<b>1.0</b>
<b>7.0</b>	<b>2.0</b>
<b>10.0</b>	<b>3.5</b>
<b>More than 10.0</b>	<b>&gt; 3.5</b>

If the effluent from UASB reactor satisfies the discharge standard of surface water bodies, namely,  $C_2 \leq 250 \text{ mg/L}$  ( $= 0.25 \text{ kg/m}^3$ ); in this study, at room temperature, the concentration of COD in influent  $C_3$  must be equal to or less than  $1000 \text{ mg/L}$  ( $= 1 \text{ kg/m}^3$ ). Therefore the ratio ( $X_2$ ) of recirculation to feed is given by Eq. 5.4:

$$X_2 \geq \frac{C_1 - 1}{1 - 0.25} = \frac{C_1 - 1}{0.75} = \frac{4(C_1 - 1)}{3} \quad (5.6)$$

Substituting COD concentration data for the feed  $C_1$  into Eq. 5.6, the ratio of recirculation to feed can be calculated and the results are listed in Table 5.2.

**Table 5.2** Ratio of Recirculation to Feed at Room Temperature (effluent directly discharges to the surface water bodies)

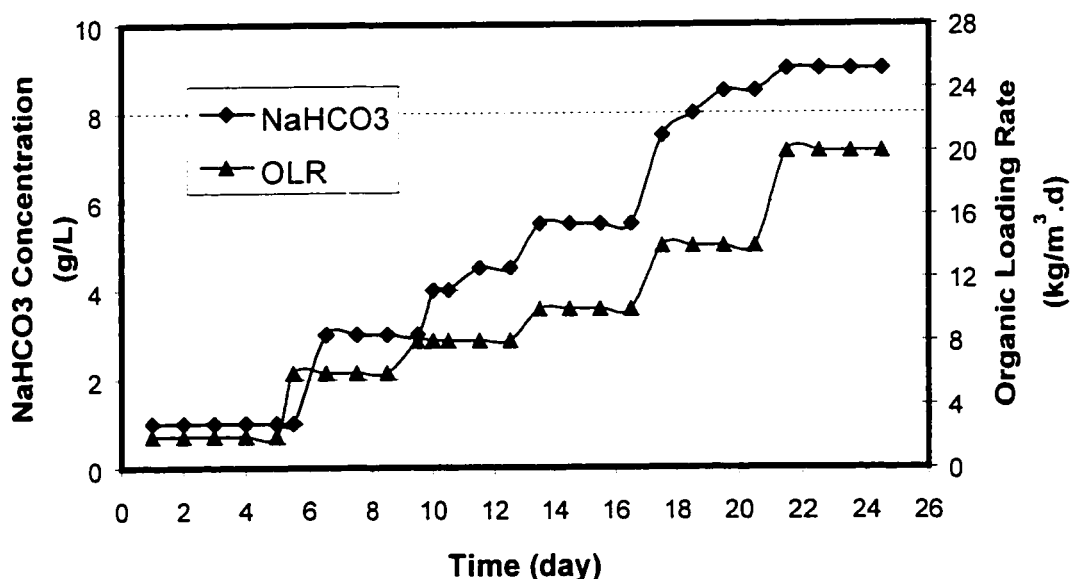
<b>COD Concentration in Feed (kg/m<sup>3</sup>)</b>	<b>Ratio of Recirculation to Feed</b>
2.0	1.3
3.0	2.7
4.0	4.0
5.0	5.3
7.0	8.0
10.0	12.0
More than 10.0	> 12.0

As illustrated in Tables 5.1 and 5.2, the ratio  $X_2$  is much bigger than the ratio  $X_1$ . Therefore, if required to maintain a high quality effluent within an UASB reactor system, a large amount of additional electrical energy will be consumed to maintain the recirculation system, which will greatly increase daily operating costs.

Comparing the ASBR and UASB reactors for the performance of soluble COD reduction, the ASBR is better than the UASB reactor, but was poor in both reactors at high organic loading rates. The soluble COD reductions showed a decreasing trend with an increase in OLR for both reactors.

### 5.1.2 pH Values

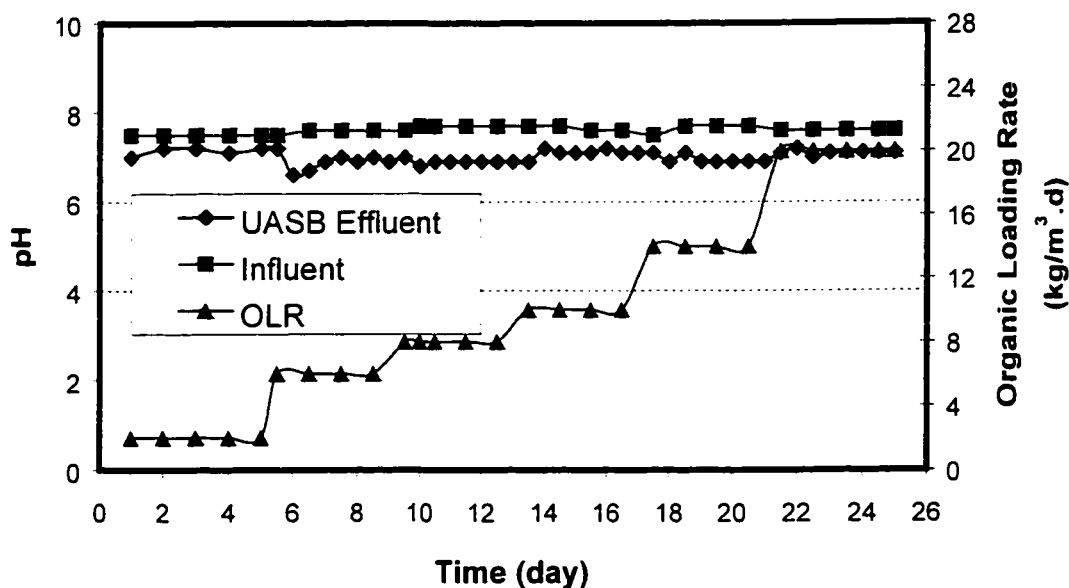
The pH value of undiluted beer used in the study is around 4.5, and diluted samples were also acidic. Addition of nutrients (nitrogen and phosphorus) in diluted samples can increase the pH value to neutral, but still cannot maintain the neutral pH value in the system during the operating period. The pH value is a very important factor for maintaining high COD removal efficiency as was mentioned in sections 1.2 and 4.1 and the literature review. In this study, sodium bicarbonate was used to adjust pH values of reactor to the optimal range of 6.9 to 7.2 for the methanogenic bacteria. As illustrated in Figure 5.3, the amount of sodium bicarbonate added into the feed solution increased with an increase in the organic loading rate in order to keep the pH in the optimal range.



**Figure 5.3** Added Amount of NaHCO<sub>3</sub> during the Operating Period at Room

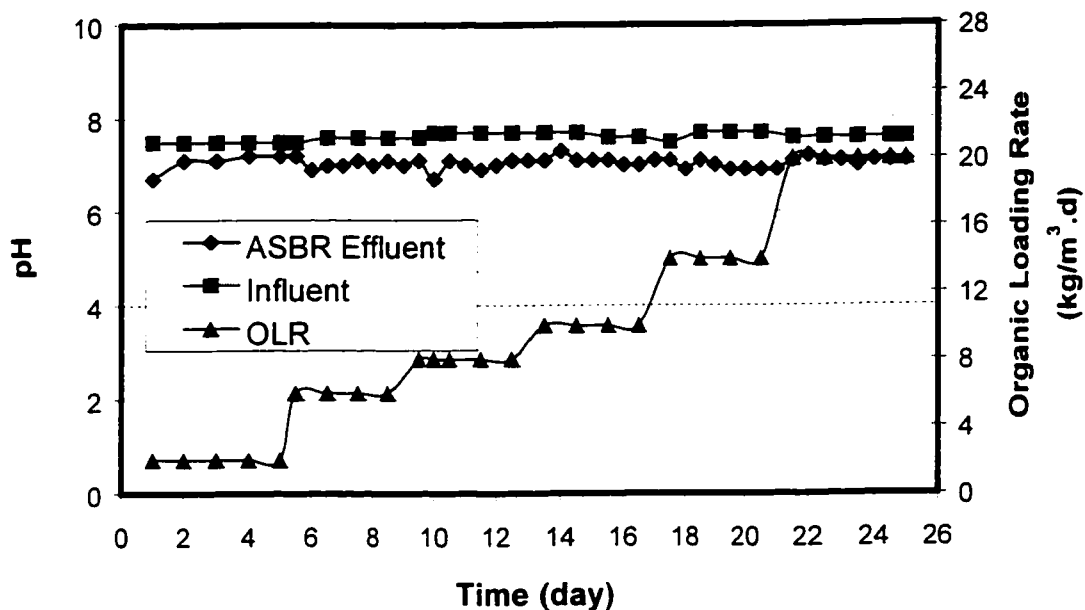
Temperature

Figure 5.3 illustrates that the added amount of  $\text{NaHCO}_3$  is in the range of 0.9 to 1.2 g  $\text{NaHCO}_3/\text{g COD}$  that is close to but less than the theoretical value of 1.2 g  $\text{NaHCO}_3/\text{g COD}$  (Speec, 1996). The pH values in both reactor effluents during the operation period are shown in Figures 5.4 and 5.5, respectively.



**Figure 5.4** Influent and Effluent pH Values and Organic Loading Rates over the Test Period at Room Temperature in the UASB Reactor





**Figure 5.5** Influent and Effluent pH Values and Organic Loading Rates over the Test Period at Room Temperature in the ASBR

Figures 5.4 and 5.5 illustrate that through adjusting the amount of added sodium bicarbonate, the pH value of the influent could be kept in the range of 7.5 to 7.7; at the same time, also could keep the pH values in both reactor effluents in the optimal range of 6.9 to 7.2. Only within short periods, the pH values were out of the optimal range appeared in both reactor effluents, such as day 1 and day 10, the pH in the ASBR effluent was 6.7; day 6, the pH in the UASB effluent was 6.6 – 6.7; day 10, the pH in the UASB effluent was 6.8. But they are still in the range required by methanogenic bacteria that was mentioned in the literature review, and the pH value could be rapidly recovered to the optimal range by adding  $\text{NaHCO}_3$ . Usually, the ability of adjusting the pH value in the ASBR is higher than that in the UASB reactor; the ASBR could adjust the pH value

to the optimal range within one cycle (6 h), but under the same condition, that in the UASB reactors required 6 to 12 hour.

### 5.1.3 Methane Production

Methane production is an important factor in anaerobic treatment that expresses the anaerobic treatment efficiency from another aspect. It is relative with the reduction of COD. At the same time, methane production and COD reduction in anaerobic treatment is also restricted each other. Theoretically, one gram of COD reduction will produce 0.35L of methane at 0°C and 1 atmosphere (Speece, 1996). Therefore, based on the “Ideal Gas Law”, at 1 atmosphere pressure and room temperature (regarded as 23°C), the theoretical methane production will be given as:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \quad (5.7)$$

Where  $V_1$  represents the volume of methane produced at 0°C and 1 atmosphere,  $T_1 = 0^\circ\text{C} = 273\text{ K}$ ,  $V_2$  represents the volume of methane produced at 23°C and 1 atmosphere,  $T_2 = 23^\circ\text{C} = 296\text{ K}$ .

Therefore,

$$V_2 = \frac{V_1 \times T_2}{T_1} = \frac{0.35\text{ L} \times 296\text{ K}}{273\text{ K}} = 0.38\text{ L} \quad (5.8)$$

The measured results of methane production at room temperature are listed in Table 5.3.

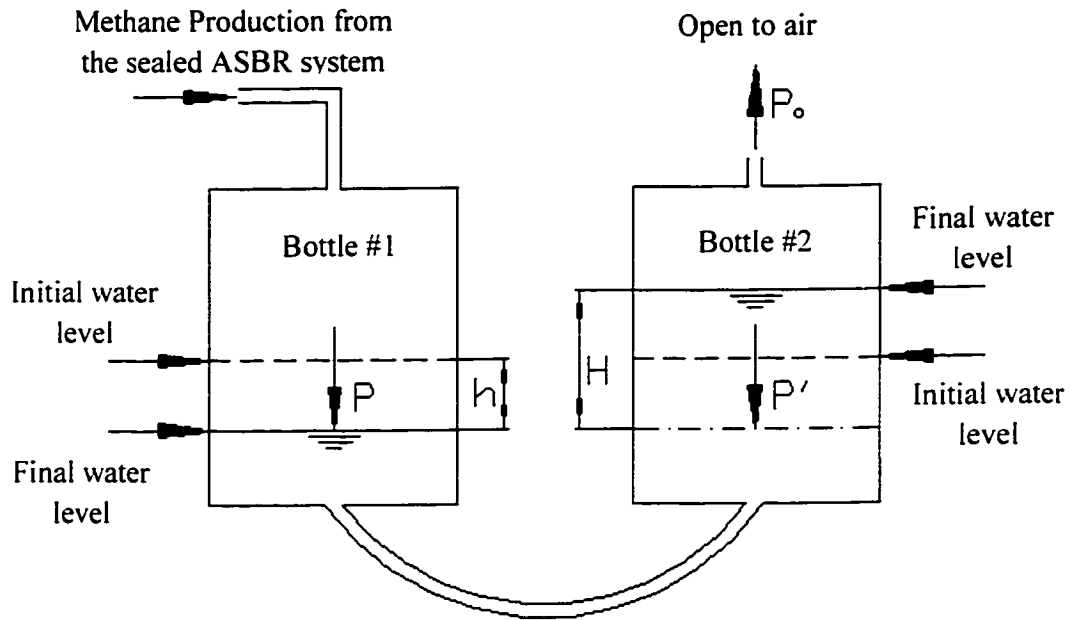
**Table 5.3** Methane Production at Room Temperature in the ASBR

<b>OLR (kg/m<sup>3</sup>.d)</b>	<b>Measured height of Methane Production h (cm/6h)</b>	<b>Measured Volume of Methane Production V<sub>3</sub> (cm<sup>3</sup>/6h)</b>	<b>Temperature when Measured (°C)</b>
2	1.00	105.6	23.0
6	2.48	262.0	23.0
8	2.85	301.1	24.1
10	2.56	270.4	23.4
14	3.31	349.6	23.0
20	3.80	401.4	23.0

The measured volume of methane production  $V_3$  is equal to the measured height of methane production ( $h$ ) in bottle #1 (see Figure 5.6) times the cross – sectional area of bottle #1 ( $A = 105.63 \text{ cm}^2$ ) and the total volume  $V_4$  of methane production per day is equal to  $V_3$  times 4 (because of 4 sequences per day), namely:

$$V_4 = V_3 \times 4 = h \times A \times 4 = 105.63 \text{ cm}^2 \times h \times 4 (\text{cm}^3 / \text{day}) \quad (5.9)$$

The gas volume changes with temperature and pressure. In order to compare, all results of measured methane production volume must be changed to the same standard, namely, the same temperature and pressure. In the first group, assuming the standard temperature is 23°C, and the standard pressure is 1 atm.



