

**REMOVAL EFFICIENCY AND KINETIC STUDY OF BOD AND COD
USING AEROBIC AND ANAEROBIC DIGESTION**

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**A project report submitted in partial fulfilment of the
requirements for the award of the degree of
Bachelor (Hons.) of Chemical Engineering**

**Faculty of Engineering and Science
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April 2011

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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REMOVAL EFFICIENCY AND KINETIC STUDY OF BOD AND COD USING AEROBIC AND ANAEROBIC DIGESTION

ABSTRACT

Biological digestions have some advantages over other treatment methods such as chemical treatment because it is relatively simple, cost effective and energy efficient. For past decades, aerobic digestion have been widely used to treat wastewater due to its high degree of efficiency and high quality of effluent; however, aerobic digestion required extra expenses for aeration and sludge disposal. Anaerobic digestion have been given more interested these few years as a cost-effective alternative but anaerobic digestion have relatively low quality of effluent. Therefore, a combined anaerobic-aerobic digestion scheme was developed in order to setup a more economical and high efficiency system. The purpose of this study was to investigate the operating conditions and performance of combined digestion system, and then compared with single aerobic and anaerobic digestion. Throughout this study, pH and DO profiles were found to be related in aerobic digestion due to nitrification and denitrification processes, and wastewater in anaerobic digestion was found to be more acidic after 8 hours of treatment in comparison with aerobic and combined digestion. The combined anaerobic-aerobic (2-6) digestion indicated the highest COD and BOD removal percentages which were 74% and 86%, respectively. While aerobic digestion achieved 69% and 84% of COD and BOD removal, respectively. Anaerobic digestion had relatively lowest COD and BOD removal percentage, 36% and 67%, as anaerobic digestion underwent fermentation process only instead of respiration process. Various COD concentrations of synthetic wastewater was prepared and treated in three digestion schemes. It is found that aerobic digestion had better COD degradation (70-80%) when treated with different COD concentration of wastewater in comparison with the combined (60-78%) and anaerobic (35 – 50%) digestion. The kinetics studies using Monod, first order, diffusional and Singh Model were performed according to the obtained data.

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LIST OF SYMBOLS / ABBREVIATIONS

C_{so}	initial substrate concentration (mg COD/L)
C_s	substrate concentration (mg COD/L)
$\frac{dC_s}{dt}$	substrate degradation (mg COD/L-h)
k_I	first order constant (h^{-1})
k_D	rate constant for Diffusional model ($mg\ COD^{0.5}/L^{0.5}h$)
k_{si}	rate constant for Singh Model (h^{-1})
K_I	product of maximum specific degradation rate and biomass concentration (mg COD/L-h)
K_s	half saturated constant of Monod's equation (mg COD/L)
t	degradation time (h)
AFB	Aerobic Fluidized Bed
AST	Activated Sludge Treatment
BOD	Biochemical Oxygen Demand
CH ₄	Methane (Biogas in this study)
CO ₂	Carbon Dioxide
COD	Chemical Oxygen Demand
CSTR	Continuous Stirred Tank Reactor
DO	Dissolve Oxygen (mg/L)
FFB	Fixed Film Bed
H ₂ O	Water
HRT	Hydraulic Retention Time (h)
MBR	Membrane Bioreactor
N	Nitrogen
NH ₄ ⁺	Ammonium Ion
P	Phosphorus
SBR	Sequential Batch Reactor

TSS	Total Suspended Solids
UASB	Upflow Anaerobic Sludge Bed
VFA	Volatile Fatty Acids
VSS	Volatile Suspended Solids

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CHAPTER 1

INTRODUCTION

1.1 Background

This study is related to reduction of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) in aerobic, anaerobic and combined anaerobic-aerobic digestion of wastewater treatment.

Aerobic digestion of waste is the natural biological degradation and purification process in an oxygen-rich environment, whereas anaerobic digestion is accomplished without oxygen in a closed system. Aerobic digestion technologies have been widely applied in organics wastewater treatment due to high degree of efficiency and high quality of effluent (Yeoh, 1995). Aerobic digestion system can achieve higher removal of biodegradable organics matters if compared to anaerobic digestion system, and the produced biomass is well flocculated and resulting lower effluent suspended solids (Cakir and Stenstrom, 2005). Interest in anaerobic for wastewater treatment has greatly increased mainly due to resource recovery and utilization, while still achieving pollution control (Seghezzi et al., 1998). In comparison with aerobic digestion, anaerobic is a cost effective system (Lettinga, 1995) due to low sludge production, low energy consumption due to unnecessary transfer of large quantities of air or oxygen and significant conversion of organics matters to methane gas which is useful for combustible gas.

Generally, anaerobic-aerobic systems that operate separately in sequential process complement each other. Chan et al. (2009) stated that aerobic digestion are more suitable for low strength wastewater (COD less than 1000 mg/L) and anaerobic treatments are more suitable for high strength wastewater (COD more than 4000 mg/L). High polluted industrial are more suitable to treat with anaerobic treatment follow by aerobic treatment due to high level of COD. Furthermore effluent produced in anaerobic (pre-) treatments consists of solubilized organics matter and aerobic (post-) treatments are required to polish the effluent and meet the standard (less than 30 mg BOD/L) (Chan et al, 2009 ; Vochten et al., 1998). Such sequential treatment scheme is potential and combines the advantages of both treatments.

1.2 Problem Statement

In fact, both aerobic and anaerobic digestions have advantages and disadvantages. A combined of both digestions was developed to minimise disadvantages and meet the requirement. However, only aerobic digestions are employed in mostly existing wastewater plant due to the quality of effluent. Implement of additional anaerobic reactor will increase the capital investment cost. Therefore, comparison of aerobic and combined system in terms of operating conditions and performance must be investigated, in order to determine the advantages of combined system over aerobic system.

1.3 Objectives

The objectives of this study are listed as follows:

1. To develop a combined anaerobic-aerobic digestion system using one anaerobic digester and one aerobic digester.
2. To study pH and DO profiles in three systems.
3. To investigate and compare the performance of anaerobic-aerobic system with aerobic and anaerobic digestion.
4. To study the effect of different initial COD concentration for three systems.
5. To perform kinetic studies on three systems.

1.4 Scope of Study

This study was to investigate and compared reduction of BOD and COD in aerobic, anaerobic and combined system. In addition, the performance for combined system was determined by manipulating residence time. During the processes, pH and DO were observed for three systems.

Furthermore, COD concentrations profiles of three systems were investigated by varying initial concentration of COD in wastewater. Then, kinetics studies were performed using four models, including Monod model, First order, Diffusional and Singh model, according to obtained data.

1.5 Hypotheses

Based on the study scope, the hypotheses made are listed as below:

1. The pH profile for anaerobic digestion has greater decrement if compare with aerobic digestion.
2. The removal efficiency of BOD and COD in combined anaerobic-aerobic digestion is the greatest followed by aerobic and anaerobic digestion.
3. The removal efficiency of COD decreases as the initial concentration of COD increases for three systems.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

Organics compounds are combination of carbon, hydrogen, oxygen, nitrogen, sulphur and other trace elements. They are generated by plants, animal and human beings such as human excreta, paper products, detergents, cosmetics, food, agricultural products, wastes from commercial activities and industrial sources (Richard, 2008). Large concentration of these organic compounds in a stream will increase biological oxygen demand (BOD) and chemical oxygen demand (COD) as a result of low level of dissolve oxygen which will endanger the aquatic organisms (Richard, 2008). Macro-nutrients (nitrogen, phosphorus) may promote eutrophication of the receiving water bodies (Duce, 2008). Excessive algae growth and subsequent dying off and mineralization of these algae, may lead to the death of aquatic life because of oxygen depletion (Verheyen et al., 1996). Agro-industrial effluents may contain compounds that are directly toxic to aquatic life (e.g. tannins and chromium in tannery effluents; un-ionized ammonia) (Verheyen et al., 1996) at pH higher than 8 (Reginatto et al., 2005).

A biological treatment is defined as the use of bacteria or other microorganism to remove contaminates or organics compounds by assimilating them (Schultz, 2005). Biological systems in wastewater treatment are relatively simple, cost effective and energy efficient. They can be used in many industrial, municipal, commercial and residential building applications (The Natural Edge Project, 2009).

The efficiency of biological treatment can be evaluated through toxicity, COD, BOD, and levels of nitrogen and sulphur compounds (Schultz, 2005).

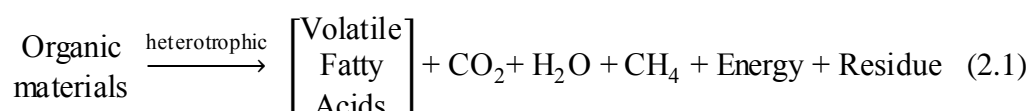
2.2 Biological Digestion

There are two basic categories of biological digestions for wastewater treatment, which are aerobic and anaerobic digestions (Schultz, 2005).

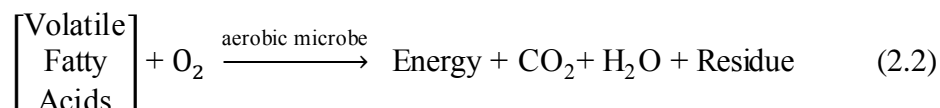
2.2.1 Aerobic Digestion

Aerobic digestion is the natural biological degradation and purification process in which bacteria that thrive in oxygen-rich environments break down and digest the waste. Microbial metabolism in aerobic digestion can be categorized into fermentation and respiration, biosynthesis, and endogenous respiration.

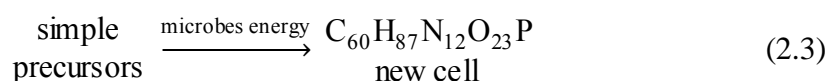
When a culture of aerobic heterotrophic microorganisms is placed in an environment containing a source of organic material, the microorganisms will remove and utilize most of this material. During fermentation metabolism, these materials will be channeled into metabolic energy and oxidized to carbon dioxide, water and soluble inert material, providing energy for both synthesis and maintenance (life support) functions (Ros and Zupacic, 2002). The equation is given as below (Seabloom and Buchanan, 2005):



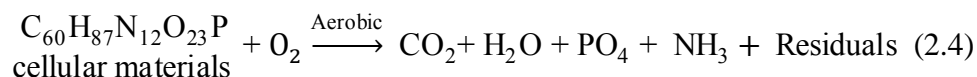
Through the process of respiration, aerobic microorganisms can further transform the volatile fatty acids to carbon dioxide, water and additional energy (Lehninger, 1973) as shown in Equation 2.2.



According to Lehninger (1973), biosynthesis is the most complex and vital energy requiring activity of all living organisms. Two kinds of ingredients are required for the biosynthesis of cell components: (1) precursors that provide the carbon, hydrogen, nitrogen, and other elements found in cellular structures, and (2) adenosine triphosphate (ATP) and other forms of chemical energy needed to assemble the precursors into covalently-bonded cellular structure. The formation of new cells through biosynthesis is given in Equation 2.3.



Once the external source of organic material is exhausted, the microorganisms will begin endogenous respiration where microbes will feed on each other at a higher rate than new cells can be produced (Ros and Zupacic, 2002 ; Seabloom and Buchanan, 2005).



Overall processes of aerobic can be represented in Figure 2.1,

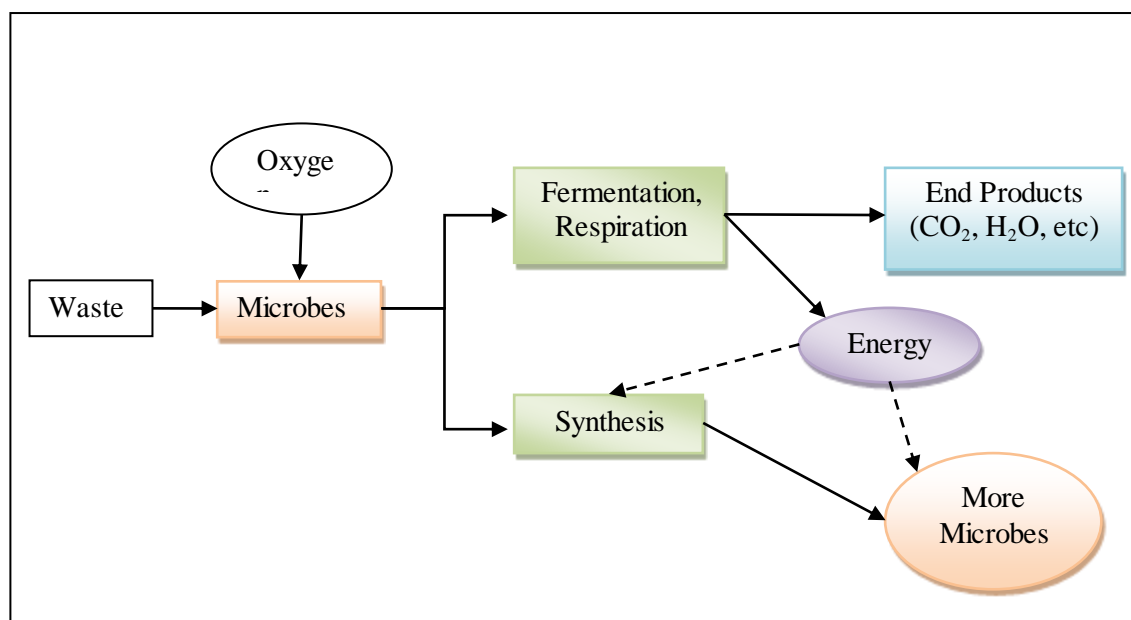


Figure 2.1: The Path of Aerobic Digestion

2.2.2 Anaerobic Digestion

Anaerobic digestion is a biological process that happens naturally when bacteria breaks down organic matter in environments without oxygen (Friend of Earth, 2007) with concurrent production of biogas (Midwest Rural Energy Council).

Anaerobic process is generally divided into four stages, which are hydrolysis, acidogenesis, acetogenesis and methanogenesis. Through hydrolysis, the complex organic molecules are broken down into simple sugars, amino acids, and fatty acids (Friend of Earth, 2007). In acidogenesis, acidogenic (acid-forming) bacteria will further product of hydrolysis to organic acids (e.g., acetic, propionic, formic, lactic, butyric, or succinic acids), alcohols and ketones, acetate, carbon dioxide, and hydrogen (United-Tech, 2010). Acetogenic bacteria convert fatty acids (e.g., propionic acid, butyric acid) and alcohols into acetate, hydrogen, and carbon dioxide, which are used by the methanogens. Under relatively high hydrogen partial pressure, acetate formation is reduced and the substrate is converted to propionic acid, butyric

acid and ethanol rather than methane (United-Tech, 2010). Last stage (methanogenesis), methane, carbon dioxide and water are produced by methanogenic bacteria (Friend of Earth, 2007). Pictures of bacteria and overall anaerobic processes can be illustrated in Figures 2.2 and 2.3, respectively.