**Figure 5.6** Gas Collection System

Figure 5.6 shows the gas collection system. In this study, the volume of trace gases is ignored because of their small amounts. The produced methane first was accumulated in bottle #1 which pushed its water level down. At the same time, the water level in bottle #2 went up (see Figure 5.6). After one cycle (6 h), the volume of methane production ( $V_3$ ) was measured.

Because,

$$P = P' = P_o + \rho_l gH \quad (5.10)$$

$$H = 2h \quad (5.11)$$

Where  $P$  is the pressure on the final water surface in bottle #1,  $P'$  is the pressure in bottle #2 at the same height with the final water surface in bottle #1 (See Figure 5.6),  $P_o$  is the

atmosphere pressure ( $P_o = 1$  atm at room temperature).  $\rho_t$  is the water density,  $g$  is gravity acceleration,  $H$  is the height difference between the final water surface in bottles #1 and #2,  $h$  is the height difference between the initial water level and final water level in bottle #1 due to methane accumulation inside (See Figure 5.6). Based on the Eq. 5.10 and 5.11, pressure ( $P$ ) can be calculated and is given in Table 5.4.

**Table 5.4** Pressure ( $P$ ) on the Final Water Surface in Bottle #1

<b>OLR (kg/m<sup>3</sup>.d)</b>	<b>Temperature T (°C)</b>	<b>Water Density (<math>\rho_t</math>) (kg/m<sup>3</sup>)</b>	<b>Pressure (P) (10<sup>5</sup> Pa)</b>
2	23.0	997.48	1.0150
6	23.0	997.48	1.0179
8	24.1	997.24	1.0186
10	23.4	997.38	1.0180
14	23.0	997.48	1.0195
20	23.0	997.48	1.0204

Based on the “Ideal Gas Law”, the specific volume of methane production  $V_5$  at  $P_5 = 1$  atm and  $T_5 = 23^\circ\text{C} = 296$  K is given:

$$(2300 + V_5) = (2300 + 4 \times V_3) \times \frac{P}{P_5} \times \frac{T_5}{T} \quad (5.12)$$

Where 2300 mL is the total space volume including the space volume in the ASBR and the space volume upon the initial water surface in bottle #1 as well as the volume of the connecting tube (see Figure 3.1);  $T$  is temperature at the time of testing;  $V_3$  and  $P$  were

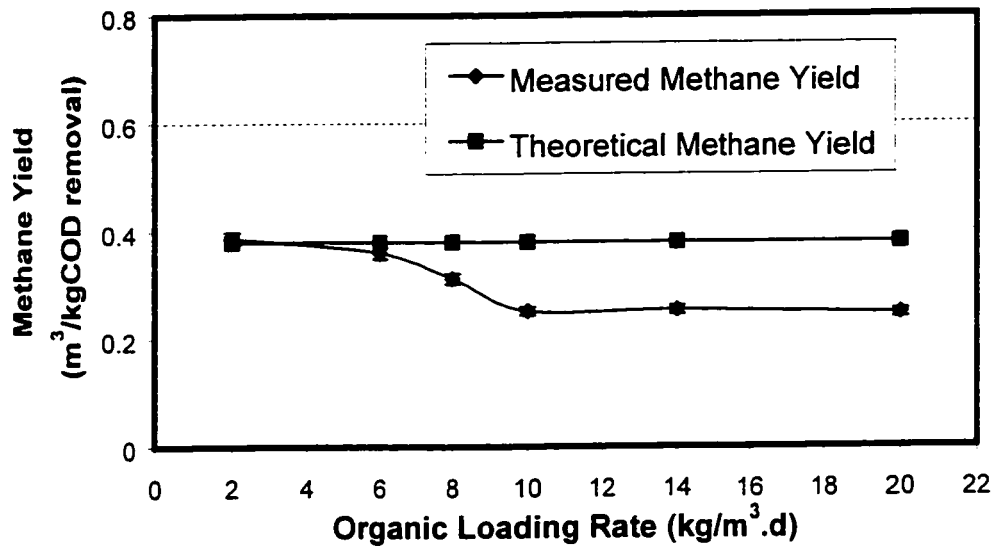
mentioned above. Based on Eq. 5.12, the calculated results of the specific volume of methane production  $V_5$  are listed in Table 5.5

**Table 5.5** Specific Volume of Methane Production ( $V_5$ ) at 1 atm and 23°C in the ASBR

<b>OLR (kg/m<sup>3</sup>.d)</b>	<b>Specific Volume of Methane Production (<math>V_5</math>) (cm<sup>3</sup>/6h)</b>
2	110.3
6	274.2
8	305.7
10	279.6
14	366.6
20	421.2

According to the standardized results shown in Table 5.5, the methane yield can be calculated by the Eq. 5.13. The methane yield curve is plotted as a function of OLR at room temperature and is shown in Figure 5.7.

$$\text{Methane Yield} = \frac{\text{Specific Volume of Methane Production (m}^3 / 6h)}{\text{COD Removal (kg / 6h)}} \quad (5.13)$$



**Figure 5.7** Methane Yield as a Function of OLR in the ASBR at Room Temperature

Figure 5.7 illustrated that the methane yield in the ASBR at room temperature decreases with an increase of OLR, and is close to the theoretical data within the range of OLR of 2 to 6 kg/m³.d; but the methane yield rapidly drops and is going to the lower level after 6 kg/m³.d compared with the theoretical data.

The gas collection system in the UASB reactor failed, so no results of methane production from the UASB reactor are presented in this study. The sludge was acclimated in one bucket for 3 months before inoculating into both reactors, therefore the initial characteristic of the sludge in both reactors was the same. The volume of methane production in the UASB reactor can be theoretically determined based on the ratio of COD reduction in both reactors, namely,

$$\frac{COD\ Reduction\ in\ the\ UASB}{COD\ Reduction\ in\ the\ ASBR} = \frac{Methane\ Production\ in\ the\ UASB}{Methane\ Production\ in\ the\ ASBR} \quad (5.14)$$

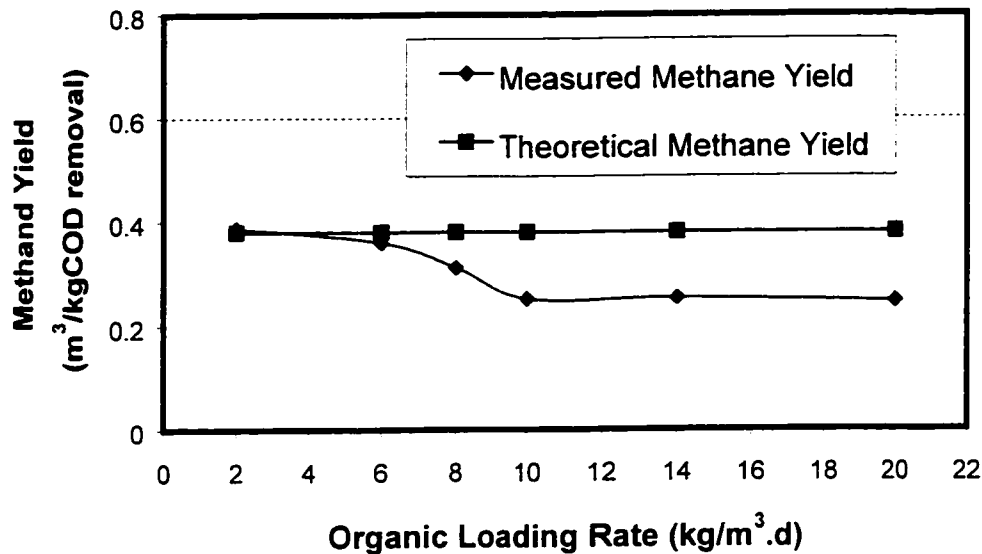
Substituting the results of COD reductions in both reactors and methane production in the ASBR into Eq. 5.14, the specific volume of methane production in the UASB reactor then can be calculated. The results are listed in Table 5.6

**Table 5.6** Specific Volume of Methane Production ( $V_6$ ) at 1atm and 23°C in the UASB Reactor

OLR (kg/m <sup>3</sup> .d)	Specific Volume of Methane Production ( $V_6$ ) (cm <sup>3</sup> /6h)
2	90.54
6	217.58
8	244.02
10	223.94
14	295.07
20	362.11

Based on Table 5.6 and Eq. 5.13, the methane yield in the UASB reactor can be calculated and can plotted its curve as a function of OLR.





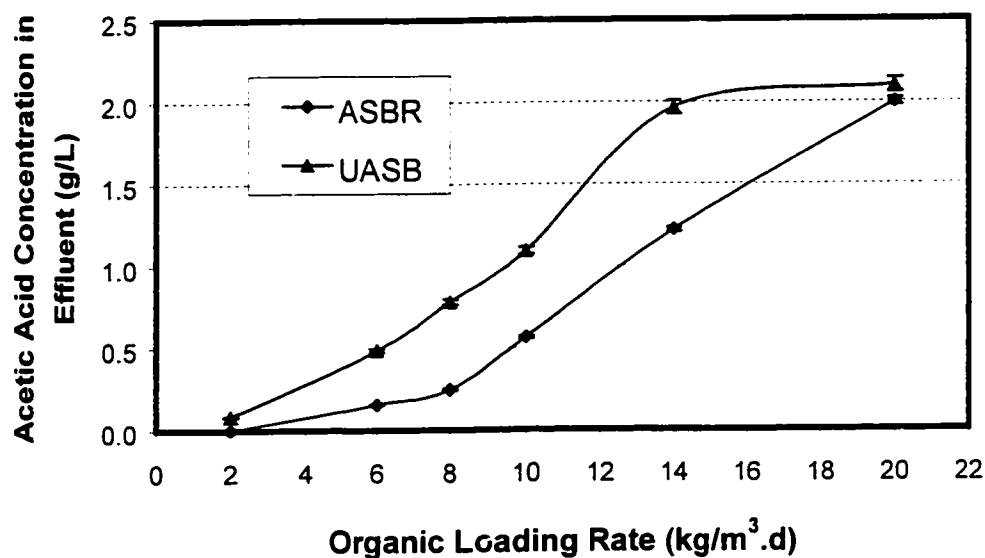
**Figure 5.8** Methane Yield as a Function of OLR in the UASB Reactor at Room Temperature

Figure 5.8 presents a comparison of the calculated methane yield in the UASB system and the theoretical methane yield at 23°C. The comparison of Figure 5.7 and Figure 5.8 shows that methane yields in both reactors are theoretically the same because of the same characteristic of sludge in both reactors. But in practice, the methane yield is also restricted by a number of factors, such as operating mode, feed condition, temperature, etc.

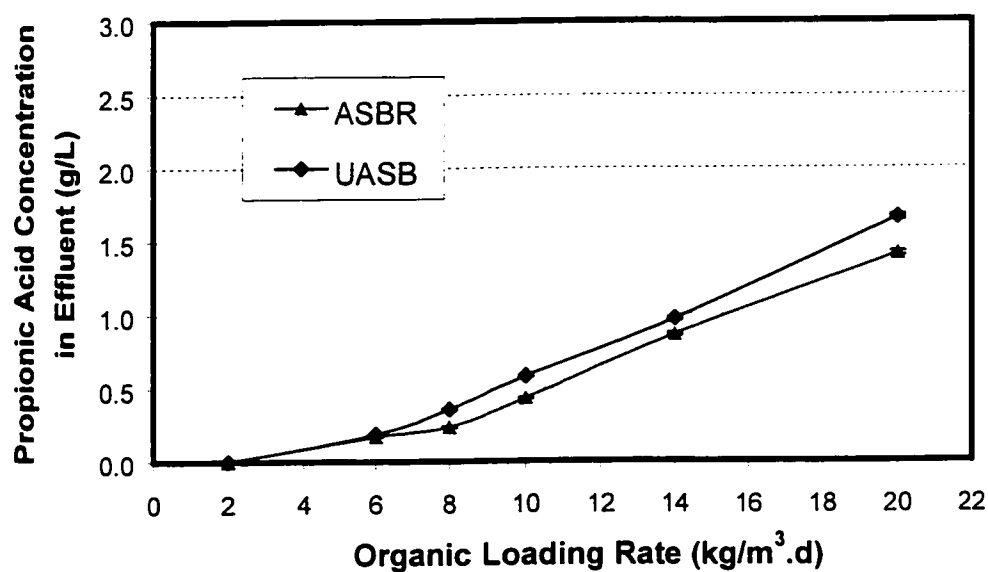
#### 5.1.4 VFA in Effluent

The results were obtained from the VFA concentration assay in the effluent using an HPLC. They were expressed as the concentration of acetic acid, propionic acid, and butyric acid. The measured concentration of butyric acid in the effluent was zero under

all organic loading rates at room temperature. The other two acid concentrations in the effluent at room temperature are shown in Figures 5.9 and 5.10, respectively.