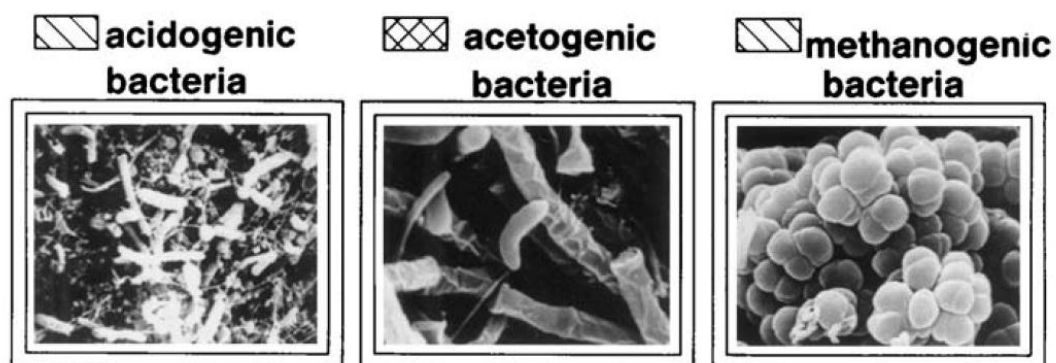


Figure 2.2: Pictures of different bacteria in anaerobic digestion (Reference: Alexander and Diamantis, 2005)

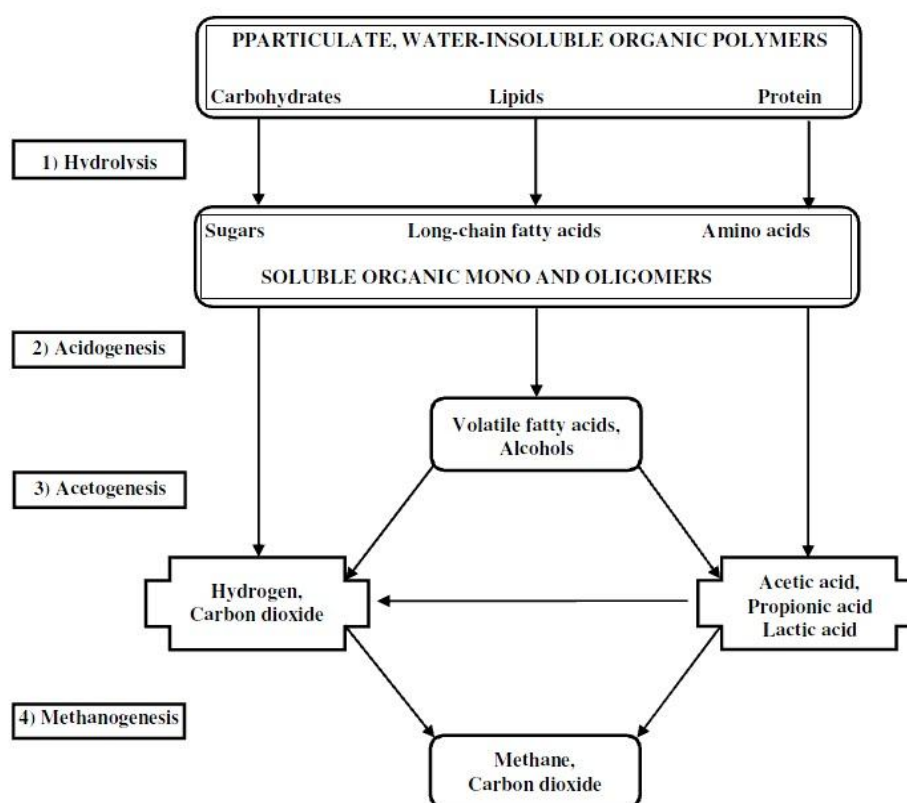


Figure 2.3: Schematic of Reaction in Anaerobic Digestion (Reference: Salsabil, 2008)

2.3 Aerobic versus Anaerobic Digestion

Both aerobic and anaerobic digestions have advantages and disadvantages in wastewater treatment. Conventional aerobic technologies based on activated sludge processes are dominantly applied for the treatment of domestic wastewater due to the high efficiency achieved, the possibility for nutrient removal and the high operational flexibility (Gavrilescu & Macoveanu, 1999), whereas anaerobic treatment of domestic wastewater can serve a viable and cost-effective alternative (Lettinga, 1995) due to its relatively low construction and operational cost, operational simplicity, low production of excess sludge, production of energy in form of biogas and applicability in small and large scales. Various merits of both treatments are listed in Table 2.1.

Table 2.1: Comparison Between Aerobic and Anaerobic Digestions (References: Yeoh, 1995 ; Leslie, 1999 ; Eckenfelder et al.)

	Aerobic	Anaerobic
Organics remove efficiency	High	High
Energy requirement	High	Low to moderate
Effluent quality	Excellent	Moderate to poor
Organics loading rate	Moderate	High
Sludge production	High	Low
Nutrient requirement	High	Low
Alkalinity requirement	Low	High for certain industrial waste
Temperature sensitivity	Low	High
Start-up time	2-4 weeks	2-4 months
Odor	Less opportunity	Potential odor problem
Bio-energy and nutrient recovery	No	Yes
Mode of treatment	Total	Essentially pre-treatment

Aerobic treatment systems are commonly used in the treatment of organic wastewaters for achieving high degree of treatment efficiency, while in anaerobic treatment systems, considerable progress has been achieved in anaerobic biotechnology for waste treatment based on the concept of resource recovery and utilization, while still achieving the objective of pollution control (Yeoh, 1995 ; Seghezzi, 1998).

Anaerobic treatment systems have some advantages over aerobic treatment systems due to removal of higher organic loading, low sludge production and high pathogen removal, methane gas production and low energy consumption (Nykova et al., 2002). Conventional activated sludge (CAS) process in aerobic treatment systems is energy intensive due to the high aeration requirement and it also produces large quantity of sludge (about 0.4 g dry weight/g COD removed) that has to be treated and disposed off (Mrowiec and Suschka). Sludge production in anaerobic systems is low and the excess sludge is already digested and can be directly dewatered, typically by drying beds, and disposed (Kassab et al., 2009). Anaerobic treatment systems have higher volumetric organic loads than aerobic processes, so smaller reactor volumes and less space may be required for treatment. Organic loading rates of 3.2 to 32 kg COD/m³/d may be achieved, compares with 0.5 to 3.2 kg COD/m³/d for aerobic processes (The AD Community, 2007). In addition, the required nutrient addition is much less for anaerobic treatment system because less biomass is produced (The AD Community, 2007). Production of methane (biogas) in anaerobic treatment can be used to generate power to satisfy the energy need of the whole treatment plant (energy recovery) or used as fuel (Last, 2006).

Nevertheless, anaerobic treatment systems have relatively poor effluent quality, high temperature sensitivity and alkalinity requirement. In terms of effluent quality, methanogens have limited substrate affinity, and thus anaerobic system is inefficient in treatment polishing. In comparison, aerobic system permits the removal of organics with, in practice, a capacity of purification down to values lower than required standard (less than 30 mg BOD/L) (Guiot, 1994). Effluent of anaerobic treatment often contains ammonium ion (NH₄⁺) and hydrogen sulfide (HS⁻) (Heijnen et al., 1991), implying a complete stabilization of organic matters is impossible, therefore anaerobic systems are essentially for pre-treatment. Furthermore, anaerobic

treatment is highly influenced by temperature because methanogenic bacteria are very sensitive to small changes in temperature, which leads to a decrease of the maximum specific growth rate, while the half-saturation constant increases. Thus, a mesophilic digester must be designed to operate at temperature between 30 and 35 °C for their optimal functioning (United-Tech, 2010). In addition, methanogenic bacteria are also pH sensitive and generally have an optimum range from pH 6.5 to pH 7.5 (Clark and Speece, 1971). Under normal conditions, acid produced by acidogenic bacteria is buffered by the bicarbonate that is produced by methanogens. Under adverse environmental conditions, the buffering capacity of the system can be upset, eventually stopping the production of methane. Acidity is inhibitorier to methanogens than of acidogenic bacteria (United-Tech, 2010) therefore alkalinity and pH are often controlled by adding bicarbonate to reactor (Eckenfelder et al., 2010).