**Figure 5.9** Acetic Acid Concentrations in both Reactor Effluents as a Function of OLR at Room Temperature

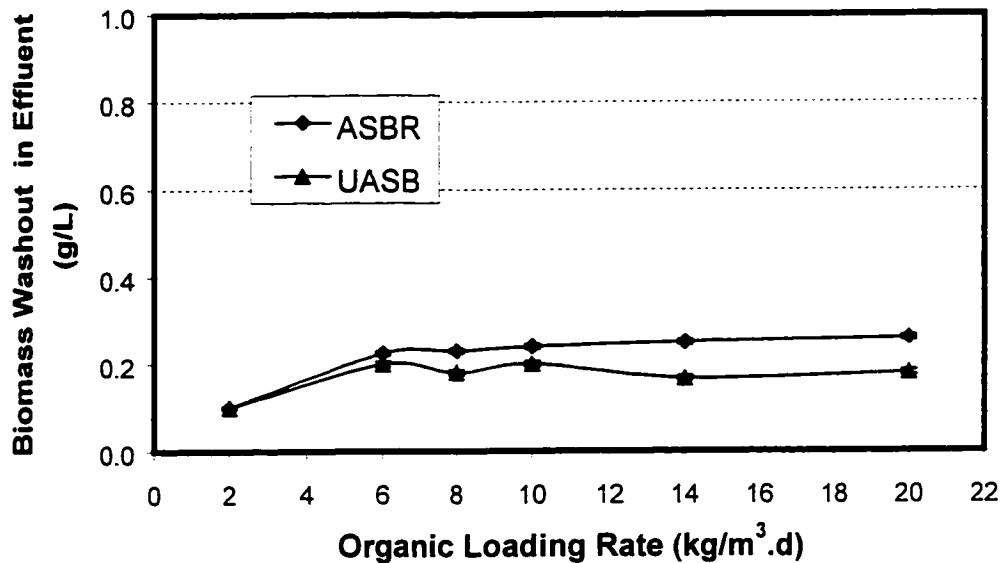


**Figure 5.10** Propionic Acid Concentrations in both Reactor Effluents as a Function of OLR at Room Temperature

Figures 5.9 and 5.10 illustrate that both concentrations of acetic and propionic acids in both reactor effluents increase with an increase of organic loading rate at room temperature. They also illustrate that acetic acid concentration in the UASB reactor effluent are higher than that in the ASBR effluent at all organic loading conditions; the propionic acid concentration in both reactor effluents was close within the range of 2 to 6 kg/m<sup>3</sup>.d of organic loading rates, but is higher in the UASB reactor effluent than that in the ASBR effluent within the range of 6 to 20 kg/m<sup>3</sup>.d.

#### **5.1.5 VSS in Effluent**

Biomass washout in effluent is an important factor for bioreactor operation because it expresses the ability of maintaining the biomass in reactor. The higher ability to maintain biomass means a longer sludge retention time (SRT) and a higher effluent quality. Volatile suspended solid (VSS) is an important parameter to express the quantity of biomass in the effluent. The results of VSS in both reactor effluents were obtained from the volatile suspended solid concentration assay and are shown in Figure 5.11.

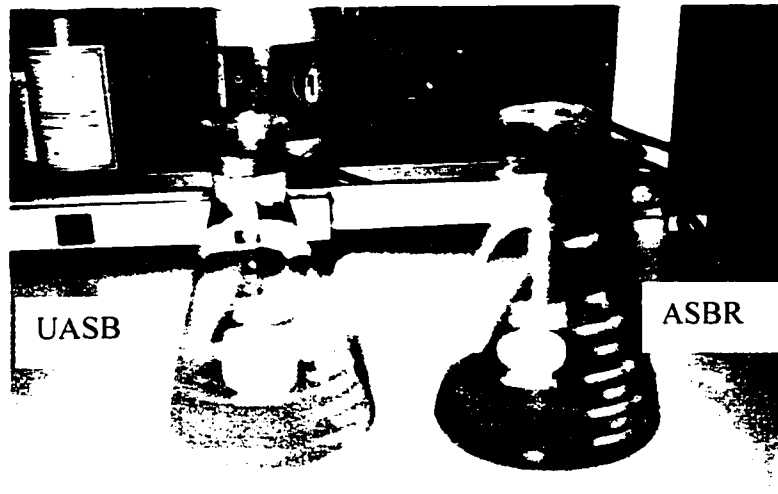


**Figure 5.11** Biomass Washout in both Reactor Effluents as a Function of OLR at Room Temperature

Figure 5.11 shows that the ability to retain biomass inside the UASB reactor is better than that in the ASBR at all organic loading rates except for  $OLR = 2 \text{ kg/m}^3.\text{d}$  at which the volatile suspended solid concentrations in both reactor effluents are almost the same. In this study, the reasons for the above results in Figure 5.11 are:

1. In the ASBR, this study adopted an intermittent mixing procedure, namely, stirring one minute per hour and the intensity for stirring was 4.5, to mix biomass and influent. It is possible that the mixing intensity was too strong which resulted in turbidity in the ASBR effluent.
2. In the UASB reactor, no mechanical mixing was used. The mixing mechanism was accomplished by upflow velocity and bubbles that were produced during the

anaerobic treatment process. Because the upflow velocity in this study was very low, this resulted in the excellent ability to keep biomass inside the UASB reactor.



**Figure 5.12** Comparison of Color in both Reactor Effluents

Figure 5.12 is a picture of both reactor effluents that was taken at  $OLR = 14 \text{ kg/m}^3 \cdot \text{d}$ . It intuitively explains the results that the VSS concentration in the UASB reactor effluent was lower than that in the ASBR effluent. The color in the ASBR effluent is deeper than that in the UASB reactor effluent. However, the ability to maintain biomass in both reactors is better in the first group test.

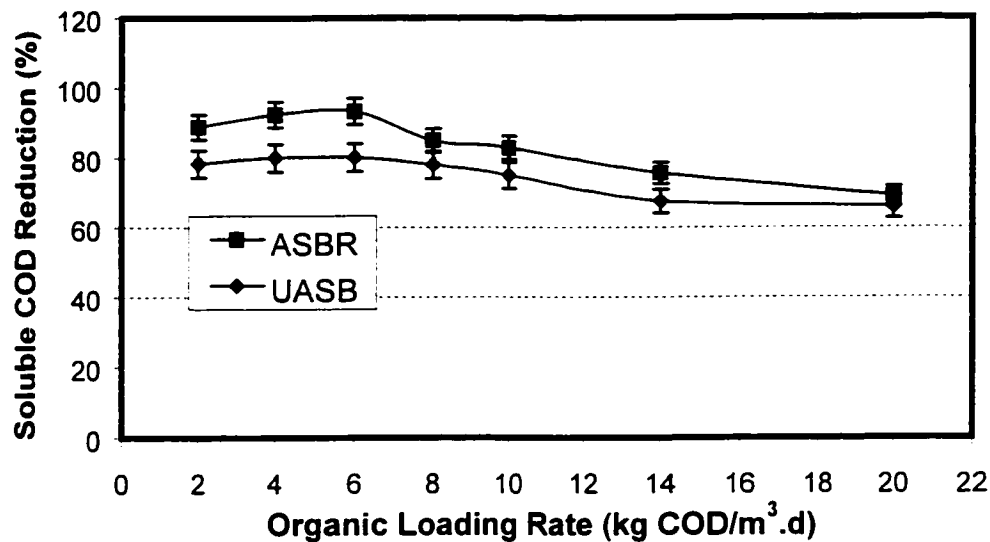
At the end of the first group test, the amount of sludge in both reactors was measured and expressed as MLVSS. The MLVSS in the UASB reactor was  $17.0 \text{ g/L}$  and was  $16.8 \text{ g/L}$  in the ASBR.

## **5.2 Anaerobic Bio-treatability of Beer Wastewater at 35°C**

The second group of experiments was run at 35°C for 29 days in an incubator. During the operating period, the following results would be obtained.

### **5.2.1 COD Reduction**

In the second group of experiments, the performance of organic removal in both reactors, the ASBR and UASB reactors, was also based on the soluble COD reduction: the maximum COD loading rate in both reactors was 20 kg/m<sup>3</sup>.d; whereas the minimum COD loading rate was 2 kg/m<sup>3</sup>.d. The feed procedure in the second group was the same as the first group, namely the influent came from one container so as to maintain a consistent feed condition into the two reactors. The results of soluble COD reduction are shown in Figure 5.13 as a function of the organic loading rate.



**Figure 5.13** Soluble COD Removal Efficiency as a Function of OLR in the ASBR and UASB Reactors at 35°C

Figure 5.13 illustrates that the soluble COD removal efficiencies at 35°C in the ASBR were 88.9% at the lowest strength loading ( $OLR = 2 \text{ kg/m}^3\cdot\text{d}$ ); were greater than 90% at lower to moderate strength organic loadings ( $3 \text{ kg/m}^3\cdot\text{d} < OLR \leq 6 \text{ kg/m}^3\cdot\text{d}$ ); were in the range of 80% to 90% at moderate to higher strength organic loadings ( $6 \text{ kg/m}^3\cdot\text{d} < OLR \leq 10 \text{ kg/m}^3\cdot\text{d}$ ), and were less than 80% at high – strength loadings ( $10 \text{ kg/m}^3\cdot\text{d} < OLR \leq 20 \text{ kg/m}^3\cdot\text{d}$ ). Based on the above description, the performance of the ASBR at 35°C was better at all organic loadings even if the activity of the inoculated sludge was poor; especially, at low and moderate strength loadings, the performance on soluble COD reduction in the ASBR was much better. The quality of the effluent from the ASBR satisfied the direct discharge standard of the surface water systems ( $COD \leq 250 \text{ mg/L}$ ) at low or moderate strength loadings ( $OLR \leq 6 \text{ kg/m}^3\cdot\text{d}$ ) and satisfied the discharge standard

of the municipal sewer systems ( $\text{COD} \leq 1000 \text{ mg/L}$ ) at moderate or high - strength loadings ( $6 \text{ kg/m}^3.\text{d} < \text{OLR} \leq 10 \text{ kg/m}^3.\text{d}$ ).

On the other hand, Figure 5.13 also illustrates that the performance of COD removal efficiencies in the UASB reactor without a recirculation system at  $35^\circ\text{C}$  was better at low to moderate strength organic loadings ( $\text{OLR} \leq 8 \text{ kg/m}^3.\text{d}$ ) with soluble COD reductions of 78% to 80%; and the organic concentration (COD) in the effluent was less than  $1000 \text{ mg/L}$ , which could be directly discharged into the municipal sewer systems; even at the lowest strength organic loading rate ( $\text{OLR} = 2 \text{ kg/m}^3.\text{d}$ ), the effluent organic concentration (COD) was less than  $250 \text{ mg/L}$  that could be directly discharged into the surface water bodies. Its performance at moderate to high strength organic loadings ( $8 \text{ kg/m}^3.\text{d} < \text{OLR} \leq 20 \text{ kg/m}^3.\text{d}$ ) without a recirculation system was poor and soluble COD reduction was lower than 78% with higher effluent concentrations than  $1000 \text{ mg COD /L}$ , which could not be discharged into the municipal sewer system directly. The UASB reactor should be set with a recirculation system at loadings higher than  $8 \text{ kg/m}^3.\text{d}$ .

Based on the above discussion of the performance in the UASB reactor, when  $\text{OLR} \leq 8 \text{ kg/m}^3.\text{d}$ , namely  $\text{COD} \leq 4000 \text{ mg/L}$  ( $= 4 \text{ kg/m}^3$ ) in the feed, the COD concentration in the effluent was less than  $1000 \text{ mg/L}$  ( $= 1 \text{ kg/m}^3$ ). Therefore in the second group, according to Eq. 5.4, the ratio ( $X_3$ ) of recirculation to feed is given:

$$X_3 > \frac{C_1 - 4}{4 - 1} = \frac{C_1 - 4}{3} \quad (5.15)$$



According to Eq. 5.15, the ratio of recirculation to feed can be calculated and listed in Table 5.7.

**Table 5.7** Ratio of Recirculation to Feed at 35°C (effluent directly discharges to the municipal sewer systems)

<b>COD Concentration in Feed (kg/m<sup>3</sup>)</b>	<b>Ratio of Recirculation to Feed</b>
5.0	0.33
7.0	1.0
10.0	2.0
More than 10.0	> 2.0

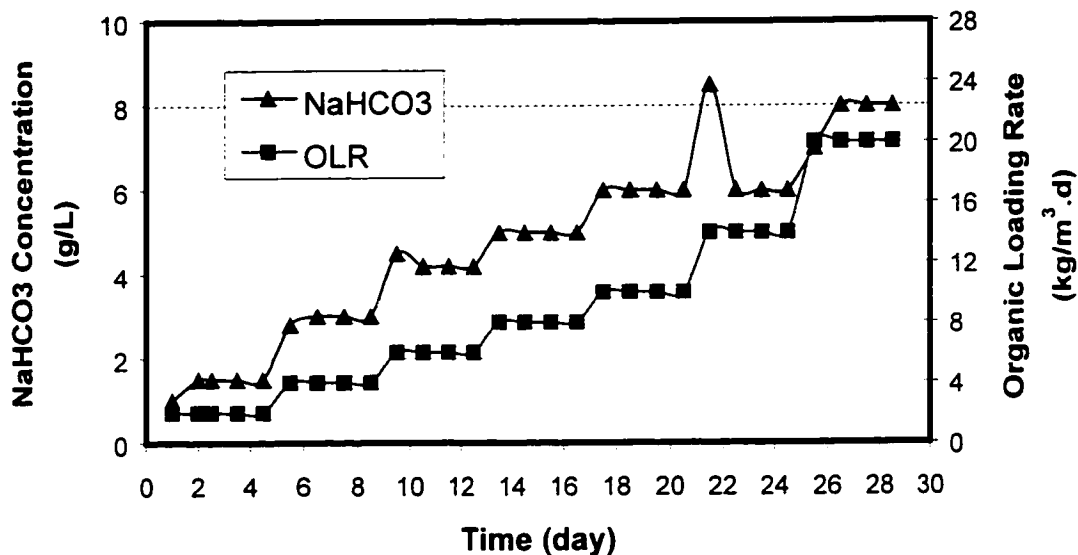
At 35°C, if the effluent in the UASB reactor can be treated to satisfy the direct discharge standard of the surface water bodies, its COD concentration must be equal to or less than 250 mg/L, then its COD concentration in influent must be equal to or less than 1000 mg/L which is the same with that at room temperature. Therefore Table 5.2 also can be used in the UASB reactor in the second group.

Comparison of the ASBR and UASB reactors shows that the performance on soluble COD reduction in the ASBR was better than that in the UASB without a recirculation system. In both reactors, the soluble COD removal efficiencies at moderate and high strength OLR ( $6 \text{ kg/m}^3\cdot\text{d} < \text{OLR} < 20 \text{ kg/m}^3\cdot\text{d}$ ) decreased with an increase of OLR; and increased with an increase of OLR at low and moderate strength OLR (2

$\text{kg/m}^3\cdot\text{d} < \text{OLR} \leq 6 \text{ kg/m}^3\cdot\text{d}$ ). The reason for this phenomenon of soluble COD reduction increasing with an increase of OLR is the sensitivity of methanogenic bacteria to temperature that was mentioned in the literature review. Because the sludge was taken out from two reactors after completing the first group test at room temperature and transferred to the incubator to acclimate at  $35^\circ\text{C}$  for 5 days, and then the sludge was equally separated into two reactors for the second group testing. Through the results of soluble COD reduction obtained from the second group, we can know the sludge was not in the optimal situation at the beginning and was continuously acclimated. Therefore even if the OLR was gradually increased, the soluble COD removal efficiencies still increased. When the OLR increased to a certain level ( $\text{OLR} < 6 \text{ kg/m}^3\cdot\text{d}$ ), due to organic overloading of the sludge, the removal efficiencies began to decrease with the increase of OLR that was confirmed in both reactors.

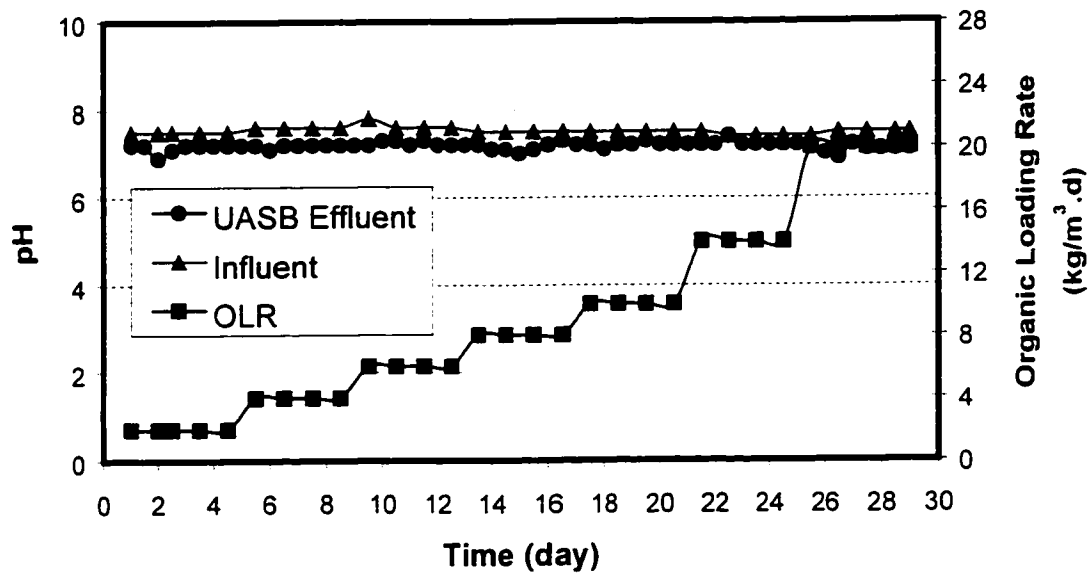
### **5.2.2 pH Values**

In the second group of tests, sodium bicarbonate was used to maintain pH values in both reactor effluents in the optimal range of 6.9 to 7.2. The added amount of  $\text{NaHCO}_3$  into the feed is plotted in Figure 5.14.

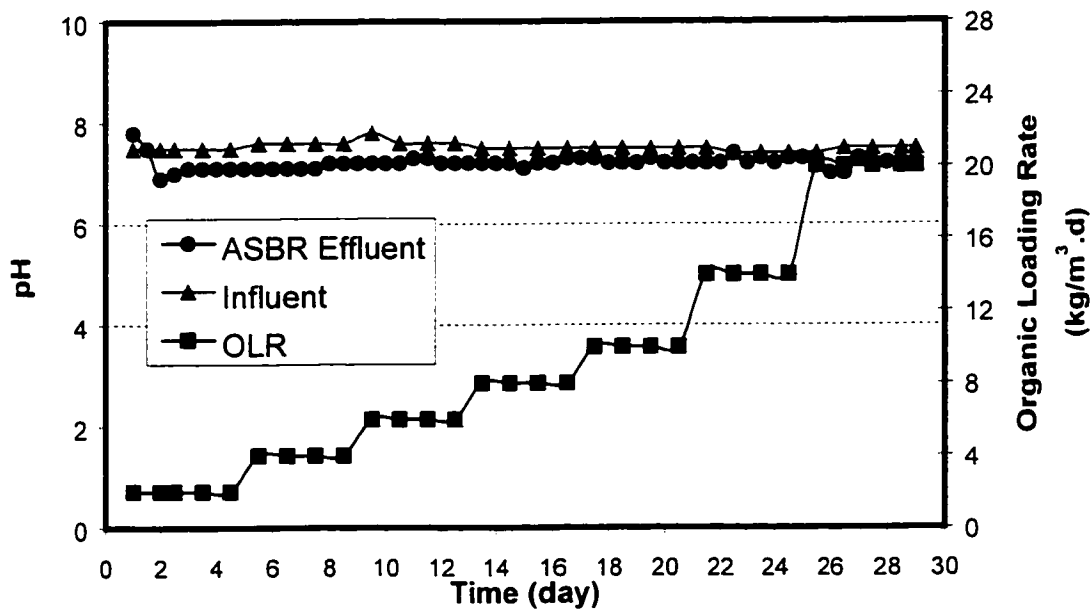


**Figure 5.14** Added Amount of NaHCO<sub>3</sub> during the Operating Period at 35°C

As illustrated in Figure 5.14, generally, the added amount of NaHCO<sub>3</sub> increased with the increase of OLR in the second group of tests. In the first day of the operating at OLR = 14 kg/m<sup>3</sup>.d, the added amount of NaHCO<sub>3</sub> was 8 g/L that resulted in the pH increasing (pH = 7.4) in both reactor effluents in the next day which was out of the optimal range shown in Figures 5.15 and 5.16. Therefore, in the other days of the operating at OLR = 14 kg/m<sup>3</sup>.d, the added amount of NaHCO<sub>3</sub> decreased to 6 g/L and the pH values in both reactor effluents were kept in the optimal range. Figures 5.15 and 5.16 show the pH values in both reactor effluents during the second test group.



**Figure 5.15** Influent and Effluent pH Values and Organic Loading Rates over the Test Period at 35°C in the UASB Reactor



**Figure 5.16** Influent and Effluent pH Values and Organic Loading Rates over the Test Period at 35°C in the ASBR

Figures 5.15 and 5.16 illustrate that the pH in both reactor effluents could be kept within the optimal range of methanogens. Even if both reactor effluents were sometimes out of that range, they still could be rapidly recovered by adjusting the added amount of  $\text{NaHCO}_3$  in both reactors.

### 5.2.3 Methane Production

As mentioned in section 5.1.3, the methane production is related to the reduction of COD. Therefore, based on the “Ideal Gas Law”, at 1 atmosphere pressure and 35°C, the theoretical methane production can be given by Eq. 5.7:

$$\frac{V_1}{V_7} = \frac{T_1}{T_7} \quad (5.16)$$

Where  $V_1$  represents the volume of methane produced at 0°C and 1 atmosphere,  $T_1 = 0^\circ\text{C} = 273 \text{ K}$ ,  $V_7$  represents the volume of methane produced at 35°C and 1 atmosphere.  $T_7 = 35^\circ\text{C} = 308 \text{ K}$ .

Therefore,

$$V_7 = \frac{V_1 \times T_7}{T_1} = \frac{0.35 \text{ L} \times 308 \text{ K}}{273 \text{ K}} = 0.395 \text{ L} \quad (5.17)$$

The measured results of methane production at 35°C are listed in Table 5.8.

**Table 5.8** Methane Production at 35°C in the ASBR

<b>OLR (kg/m<sup>3</sup>.d)</b>	<b>Measured height of Methane Production <math>h_1</math> (cm/6h)</b>	<b>Measured Volume of Methane Production <math>V_8</math> (cm<sup>3</sup>/6h)</b>
2	0.85	89.8
4	1.96	207.0
6	3.00	316.9
8	3.15	332.7
10	3.30	348.6
14	4.10	433.1
20	5.50	581.0

The volume of methane production  $V_8$  per 6 h is equal to  $h_1$  times the cross-sectional area of bottle #1 ( $A = 105.62 \text{ cm}^2$ ) (see Figure 5.6). The total volume of methane production per day ( $V_9$ ) can be calculated by Eq. 5.9:

$$V_9 = V_8 \times 4 \quad (5.18)$$

According to Figure 5.6 and Eqs. 5.10 and 5.11, in the second test group, the pressure on the final water surface in bottle #1 can be calculated and is listed in Table 5.9. The water density at 35°C is 993.95 kg/m<sup>3</sup>.

**Table 5.9** Pressure ( $P_8$ ) on the Final Water Surface in Bottle #1

<b>OLR (<math>\text{kg/m}^3 \cdot \text{d}</math>)</b>	<b>Pressure (<math>P_8</math>) (<math>10^5 \text{ Pa}</math>)</b>
2	1.0147
4	1.0168
6	1.0189
8	1.0191
10	1.0194
14	1.0210
20	1.0237

Based on the “Ideal Gas Law”, the specific volume of methane production ( $V_{10}$ ) at  $P_{10} = 1 \text{ atm}$  and  $35^\circ\text{C}$  is given:

$$(2300 + V_{10}) = (2300 + 4 \times V_8) \times \frac{P_8}{P_{10}} \quad (5.19)$$

Rewriting Eq. 5.19,

$$V_{10} = (2300 + 4 \times V_8) \frac{P_8}{P_{10}} - 2300 \quad (5.20)$$

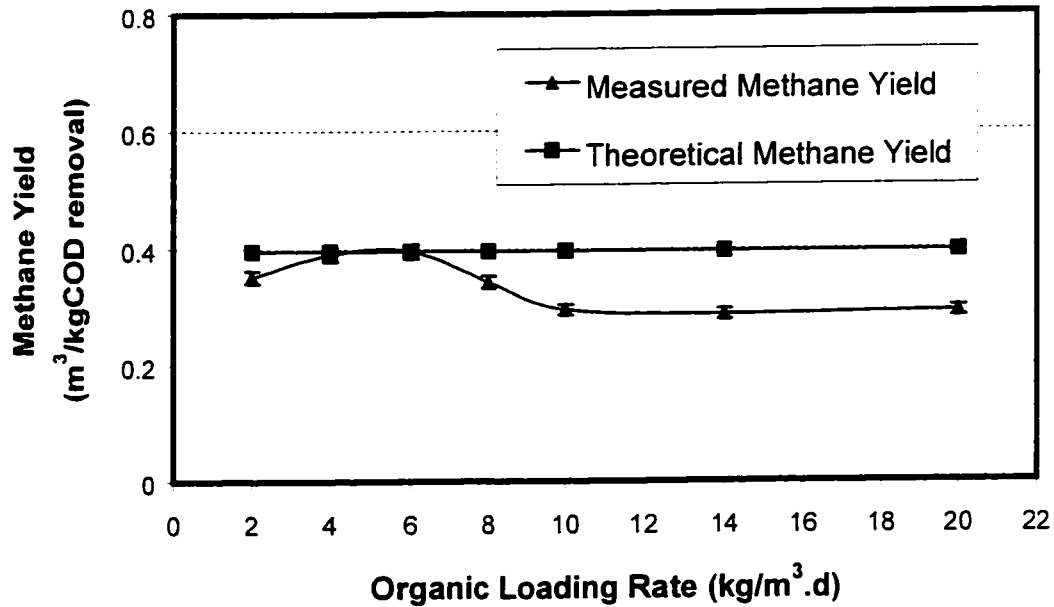
Based on Eq. 5.20, the specific volumes of methane production  $V_{10}$  are calculated and are listed in Table 5.10.