Generally, highly polluting industrial wastewaters (more than 4000 mg COD/L) are preferably treated in an anaerobic reactor due to the high potential for energy generation and low surplus sludge production (Chan et al., 2009), while aerobic treatment systems are suitable for the treatment of low strength wastewaters such as municipal wastewater (less than 1000 mg COD/L) (Mrowiec and Suschka, 2010).

2.4 Combined Anaerobic-Aerobic Digestion

In a combined anaerobic-aerobic treatment, two stages involving anaerobic degradation of the main fraction of organic matter, and a polishing step of the partially treated wastewaters by aerobic treatment to lower the final organic load of the effluent sequentially take place, so the discharge requirements can be met (Cocci et al., 1991; Monroy et al., 1995). Treatment of domestic wastewater in the combined anaerobic–aerobic treatment exploits the advantages of the two systems in the most cost-effective set-up if compared with aerobic treatment alone (Vera et al., 1999).

Benefits of combined anaerobic-aerobics identified by Frostell (1983) and Cervantes et al. (2006) and reorganized by Chan et al. (2009) are listed as below:

- Great potential of resource recovery: Anaerobic pretreatment removes most of the organic pollutants and converts them into a useful fuel, namely biogas.
- High overall treatment efficiency: Aerobic post-treatment polishes the anaerobic effluent and results in very high overall treatment efficiency. The aerobic treatment also smoothes out fluctuations in the quality of the anaerobic effluent.
- Less disposal of sludge: By digesting excess aerobic sludge in the anaerobic tank, a minimum stabilized total sludge is produced which leads to a reduction in sludge disposal cost. As an additional benefit, a higher gas yield is achieved.
- Low energy consumption: anaerobic pretreatment acts as an influent equalization tank, reducing diurnal variations of the oxygen demand and resulting in a further reduction of the required maximum aeration capacity.
- When volatile organics are present in the wastewater, the volatile compound is degraded in the anaerobic treatment, removing the possibility of volatilization in the aerobic treatment.

Ros and Zupancic (2004) agreed that it is operationally and economically advantageous to adopt anaerobic–aerobic processes in the treatment of high strength industrial wastewaters since it coupled the benefit of anaerobic digestion (i.e. biogas production) with the benefits of aerobic digestion (i.e. better COD and volatile suspended solid (VSS) removal) and increase their capability to biodegrade organic matter.

2.4.1 Type of Combination

Generally there are three types of combination for aerobic-anaerobic treatment system, which are conventional anaerobic-aerobic system, anaerobic-aerobic system using high rate reactor and integrated anaerobic-aerobic system as shown in Figure 2.4,

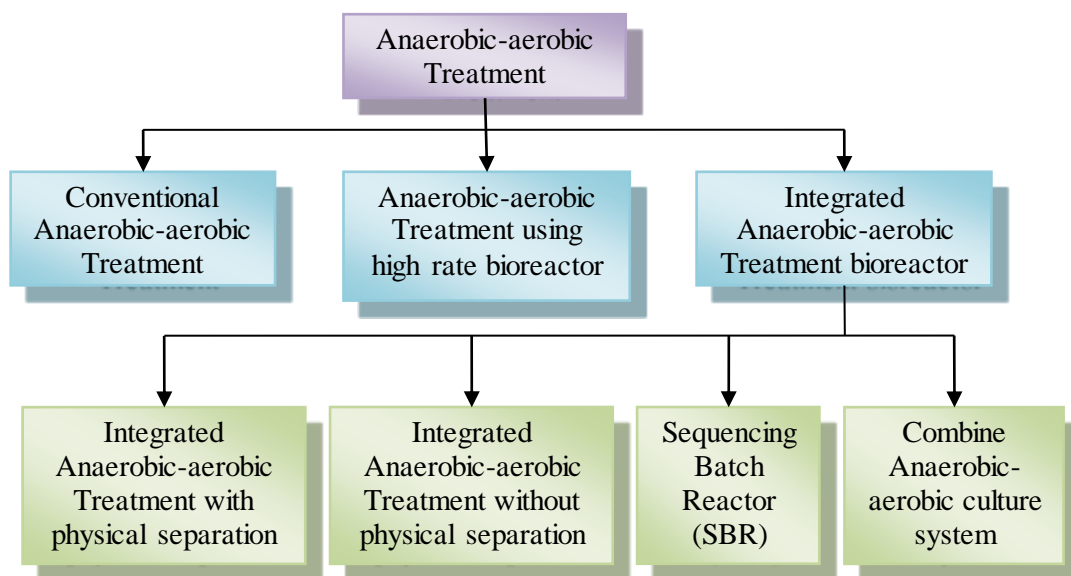


Figure 2.4: Type of Combine Anaerobic-Aerobic System (Adapted from Chan et al., 2009)

The simplest approach for the anaerobic–aerobic treatment is the use of conventional systems such as aerated stabilization ponds, aerated and non-aerated lagoons, as well as natural and artificial wetland systems (Chan et al., 2009). Figure 2.5 shows an aerated lagoon. Aerobic treatment occurs in the upper part of these systems while anaerobic treatment occurs at the bottom end. However, conventional anaerobic-aerobic system has disadvantages including large space requirement, emissions into populated environments from large open reactors, low process efficiencies, large surplus sludge production and high energy consumption.



Figure 2.5: Aerated Lagoons

In anaerobic-aerobic treatment scheme, pre-treatment (anaerobic system) and post treatment (aerobic system) are operated in two separated high rate reactor. Various types of high rate reactors, such as upflow anaerobic sludge blanket (UASB), filter bioreactor, aerobic fluidized bed (AFB), membrane bioreactor (MBR) and others, have been developed for years in order to overcome the disadvantages of conventional anaerobic-aerobic system. Figures 2.6 and 2.7 show schematic diagrams of UASB and AFB.

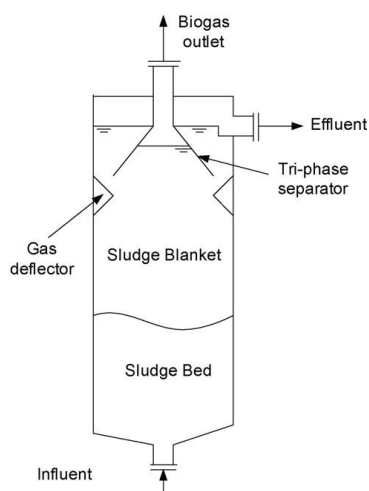


Figure 2.6: Schematic Diagram of UASB Reactor (Reference: Sperling, 2005)

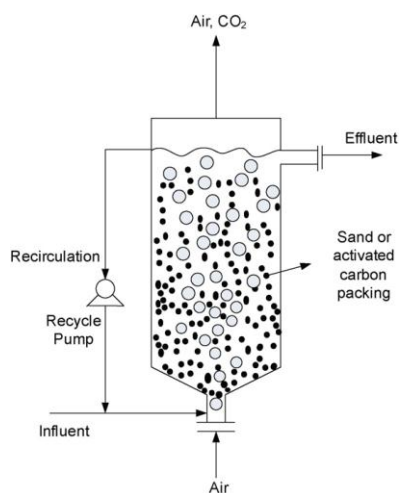


Figure 2.7: Schematic Diagram of AFB Reactor (Reference: Sperling, 2005)

Various combinations of high rate reactors have been applied for industrial wastewater treatment plants. For example, UASB and continuous stirred reactor (CSTR) are used to treat wastewater from pulp and paper industry (Tezel et al., 2001), pharmaceutical industry (Spooza and Demidran, 2008), simulate textile industry (Isik and Spooza, 2008) and etc. Figure 2.8 shows a typical example of anaerobic-aerobic treatment for combined fixed film bed (FFB) system.