**Table 5.10** Specific Volume of Methane Production ( $V_{10}$ ) at 1atm and 35°C in the ASBR

<b>OLR (kg/m<sup>3</sup>.d)</b>	<b>Specific Volume of Methane Production (<math>V_{10}</math>) (cm<sup>3</sup>/6h)</b>
2	93.7
4	216.5
6	332.0
8	348.7
10	365.4
14	454.7
20	611.5

According to the standardized results shown in Table 5.10, the methane yield can be calculated by Eq. 5.13 and its curve can be plotted as a function of OLR at 35°C.





**Figure 5.17** Methane Yield as a Function of OLR in the ASBR at 35°C

Figure 5.17 illustrates methane yield in the ASBR at 35°C as a function of OLR. in which methane yield increased with an increase in OLR within the range of  $2 \text{ kg/m}^3.\text{d} \leq \text{OLR} \leq 6 \text{ kg/m}^3.\text{d}$ , and decreased with an increase in OLR within the range of  $6 \text{ kg/m}^3.\text{d} < \text{OLR} \leq 20 \text{ kg/m}^3.\text{d}$ . Because of the strong sensitivity of methanogenic bacteria to temperature, at the beginning of the second group test, the methane yield increased with an increase of OLR. This trend is the same with the trend of COD reduction at 35°C that proves again the close relationship between COD reduction and methane yield.

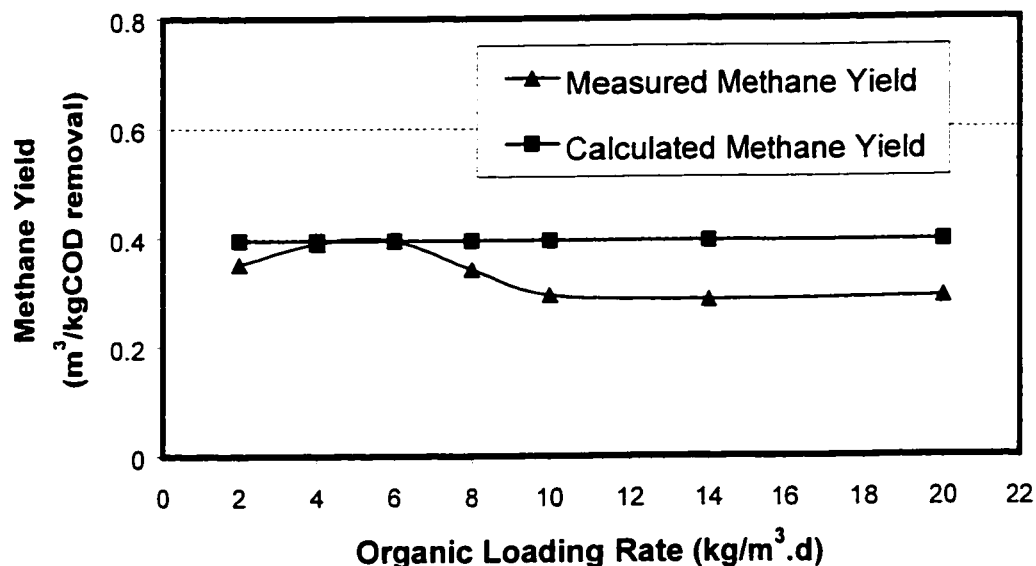
The same calculation method as mentioned in section 5.1.3 can be used to calculate the volume of methane production at 35°C in the UASB reactor. The results are listed in Table 5.11.

**Table 5.11** Specific Volume of Methane Production ( $V_{11}$ ) at 1atm and 35°C in the UASB

Reactor

OLR (kg/m <sup>3</sup> .d)	Specific Volume of Methane Production	
	(V <sub>11</sub> ) (cm <sup>3</sup> /6h)	
2	82.6	
4	187.4	
6	285.1	
8	320.2	
10	330.6	
14	406.5	
20	576.5	

Based on Table 5.11, the methane yield in the UASB reactor can also be calculated by Eq. 5.13 and can be plotted as a function of OLR.

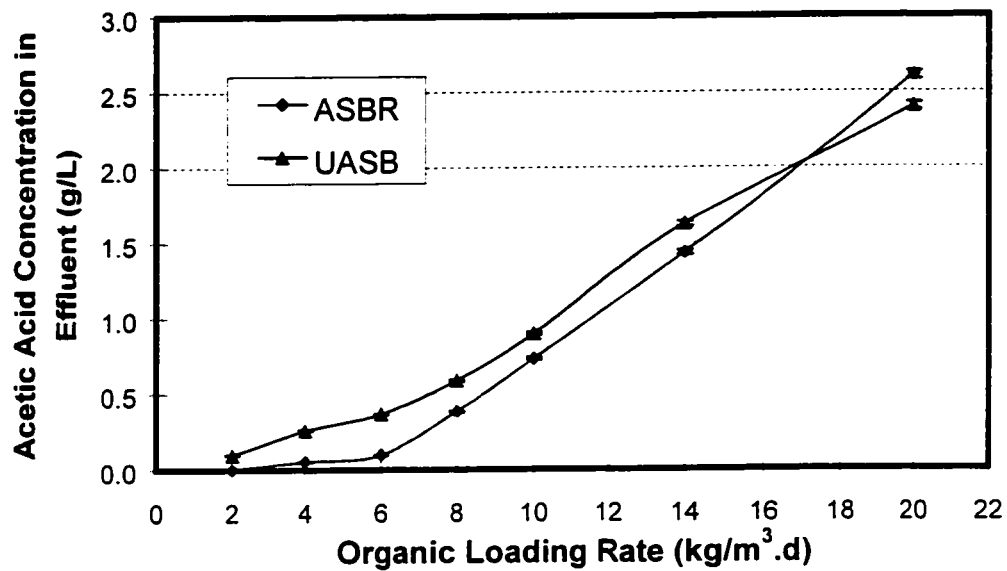


**Figure 5.18** Methane Yield as a Function of OLR in the UASB Reactor at 35°C

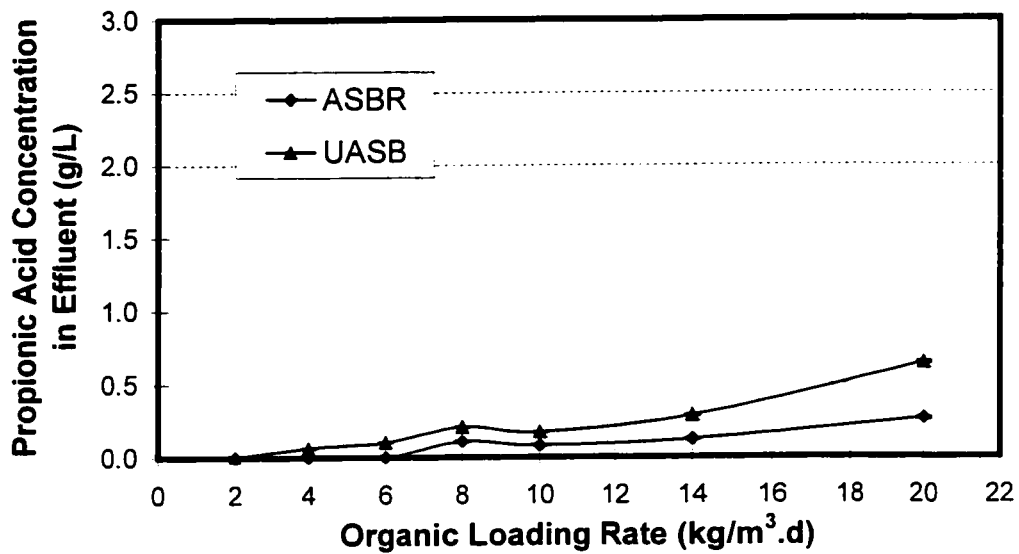
Figure 5.18 presents the results of the comparison of methane yield in the UASB reactor system and the theoretical value of methane yield at 35°C. It also illustrated the same results with that in the ASBR, namely, the methane yields in both reactors are theoretically the same at 35°C.

#### 5.2.4 VFA in Effluent

The results of VFA concentration in the effluent at 35°C were based on the same analysis procedure as room temperature. The VFA also was expressed as the concentrations of acetic acid, propionic acid and butyric acid. The measured concentration of butyric acid in the effluent at 35°C was zero under all organic loading levels in the second test group, and other two types of acids in the effluent are shown in Figures 5.19 and 5.20.



**Figure 5.19** Acetic Acid Concentrations in both Reactor Effluents as a Function of OLR  
at 35°C

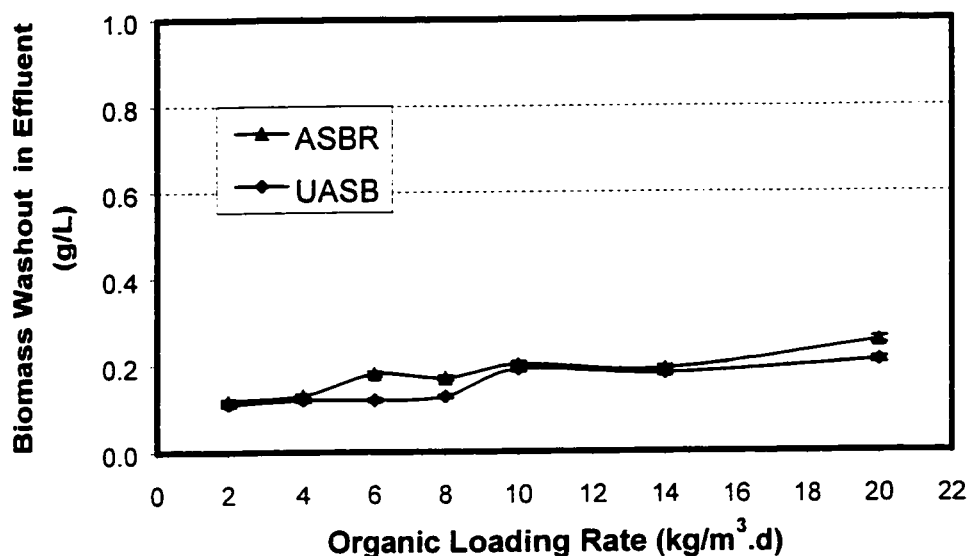


**Figure 5.20** Propionic Acid Concentrations in both Reactor Effluents as a Function of  
OLR at 35°C

Figures 5.19 and 5.20 illustrate that acetic acid and propionic acid concentrations in both reactor effluents gradually increased with an increase of OLR at 35°C. Generally, both acid concentrations in the UASB reactor are higher than that in the ASBR except the acetic acid concentration at  $OLR = 20 \text{ kg/m}^3 \cdot \text{d}$ ; at that point, the acetic acid concentration in the ASBR is higher than that in the UASB reactor. Figures 5.19 and 5.20 also show that both acid concentrations in the ASBR at low and moderate strength loadings ( $OLR \leq 6 \text{ kg/m}^3 \cdot \text{d}$ ) are very low, which means that almost all VFAs were utilized by acetogenic bacteria to produce  $\text{H}_2$ ,  $\text{CO}_2$  and acetate, which then were converted to  $\text{CH}_4$  by methanogenic bacteria, this can be confirmed by Figure 5.17, in which the methane yields under  $OLR \leq 6 \text{ kg/m}^3 \cdot \text{d}$  are close to the theoretical data.

#### **5.2.5 VSS in Effluent**

The results of VSS in both reactor effluents at 35°C were measured and are plotted in Figure 5.21.



**Figure 5.21** Biomass Washout in both Reactor Effluents as a Function of OLR at 35°C

Figure 5.21 shows that the ability to retain biomass inside the UASB reactor is better than that in the ASBR, but both reactors have a high ability to keep biomass within reactors. The VSS in both reactor effluents are from 0.12 to 0.26 g/L in the ASBR and from 0.11 to 0.21 g/L in the UASB. These values are comparable with those obtained during a study characterizing a 19.2L UASB at a 12h HRT and temperature of 34°C (El-Mamouni, 1992), which the VSS concentration in the effluent was between 0.2 to 0.68 g/L in the range of  $4 \text{ kg/m}^3.\text{d} \leq \text{OLR} \leq 20 \text{ kg/m}^3.\text{d}$ .