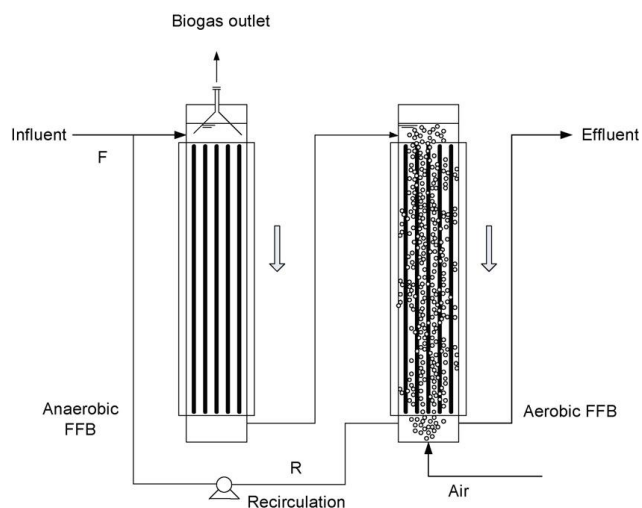


Figure 2.8: Schematic Diagram for Anaerobic-Aerobic FFBs (Pozo & Diez, 2005)

Integrated anaerobic-aerobic treatments are more intensive form of biodegradation by integrating anaerobic and aerobic area within single reactor. Typical example for these treatment systems are bubble column with draught tube and upflow anaerobic-aerobic fix bed (UA/AFB) integrated bioreactor, as shown in Figures 2.9 and 2.10, respectively.

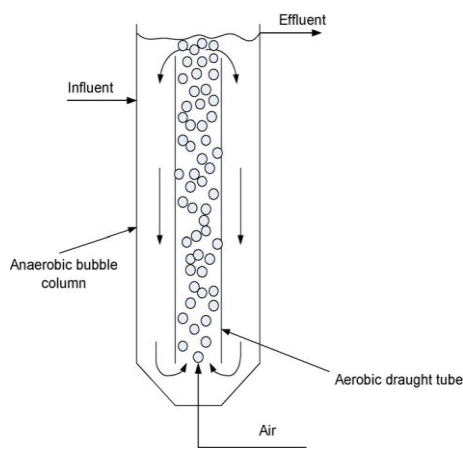


Figure 2.9: Bubble Column with Draught Tube (Reference: Hano et al., 2005)

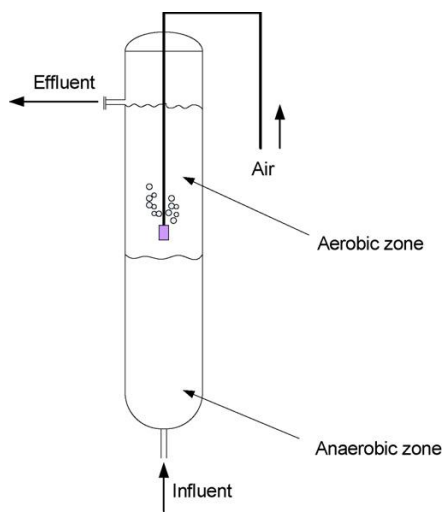


Figure 2.10: UA/AFB Integrated Reactor (Reference: Moosavi et al., 2004)

2.5 Case Study

2.5.1 Paper Mill Wastewater Treatment (References: Lerner et al., 2007)

This study was performed at American Israel Paper Mills (AIPM group) full-scale wastewater treatment plant in Hedera, Israel from 1997 to 2004. Full-scale activated sludge treatment (AST) system worked as the only bio treatment from 1997 – 2001, upflow anaerobic sludge blanket was installed as pre-treatment for AST from 2001 – 2004. Based on Figure 2.11, improvement was observed in terms of organic matter removal: 220-250 mg/L decreased to 80-120 mg/L as COD_t , and 20-40 mg/L decreased to 4-7 mg/L as BOD_t .

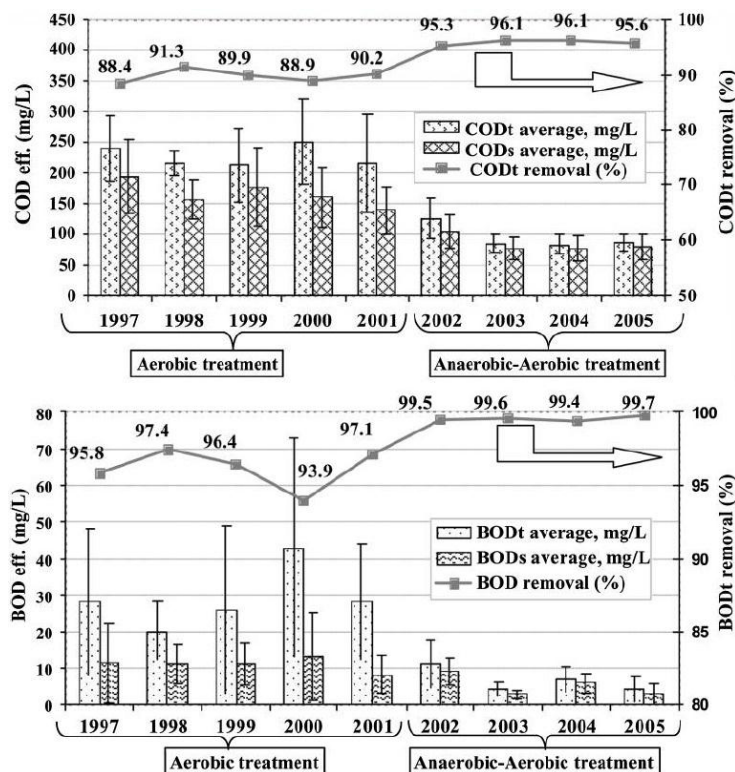


Figure 2.11: COD and BOD Removal In Aerobic and Combined Treatment

Based on the study, it is found that much lower level of sludge were produced in the UASB, 5 – 10 mg/L, compared to 50 – 85 mg/L in AST. During 1997 – 2001 the average quantity of excess sludge was 4 – 7 ton/day; however, the average daily excess sludge amount decreased to 1 – 2 ton/day after installation of UASB. The biogas production varied from 3300 to 6200 m³/day. Furthermore the chemical

consumption and cost comparison is shown in Table 2.2. Polymer consumption was reduced 50% due to low production of biosolids. The nutrient demand and electricity consumption of anaerobic digestion was only 60% and 70%, respectively of AST plant. Nevertheless anaerobic treatment required caustic soda to control pH level as methanogenesis deactivated when pH dropped below pH 6.

Table 2.2: Wastewater Treatment Plant Main Expenses

Parameter	Unit	Aerobic treatment only			Combined treatment		
		1999	2000	2001	2002	2003	2004
Electricity	kWh/day	10800	10100	10200	7100	7100	7000
Polymers	kg/day	74	64	67	34	19	31
Nutrients	kg/day	783	1464	1186	679	747	708
Caustic Soda	kg/day	-	-	-	3600	1900	1000

2.5.2 Grey Wastewater Treatment (References: Zeeman, 2009)

This study employed three systems: aerobic, anaerobic and anaerobic-aerobic system to treat grey wastewater. Grey wastewater was collected from Sneek, The Netherland, which contained total COD and nutrient concentration of 800 and 30 mg/L, respectively. Hydraulic retention times (HRT) were 12 hours for both Sequential batch reactor (SBR) and upflow anaerobic sludge blanket (UASB), and 7 hours in UASB followed by 6 hours in SBR for combine system. Figure 2.12 shows the setup of the reactors in this study.