**Figure 5.22** Comparison of Color in both Reactor Effluents

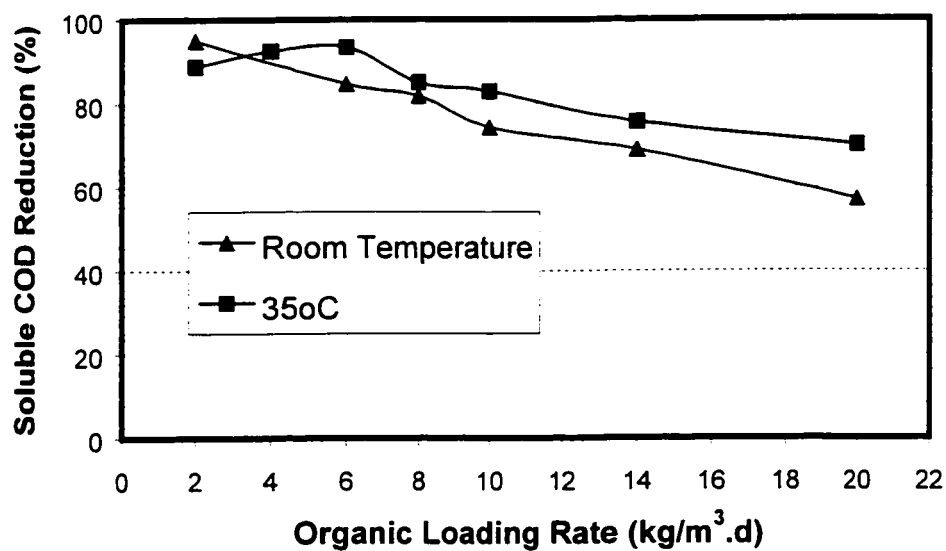
Figure 5.22 is a picture of both reactor effluents that was taken at a OLR of 20  $\text{kg/m}^3\cdot\text{d}$ . The result shown in Figure 5.22 is similar to that shown in Figure 5.12. It also intuitively confirms the analytical result regarding biomass in the UASB reactor is better than that in the ASBR at 35°C.

At the end of second test group, the amount of sludge in both reactors was also measured and expressed as MLVSS. The MLVSS in the UASB reactor was 17.0 g/L and was 16.4 g/L in the ASBR.

### 5.3 Comparison of Anaerobic Bio-treatability of Beer Wastewater between Room Temperature and 35°C

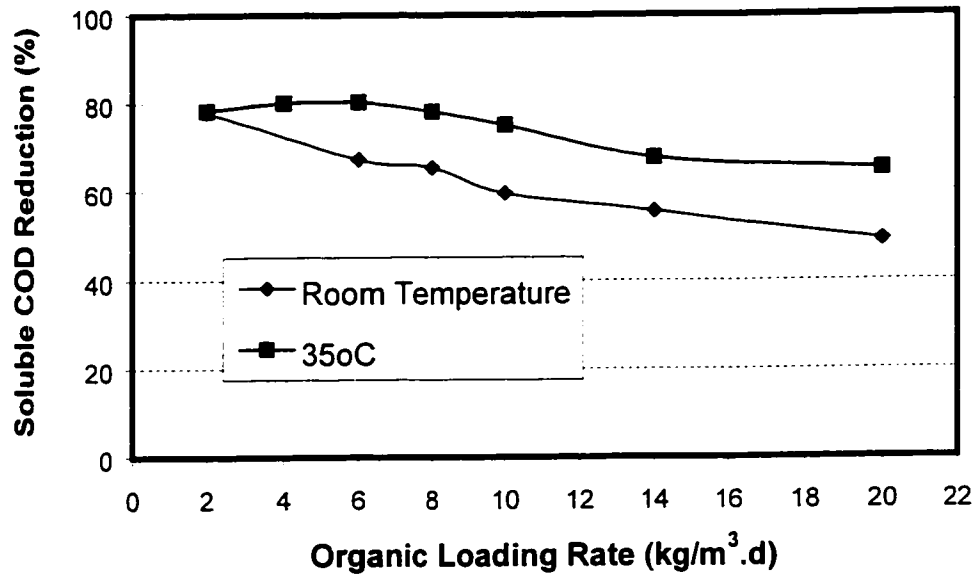
The two group tests were done under the same conditions except for the temperature. Therefore, the results can be compared. In this section, the comparison of all obtained results between room temperature and 35°C will be presented.

#### 5.3.1 COD Reduction



**Figure 5.23** Comparison of Soluble COD Removal Efficiency in the ASBR between Room Temperature and 35°C as a Function of OLR





**Figure 5.24** Comparison of Soluble COD Removal Efficiency in the UASB Reactor between Room Temperature and 35°C as a Function of OLR

The performance in terms of soluble COD removal in both reactors at both temperatures is shown in Figures 5.23 and 5.24, respectively. Comparing the two temperatures, the performance in both reactors at 35°C is much better than that at room temperature, especially in the UASB reactor as illustrated in Figures 5.24. Those results are consistent with the theory, in which the optimal temperature of anaerobic bacteria is 35°C. At this temperature, the efficiency of anaerobic bacteria on COD removal should be better than that at room temperature at all loading levels.

In addition, we also can observe in Figures 5.23 and 5.24 that the soluble COD reduction at a OLR of 2 kg/m³.d at 35°C was lower than that at room temperature in the

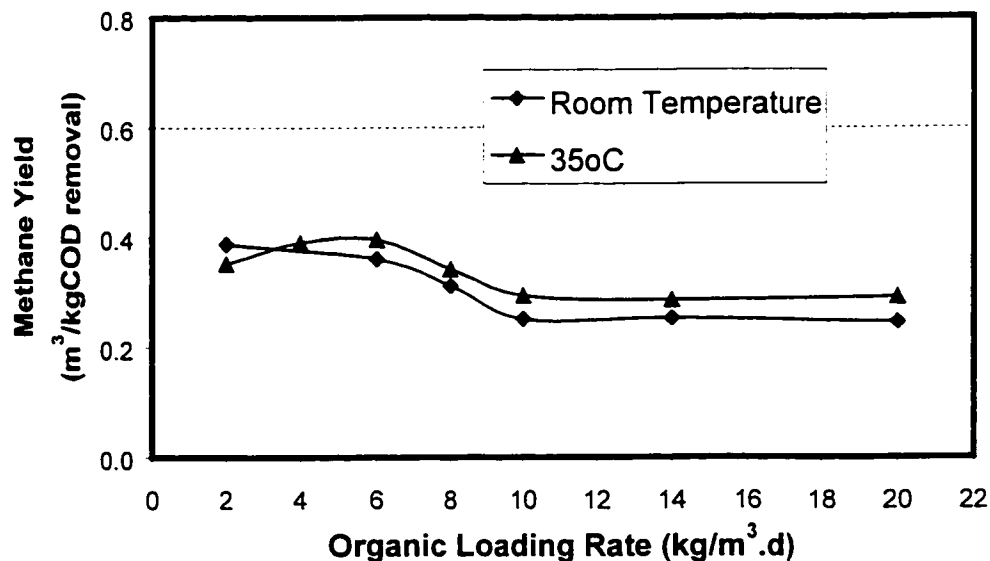
ASBR and there was similar performance at the two temperatures in the UASB reactor (actually the performance at room temperature is appreciably higher than that at 35°C). The sensitivity of methanogenic bacteria to temperature is clearly shown here. In this study, the sludge was acclimated at room temperature before starting the second test group; the sludge had already acclimatized to room temperature. Therefore when they were transferred to 35°C, they would not yet present the optimal treatment characteristic at the beginning. But with time, the characteristics of anaerobic bacteria were gradually developed and showed the increasing removal efficiency of soluble COD with an increase of OLR in both reactors. This increasing trend of soluble COD reduction is shown in those results obtained from both reactors at 35°C under  $2 \text{ kg/m}^3\cdot\text{d} \leq \text{OLR} \leq 6 \text{ kg/m}^3\cdot\text{d}$ , but it did not show the same trend in the results obtained from both reactors at room temperature. After that, when  $6 \text{ kg/m}^3\cdot\text{d} < \text{OLR} \leq 20 \text{ kg/m}^3\cdot\text{d}$ , soluble COD reduction decreased with an increase of OLR. The trends of soluble COD reduction within that range of OLR were the same in both reactors at both temperatures.

### **5.3.2 pH Values**

The pH values in both reactor effluents at both temperatures were all kept in the optimal range of 6.9 to 7.2 by addition of sodium bicarbonate. Even if the pH values were sometimes out of that range, they also could be rapidly adjusted by adding  $\text{NaHCO}_3$ . This was proven in both group tests.

In addition, the amount of  $\text{NaHCO}_3$  added in  $35^\circ\text{C}$  was less than that at room temperature at high levels of OLR (OLR = 14 and  $20 \text{ kg/m}^3.\text{d}$ ). The reason is that the pH value in the feed solution at high loading levels was easy to increase at  $35^\circ\text{C}$  even if the feed solution was changed everyday to keep fresh. It resulted in the increase of pH values in both reactor effluents throughout the day. Therefore the amount of  $\text{NaHCO}_3$  was decreased under high loading levels at  $35^\circ\text{C}$ . The measured results in both reactors at  $35^\circ\text{C}$  proved that the decrease of the amount of  $\text{NaHCO}_3$  at high loading level did not result in a decrease in the pH values in both reactor effluents, but was able to maintain pH values of effluents in the optimal range.

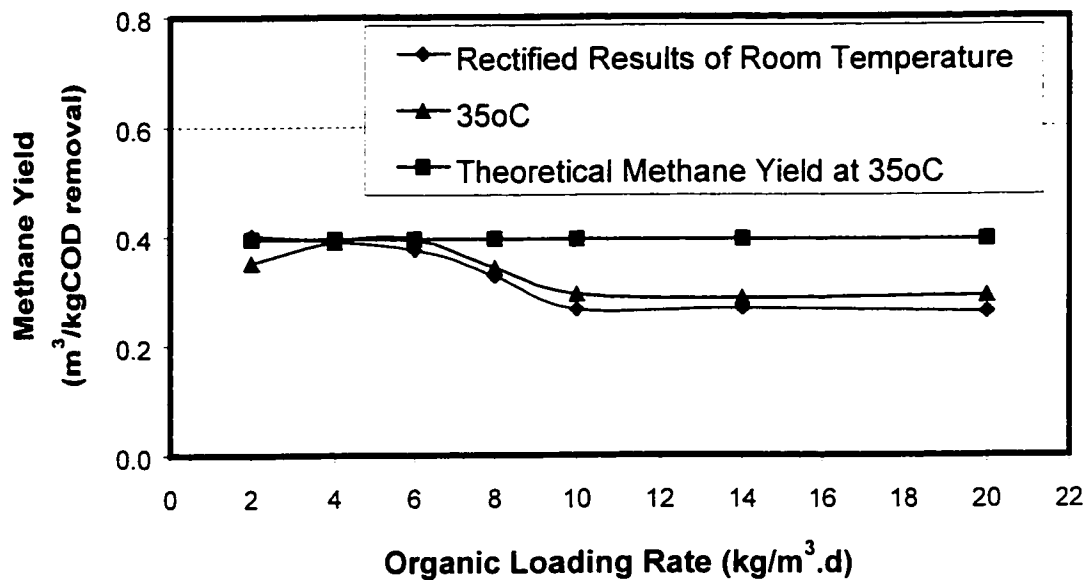
### 5.3.3 Methane Production



**Figure 5.25** Comparison of Methane Yield in the ASBR between Room Temperature and  $35^\circ\text{C}$  as a Function of OLR

Figure 5.25 illustrates the comparison of the performance of methane yield in the ASBR at both temperatures. The performance at 35°C is better than that at room temperature except for the performance at  $OLR = 2 \text{ kg/m}^3.\text{d}$ , at which methane yield at room temperature is better than that at 35°C.

Theoretically, the difference of methane yield between 35°C and room temperature should be  $0.015 \text{ m}^3/\text{kg COD removal}$ . Therefore, using the standard of  $0.015 \text{ m}^3/\text{kg COD removal}$  rectifies methane yield at room temperature.

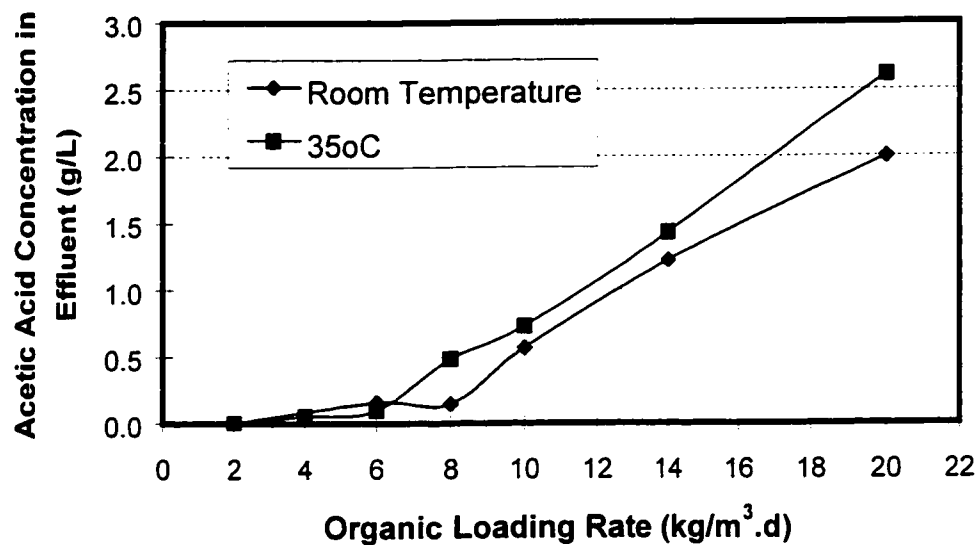


**Figure 5.26** Comparison of Methane Yield in the ASBR between 35°C and the Rectified Results of Room Temperature as a Function of OLR

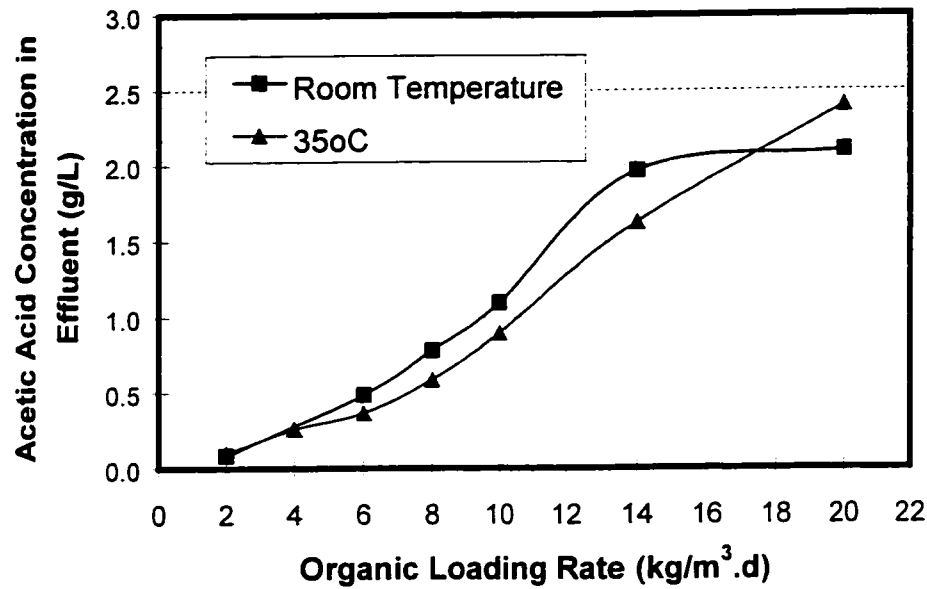
Figure 5.26 illustrates that after adjustment, the methane yield at room temperature was still lower than that in 35°C and shows a similar trend at both

temperatures except for at  $OLR = 2 \text{ kg/m}^3 \cdot \text{d}$ . Within  $2 \text{ kg/m}^3 \cdot \text{d} < OLR \leq 6 \text{ kg/m}^3 \cdot \text{d}$ , the methane yield was close to the theoretical data; within  $6 \text{ kg/m}^3 \cdot \text{d} < OLR \leq 20 \text{ kg/m}^3 \cdot \text{d}$ , the methane yield decreased with an increase in OLR and lower than the theoretical data: at  $OLR = 2 \text{ kg/m}^3 \cdot \text{d}$ , the methane yield at room temperature was higher than that at  $35^\circ\text{C}$  because of the sensitivity of methanogenic bacteria.

#### 5.3.4 VFA in Effluent



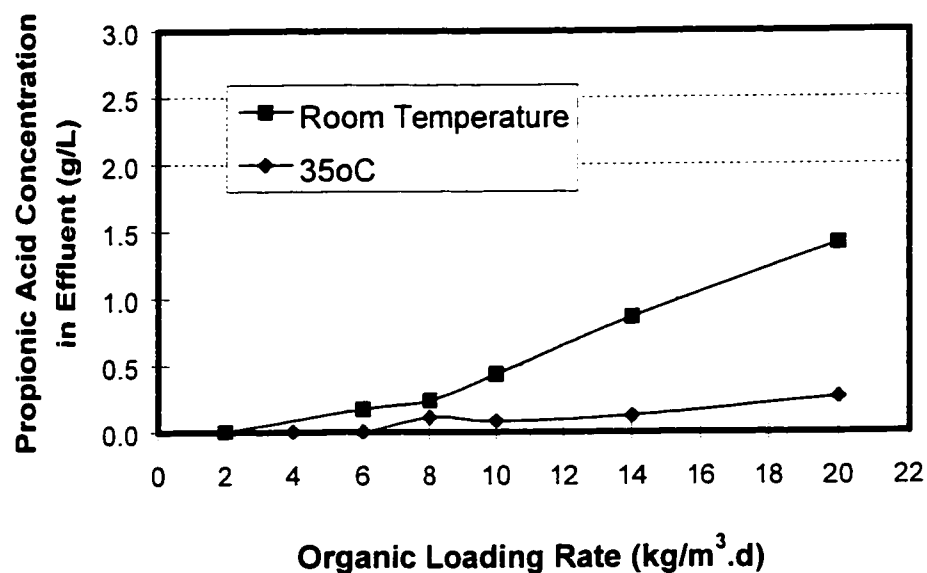
**Figure 5.27** Comparison of Acetic Acid Concentration in the Effluent of the ASBR between Room Temperature and  $35^\circ\text{C}$  as a Function of OLR



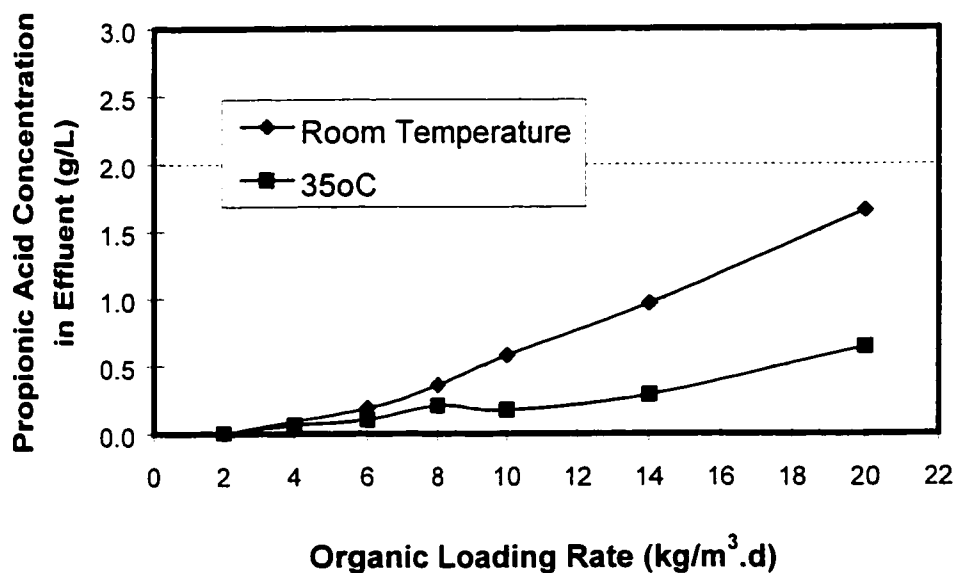
**Figure 5.28** Comparison of Acetic Acid Concentration in the Effluent of the UASB

Reactor between Room Temperature and 35°C as a Function of OLR

Figures 5.27 and 5.28 show the comparison of the acetic acid concentration in both reactor effluents at the two temperatures. In the ASBR, within the range of  $2 \text{ kg/m}^3.\text{d} \leq \text{OLR} \leq 6 \text{ kg/m}^3.\text{d}$ , the acetic acid concentration in the effluent at 35°C was lower than that at room temperature; within  $6 \text{ kg/m}^3.\text{d} < \text{OLR} \leq 20 \text{ kg/m}^3.\text{d}$ , the acetic acid concentration in the effluent at 35°C was higher than that at room temperature. In the UASB reactor, the acetic acid concentration in the effluent at 35°C was lower than that at room temperature except for at  $\text{OLR} = 20 \text{ kg/m}^3.\text{d}$ , at this point, the acetic acid concentration in the effluent at 35°C was higher than that at room temperature.



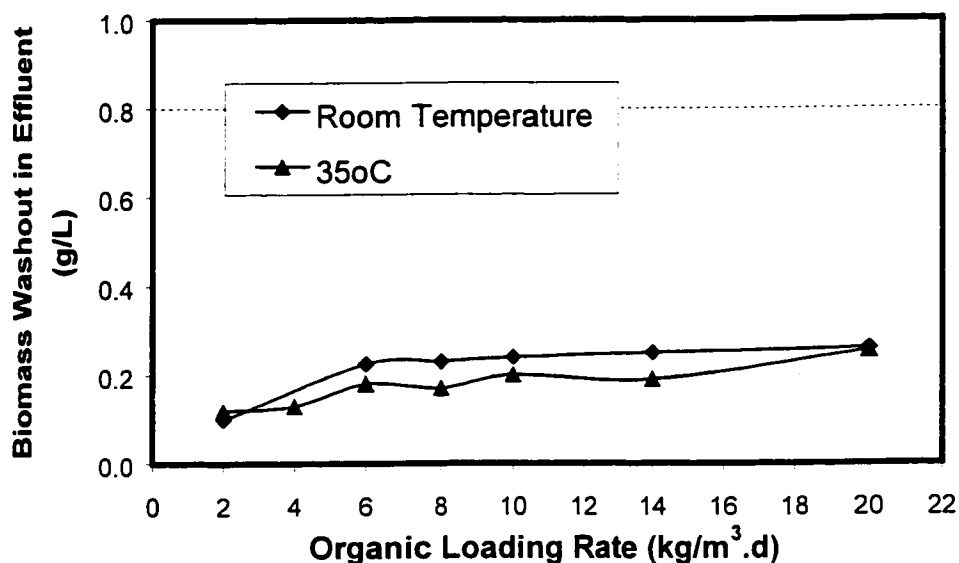
**Figure 5.29** Comparison of Propionic Acid Concentration in the Effluent of the ASBR between Room Temperature and 35°C as a Function of OLR



**Figure 5.30** Comparison of Propionic Acid Concentrations in the Effluent of the UASB Reactor between Room Temperature and 35°C as a Function of OLR

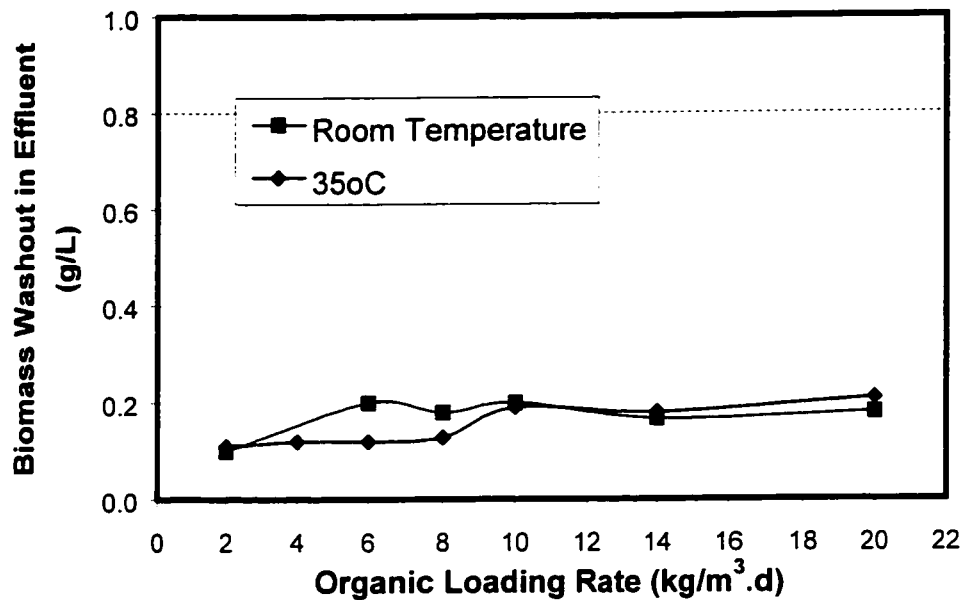
Figures 5.29 and 5.30 illustrate the comparison of the propionic acid concentration in both reactor effluents at two temperatures, respectively. These show that the propionic acid concentrations in both reactor effluents at 35°C at all loading levels were lower than that at room temperature, especially at high loading levels. The difference between 35°C and room temperature was gradually increased with the increase of OLR shown in both reactor effluents.

### 5.3.5 VSS in Effluent



**Figure 5.31** Comparison of Biomass Washout in the Effluent in the ASBR between Room Temperature and 35°C as a Function of OLR





**Figure 5.32** Comparison of Biomass Washout in the Effluent in the UASB Reactor between Room Temperature and 35°C as a Function of OLR

Figures 5.31 and 5.32 present the comparison of biomass washout in both reactors effluents at two temperatures, respectively. Through comparison, in the ASBR, biomass washout at 35°C was appreciably lower than that at room temperature under  $2 \text{ kg/m}^3.\text{d} < \text{OLR} \leq 20 \text{ kg/m}^3.\text{d}$ ; in the UASB reactor, biomass washout at 35°C was appreciably lower than that at room temperature at  $2 \text{ kg/m}^3.\text{d} \leq \text{OLR} \leq 10 \text{ kg/m}^3.\text{d}$ ; was higher at  $10 \text{ kg/m}^3.\text{d} < \text{OLR} \leq 20 \text{ kg/m}^3.\text{d}$ .

However, the difference of biomass washout in both reactor effluents between two temperatures was not large. Both reactors demonstrated a good ability to retain the biomass inside.

## ***CHAPTER 6***

### **CONCLUSIONS AND RECOMMENDATIONS**

This study of anaerobic treatment technology compared treatment efficiencies for the wash wastewater from returned beer bottles based on two types of anaerobic bioreactors– the ASBR and UASB reactors. According to those results collected from two groups of tests, the following conclusions were made:

1. Both reactors achieved COD removal and methane production under gradually increasing organic loading rate at room temperature and 35°C.
2. Anaerobic treatment technology can be applied to treat wash wastewater from returned beer bottles, and can obtain better effluent quality under low or moderate strength loading conditions at both temperatures in the ASBR and UASB reactors without a recirculation system.
3. The two group tests prove that wash wastewater from returned beer bottles is highly biodegradable.
4. The performance of each parameter at 35°C is better than that at room temperature.
5. The performance for soluble COD removal efficiency in the ASBR is better than that in the UASB reactor without effluent recirculation system at room temperature and 35°C.