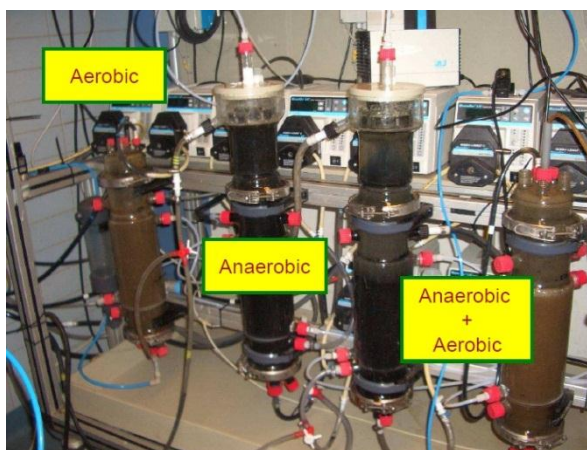


Figure 2.12: Apparatus Setup in Grey Wastewater Treatment

Based on Table 2.3, the COD removal percentages for aerobic and combine systems were both 88%, and 47% for anaerobic digestion. Effluent COD concentrations were reported as 91, 408 and 100 mg/L for aerobic, anaerobic and combined system respectively. For biogas production, anaerobic treatment produced 123 NL/m³ and combined system produced 72 NL/m³. Aerobic treatment achieved relatively high removal of nitrogen and phosphorus.

The study concluded that combine system did not give any advantages in grey wastewater treatment in terms of COD removal and sludge yield. However, the benefits of this configuration depend on gas used and energy input.

Table 2.3: Performance of Biological Treatment on Grey Wastewater

	Aerobic	Anaerobic	Combine
HRT (h)	12	12	13.2
COD removal (%)	88	47	88
COD effluent (mg/L)	91	408	100
Yield (g VSS/g COD)	0.11	0.08	0.19
Bio-gas production (NL/m ³)	-	123	72
N removal (%)	24	3	2
P removal (%)	8	6	3

CHAPTER 3

METHODOLOGY

3.1 Experimental Setup and Procedure

3.1.1 Wastewater and microbial culture

The synthesis wastewater employed in this study was prepared at various COD concentrations in the range of 2000 to 2500 mg COD/L as shown in Table 3.1. The pH of wastewater was adjusted manually close to neutral by adding HCL or NaOH solution. The concentration of sucrose was manipulated for preparation of other COD concentrations in wastewater, e.g., 850, 4500 and 5000 mg/L.

Table 3.1: Composition of Synthetic Wastewater (Reference: Kocadagistan et al, 2005)

Chemical	Amount (mg/l)
Bactopeptone	188
Sucrose	1500
MgSO ₄	125
CaCl ₂	15.5
KH ₂ PO ₄	250
FeCl ₃	11.3
NH ₄ Cl ₂	200

Activated sludge was collected from a wastewater treatment plant of Indah Water Konsordium (I.W.K.) at Bangi. Both aerobic and anaerobic digesters were seeded with this sludge and cultivated for three weeks before experiments were performed. During the cultivation process, concentration of COD was measured daily until the variation is less than 5% (Sponza and Demirden, 2010).

3.1.2 Safety and Precautions

Some safety and precautions must be emphasized and followed prior to the experiment. Heater and thermocouple must be fully ensured that immersed into liquid before the heater is switched on. The temperature controller must not be set higher than 60°C as the reactor can be damage at this temperature. The electrical control box must be always kept dry. In event of spillage, any spilled liquid off the surface of electrical control must be wiped immediately using a clean dry cloth.

3.1.3 Experiment A: Batch Aerobic Digestion

The objective of this experiment was to investigate the removal efficiency of organics matter in the wastewater in aerobic digestion. The experiment was performed in batch mode using a LS-26101 aerobic digester, shown in Figure 3.1. The digester has a height of 180 cm and a diameter of 18cm, which has an operating volume up to 10 L. However, in this experiment only 3 L wastewater were treated in aerobic digester. The digester was equipped with four air-spargers in order to maintain an excess of 2 mg DO/L (Salsabil, 2008) and operated at Psychrophilic temperature of 20°C. pH and DO were monitored during the digestion processes.

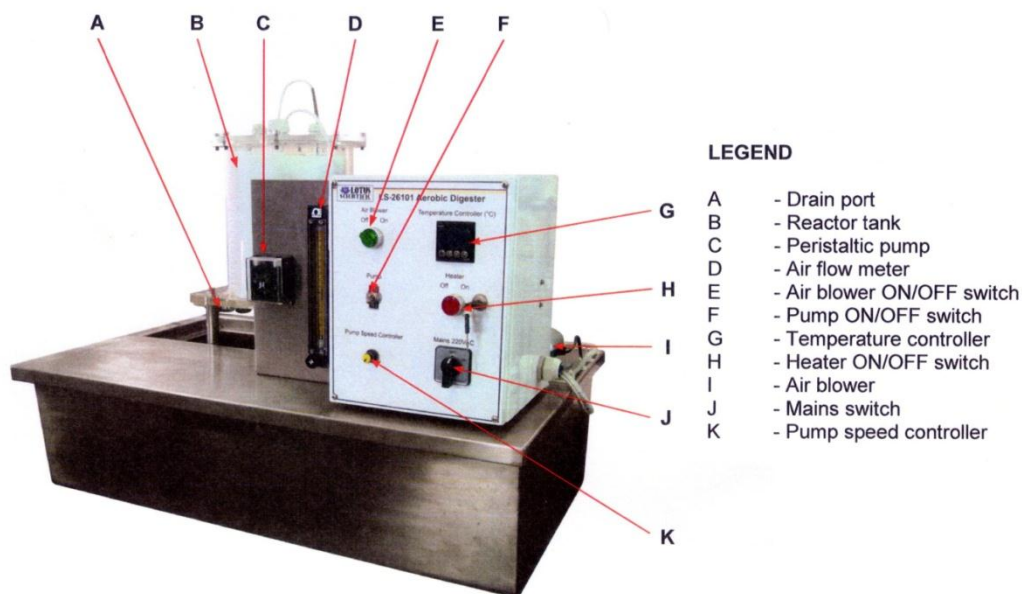


Figure 3.1: LS-26101 Aerobic Digester

3.1.4 Experiment B: Anaerobic Digestion

The experiment of anaerobic digestion was performed using LS-26102 anaerobic digester (Figure 3.2). The anaerobic digester has operating volume of 3 L equipped with bio-balls. These bio-balls served similar functions as the pumice used in experiment of wastewater treatment using upflow anaerobic fixed bed (UAF-B) and suspended aerobic reactor (SAR) by Kocadagistan (2005); they are used as a bio film support material due its large surface area. Experiments were conducted at Psychrophilic temperature of 20°C. pH and DO were monitored by using Eutech CyberScan pH 300 and Eutech CyberScan DO 300 throughout the digestion process.