6. At room temperature and 35°C, the methane yield in the ASBR under low or moderate strength organic loading rates ( $2 \text{ kg/m}^3 \cdot \text{d} \leq \text{OLR} \leq 6 \text{ kg/m}^3 \cdot \text{d}$ ) is close to the theoretical level, but lower than the theoretical level under moderate or high – strength organic loading rates ( $6 \text{ kg/m}^3 \cdot \text{d} < \text{OLR} \leq 20 \text{ kg/m}^3 \cdot \text{d}$ ).
7. In order to obtain high quality effluents, the performance of the UASB reactor requires recirculation system under  $\text{OLR} < 6 \text{ kg/m}^3 \cdot \text{d}$  at room temperature and  $\text{OLR} < 8 \text{ kg/m}^3 \cdot \text{d}$  at 35°C. The ratio of recirculation to feed in the UASB reactor system is different between room temperature and 35°C.
8. In this study,  $\text{NaHCO}_3$  proved to be a good reagent for adjusting the pH values in the influent, and at the same time, can keep the pH values in both reactor effluents within the optimal range of anaerobic treatment (6.9 to 7.2) so as to gain the best performance for each parameter.
9. The results obtained for the two group tests adequately show the relationship among each parameter. In the anaerobic treatment process, the COD reduction is completed by two stages: the acid digestion stage and the methane production stage. The main removal of COD occurred in the methane production stage. The amount of methane production restricts the removal efficiency of COD. In contrast, the COD removal also restricts the methane production. In the two group tests, the trend of performance of soluble COD removal with OLR is the same

with the trend of performance of methane yield with OLR in both reactors, which is consistent with the theory of anaerobic technology.

10. Theoretically, VFA concentration in effluent is an indication of methane production. In anaerobic processes, acetogenic bacteria use VFA as substrates to produce  $H_2$ ,  $CO_2$  and acetate that are used as substrates by methanogenic bacteria to produce methane (the processes are shown in Figure 2.6). Therefore if the VFA concentration in the effluent is high that means there is less VFA has been transferred to  $H_2$ ,  $CO_2$  and acetate so as to produce less methane, which further resulted in the low removal efficiency of COD. In the two group tests, the results of VFA (acetic and propionic acid) concentrations in both reactor effluents showed an increasing trend with an increase of OLR. Correlating with the decreasing methane yield and soluble COD removals in both reactors.

Based on the above conclusions, the following recommendations may be made:

1. The results obtained in this study prove that the effluent quality of treated wash wastewater under high – strength organic loading rate does not satisfy the discharge standard of municipal sewer systems or surface water bodies. Therefore an aerobic treatment unit is recommended after an anaerobic treatment unit in order to obtain high quality effluent.
2. Since breweries produce lots of wastewater effluent, the reuse of effluent is desirable. This not only saves the requirement of water but also protects the

environment. The study recommends adopting advanced treatment units, such as an aerobic treatment unit for tertiary treatment level after an anaerobic treatment unit, to achieve the goal of reusing the effluent.

3. Based on the conclusions, the anaerobic treatment technology is a sustainable treatment method due to methane production which can be used for energy purposes with the plant.

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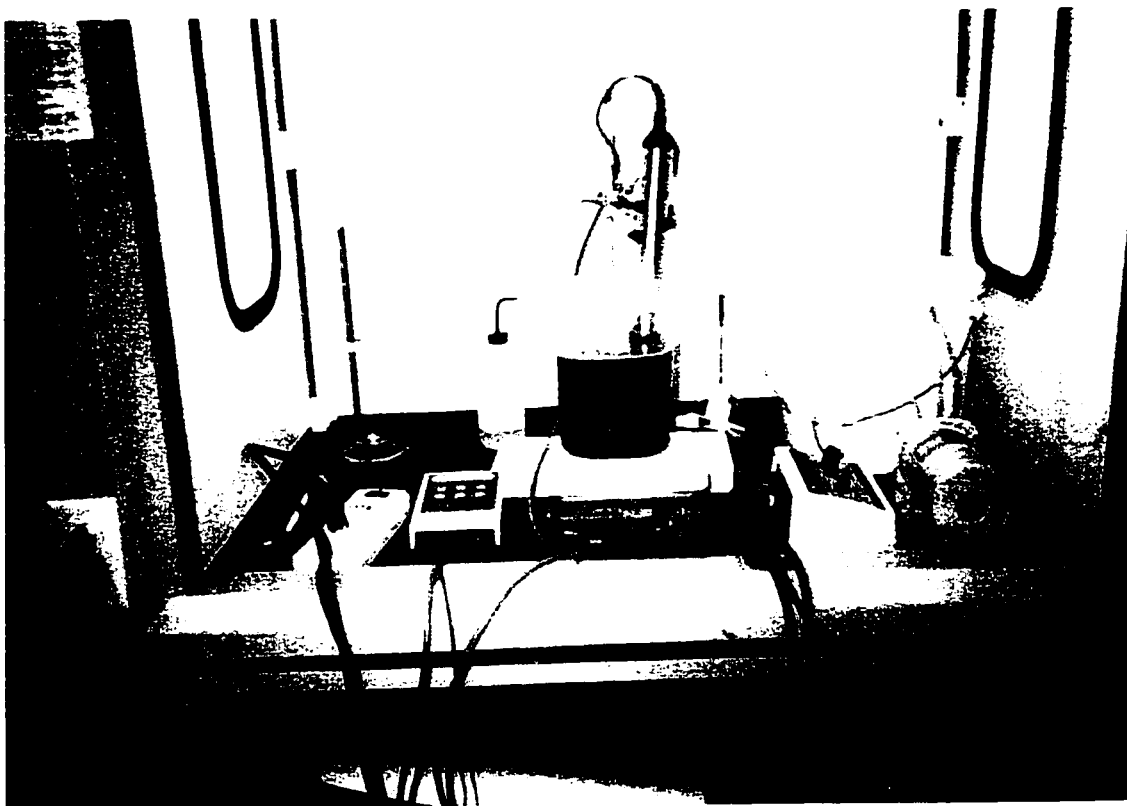
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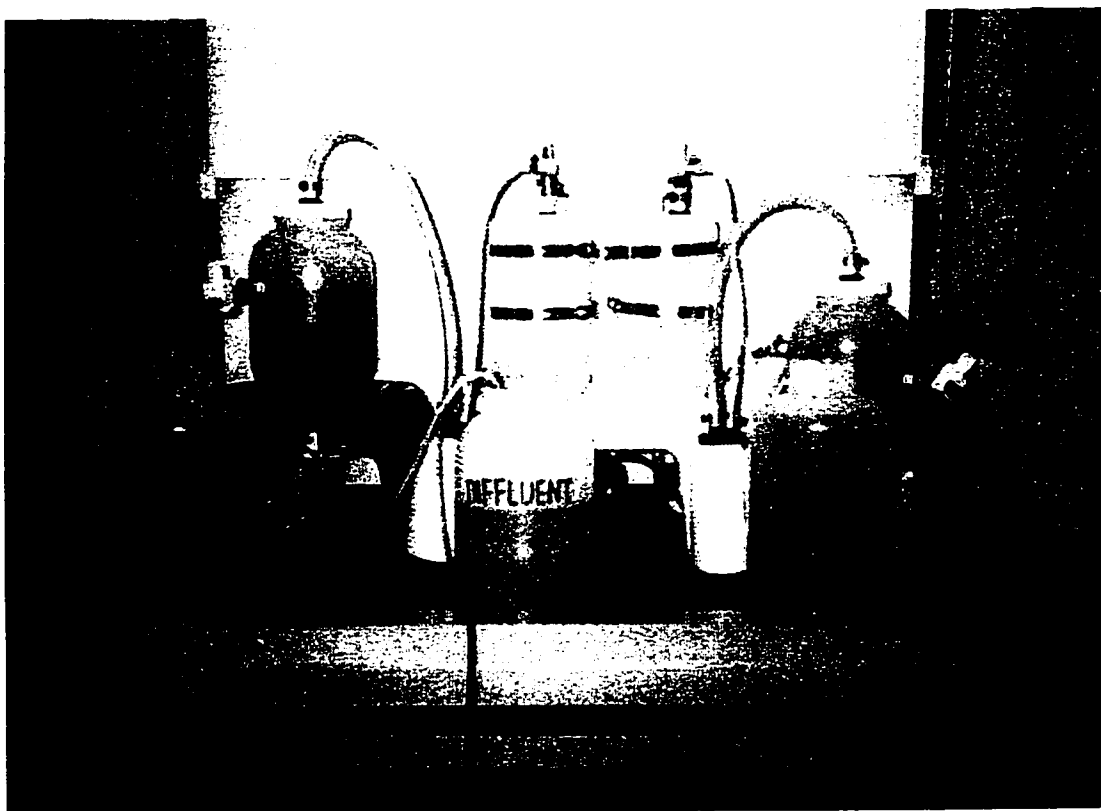
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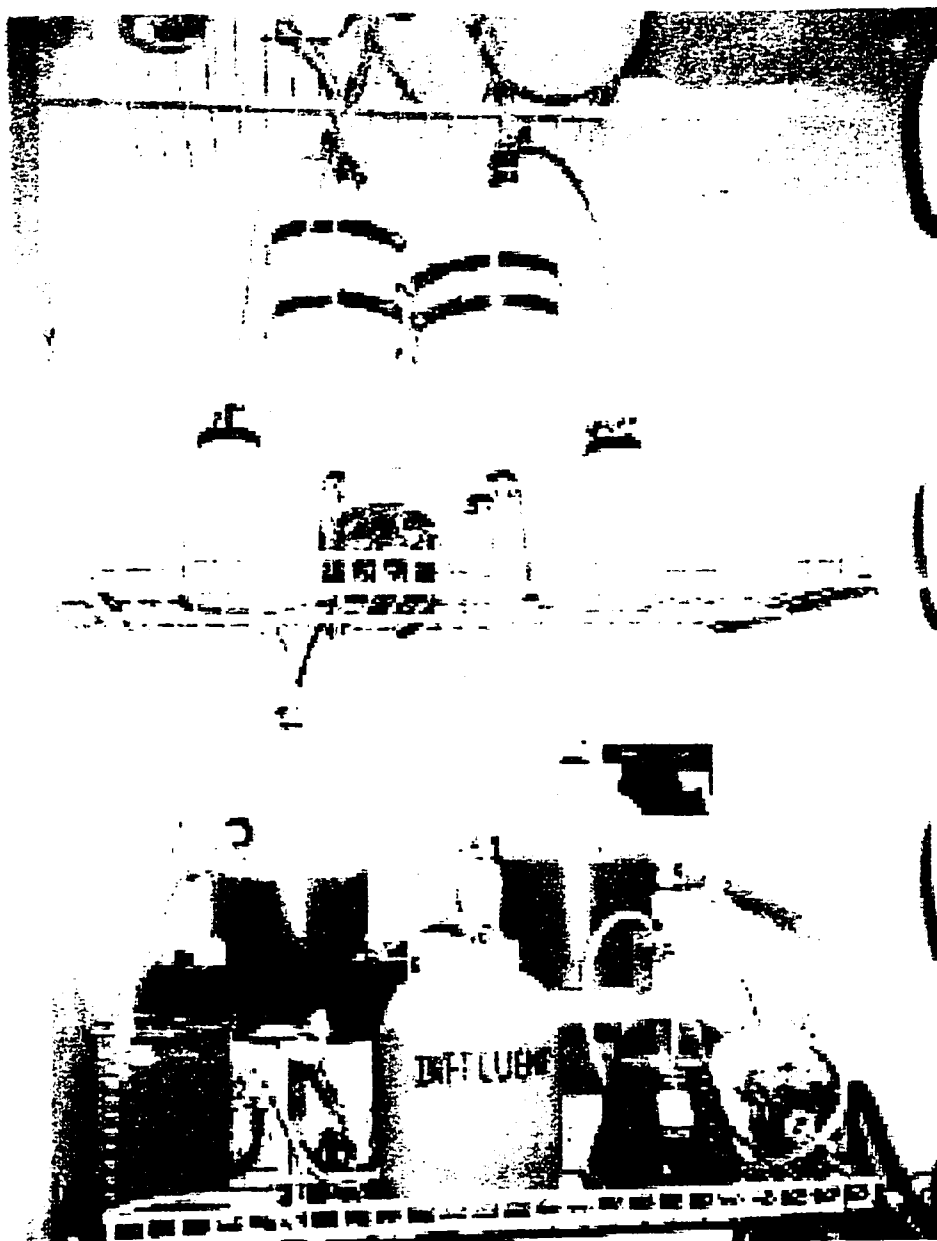
## **APPENDIX**



**Anaerobic Batch Reactor**



**Setup of the First Group Test**



**Setup of the Second Group Test**

## **NOMENCLATURE**

COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
DO	Dissolved Oxygen
HRT	Hydraulic Retention Time
OLR	Organic Load Rate
SS	Suspended Solid
TSS	Total Suspended Solid
MLVSS	Mixed Liquor Volatile Suspended Solid
VSS	Volatile Suspended Solid
VFA	Volatile Fatty Acid
ATU	Aerobic Treatment Unit
UASB	Upflow Anaerobic Sludge Blanket
ASBR	Anaerobic Sequencing Batch Reactor
ABR	Anaerobic Batch Reactor
EGSB	Expanded Granular Sludge Blanket
CSR	Continuously Stirred Reactor
FB	Fluidized Bed Reactor
AFBR	Anaerobic Fluidized Bed Reactor
SRT	Sludge Retention Time
KHP	Potassium Hydrogen Phthalate
HPLC	High Pressure Liquid Chromatography