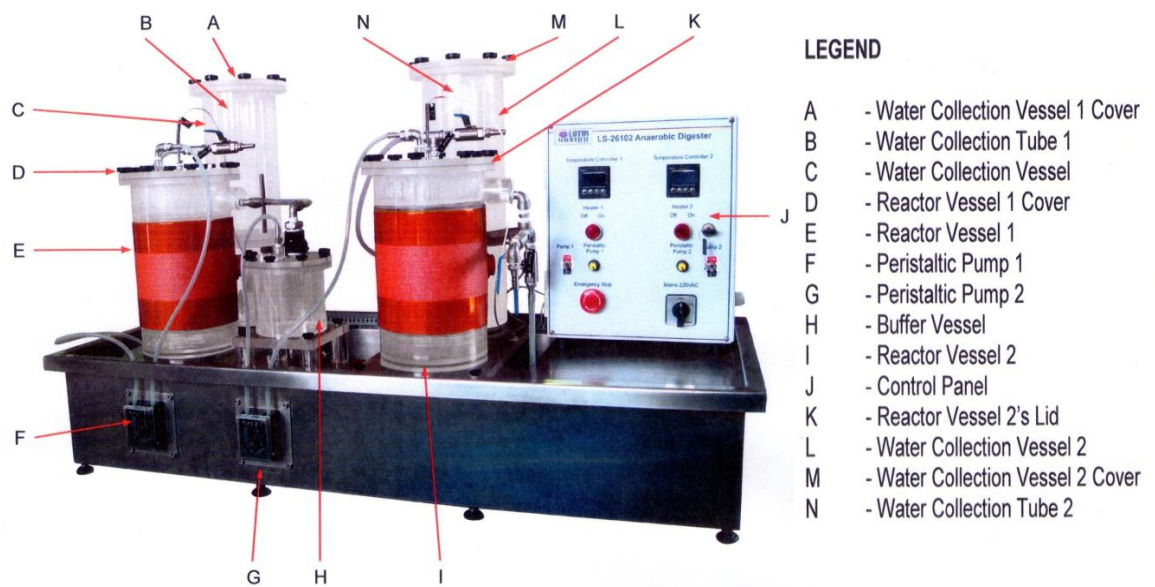


Figure 3.2: LS-26102 Anaerobic Digester

3.1.5 Experiment C: Anaerobic-aerobic Digestion

Anaerobic-aerobic digestion scheme was to combine both anaerobic and aerobic digestion in a sequence process, but was operated in two separated reactors. The experiments of anaerobic-aerobic digestion were carried out by varying the residence time in anaerobic and aerobic digestions, the synthesis wastewater were treated in anaerobic digester for 2, 4 and 6 hours followed by aerobic digestion for 6, 4 and 2 hours, respectively or referred as 2-6, 4-4, 6-2 combined system. pH and DO were monitored during the process. The process scheme is illustrated in Figure 3.3.

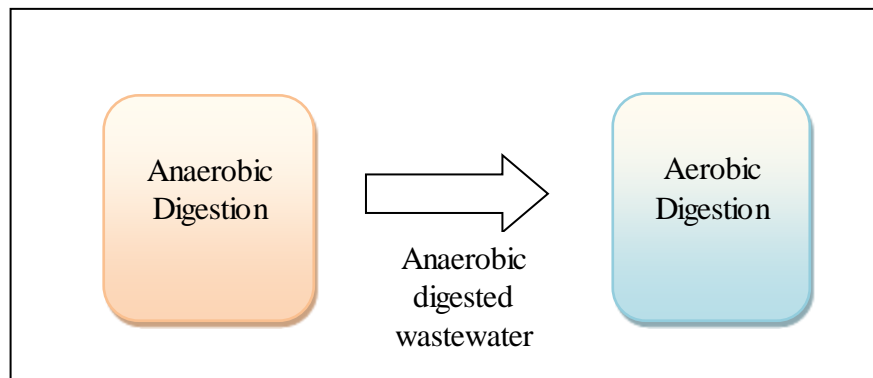


Figure 3.3: Anaerobic-Aerobic Process Scheme

3.2 Analysis Setup and Procedure

3.2.1 Biochemical Oxygen Demand (BOD) Test

Biochemical oxygen demand (BOD) determination is a laboratory test used to determine the relative oxygen requirement of wastewater. This test was conducted according to Standard Method 5210B (5-day BOD test). The test measures the molecular oxygen utilized during a specified incubation period for biochemical degradation of organic material and oxidation of inorganic material (e.g., sulfides and ferrous ion).

3.2.1.1 Materials and Apparatus

A BOD incubator serves to maintain the process temperature at 20 °C for five days and prevent the sunlight exposure. Other materials and apparatus are needed to prepare are listed as following

- BOD bottles (300 mL each)
- 200 – 250 mL beakers
- Dilution water (prepared 24 hours before performed BOD test)
- DO probe (Eutech CyberScan pH 300).

3.2.2 Chemical Oxygen Demand (COD) Test

Chemical Oxygen Demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled condition. This test was performed according to standard method 5220D (Closed reflux, colorimetric method). The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Oxidising agent, potassium dichromate ($K_2Cr_2O_7$), are used to determine COD because it is shown to be the most effective, relatively cheap and easy to purify, and is able to nearly completely oxidize almost all organic compounds. In this test, dichromate ion ($Cr_2O_7^{2-}$) is reduced to chromic ion (Cr^{3+}). Based on American Public Health Association (1998), both of these chromium species absorb in the visible region of the spectrum. Dichromate ion absorbs strongly in the 600 nm region, where chromic ion absorption is much less. The chromic ions absorb strongly in the 400 nm region, where dichromate has nearly zero absorption.

3.2.2.1 Safety and Precautions

Potassium dichromate ($K_2Cr_2O_7$) is identified as very hazardous to health in case of skin contact (permeator, corrosive, and irritant), inhalation (irritant) and swallow. Furthermore potassium dichromate is a strong oxidising agent reacts vigorously or explosively with wide variety of reducing agents.

Some safety and precautions steps are required to follow when performing the COD analysis,

- Always wear safety glasses and glove while performing tests.
- Ensure working environment is well ventilated.
- Ensure any spills are cleaned up without any delay.
- Dispose unused chemical in appropriate lab manner after used.
- Rinse with running water immediately in case of skin or eye contact.

Other safety information can be referred to Material Safety Data Sheet (MSDS) Chemical Safety Data: Potassium Dichromate as attached in appendices.

3.2.2.2 Materials and Apparatus

Main equipments required to perform this analysis tests were DRB200 Reactor and DR2800 spectrophotometer. DRB200 reactor served to heat up the wastewater sample to 150 °C for 2 hours, and COD concentrations were measured by using DR2800 Spectrophotometer. Other materials and apparatus are listed as follows:

- Beaker (250 ml)
- COD digestion reagent vials
- Magnetic Stirrer and stir bar
- Opaque shipping container for storage of unused
- Pipet, Tensette ®, 0.1 to 1.0 mL, with tips (for 200-15000 mg/L range)
- Test Tube Rack

3.3 Kinetics Model Formulation

Kinetic modelling is an interest exercise that used for design, prediction and control purposes for a digestion system (Lyberatos and Skiadas, 1999; Gavala et al., 2003). Experimental data obtained from the batch digestion studies were fitted into four models namely, Monod model, First model, Diffusional and Singh Model.

3.3.1 Monod Model

$$-\frac{dC_s}{dt} = \frac{k_1 C_s}{K_s + C_s} \quad (3.1)$$

$$\frac{1}{r} = \frac{1}{\frac{dC_s}{dt}} = -\left(\frac{K_s}{K_1}\right) \left(\frac{1}{C_s}\right) - \frac{1}{K_1} \quad (3.2)$$

where K_s , K_1 and C_s correspond to half saturated constant of Monod's equation (mg COD/L), the product of maximum specific degradation rate and biomass

concentration (mg COD/ L-h), and substrate concentration (mg COD/L), respectively, while the term $\frac{dc_s}{dt}$ represents the substrate degradation (mg COD/L-h).

3.3.2 First Order Model

The First order model is given by,

$$-\frac{dc_s}{dt} = k_1 C_s \quad (3.3)$$

On integration between known limits, the model can be written as

$$\ln\left(\frac{C_s}{C_{s0}}\right) = -k_1 t \quad (3.4)$$

The terms C_{s0} , C_s and t correspond to initial substrate concentration (mg COD/L), substrate concentration (mg COD/L), and degradation time (h) respectively. This equation is used to determine first order constant, k_1 (h^{-1}).

3.3.3 Diffusional Model

The diffusional model is given by,

$$-\frac{dc_s}{dt} = k_D C_s^{0.5} \quad (3.5)$$

When integration with known limits, the above equation becomes

$$\sqrt{C_s} - \sqrt{C_{s0}} = \frac{k_D}{2} t \quad (3.6)$$

where k_D ($\text{mg COD}^{0.5}/\text{L}^{0.5}\text{h}$) is rate constant for Diffusional model .

3.3.4 Singh Model

The Singh Model is given by,

$$-\frac{dC_s}{dt} = \frac{k_{Si}C_s}{1+t} \quad (3.7)$$

Integrating the above equation between proper limits, it becomes

$$\ln \frac{C_s}{C_{s0}} = -k_{Si} \ln(1+t) \quad (3.8)$$

where $k_{Si} (\text{h}^{-1})$ is rate constant for Singh Model.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Comparison of pH and DO in Three Systems

The changes of pH and DO of synthetic wastewater in three systems is given in Figure 4.1. Initially, pH values of the synthetic wastewater were adjusted to about pH 7.40. Three systems: aerobic, anaerobic and combined system started off in neutral conditions at the beginning of the experiments.

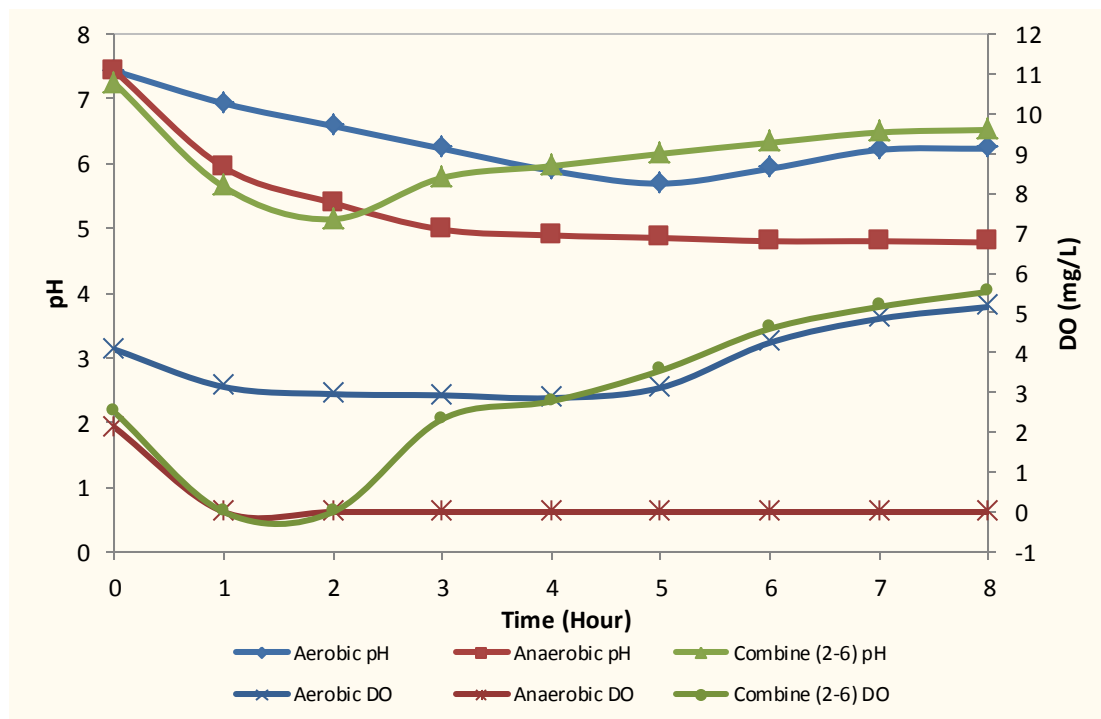


Figure 4.1: pH and DO Profiles for Three Systems

Initially pH value in the aerobic digester was decreased slowly until it reached pH 5.69. However, the pH value increased slowly after fifth hour of digestion. The change of pH in the aerobic digestion was mainly due to nitrification and denitrification activities. Metcalf and Eddy (1991) stated that optimum pH ranges for both nitrification and denitrification activities: pH 7.5 to 8.5 favoured nitrification and pH 6 to 8 for denitrification activity. Based on Figure 4.1, nitrification activity occurred in five hours from the beginning of aerobic digestion which consumed alkalinity (Grady et al., 1999) and decreased pH; it converted nitrite and nitrate in the presence of high DO conditions. Theoretically denitrification occurs under a low DO condition which reduces nitrate acids to nitrogen gas. However, both pH and DO profile were increased after fifth hour of digestion. This can be explained due to completely removal of NH_4^+ , therefore the consumption of DO by nitrifiers to oxidise NH_4^+ decreased. Although NH_4^+ concentration was not measured throughout this experiment, this phenomenon was, however, supported by Hassimi et al. (2010).

Furthermore, decrease in pH can also be caused by production of CO_2 as it will dissolve in water to form carbonic acid (H_2CO_3). Theoretically, pH in aerobic digester is more alkaline than anaerobic digester (O'Keefe and Chynoweth, 2000; Kim, 2005) because CO_2 will be stripped by air. This decrease in CO_2 will leads to decrease of the H_2CO_3 and bicarbonate ion concentrations (HCO_3^-) consuming H^+ ions (Kim, 2005). In comparison to aerobic digestion, the pH value in anaerobic digester decreased more rapidly until it achieved almost constant value at pH 4.8. Furthermore, a complete anaerobic process required to undergo four stages as mentioned in Chapter 2, product form from each stage will cause the pH of leachate to change. In fact last stage of anaerobic process, methanogenesis, will neutralise the acids produced from acidogenesis and acetogenesis by converting acetic acid, propionic acid and volatile fatty acid (VFA) to final product of methane and carbon dioxide gas. Nevertheless, Lay et al. (1997) proposed that methanogenesis rate would decrease at pH lower than 6.3, as low pH would inhibit methanogens and cause organic acids accumulate in the digester which would probably lead to a failure system. However, the pH profile that shown in Figure 4.1 is still reasonable to be obtained from a non-failure anaerobic system. According to the research performed

by Erses et al. (2008), the pH value in the anaerobic digester remained at about 5.0 when treated with municipal solid waste. After certain period of time, transition from acetogenic to methanogenic condition would occur and VFA would be utilised as substrate, and hence the pH would increase again. Metcalf and Eddy (1991) also suggested methanogen are strict anaerobes, hence their metabolism considered rate-limiting and long detention time is required. It is believed that the anaerobic system in this experiment still remained in acidogenesis and acetogenesis condition during the eight hours of digestion.

In combined system, the pH of synthetic wastewater dropped drastically when it was treated in the anaerobic digester for two hours, and then the pH increased rapidly when treated in the aerobic digester. As discussed, CO₂ produced would be dissolved and formed H₂CO₃ and other acids might be formed during the anaerobic digestion. After synthetic wastewater was transferred to aerobic digester, CO₂ was purged out by aeration and VFA would be utilised as substrate. Throughout the aerobic processes the pH remained at 6.52, and hence denitrification was favoured and less DO was consumed.

4.2 Reduction of COD and BOD in Three Systems

Chemical oxygen demand (COD) is adopted as indicators of synthetic wastewater organic strength. The COD concentrations of the synthetic wastewater for three systems are presented in Figure 4.2. The initial concentrations of COD for all the systems were similar 2100 mg/L. The COD concentration in the aerobic digester decreased drastically within eight hours of digestion if compared to that in the anaerobic digester. This result showed that aerobic digestion had higher digestion rate of 191.3 mg COD/L-h (Table 4.1), when compared with the anaerobic digestion rate of 96.3 mg COD/L-h. It is proposed that anaerobic digestions are limited to fermentation process, where higher organic compound will be reduced to lower organic (e.g. methane and carbon dioxide) through this process (Buchanan and Seabloom, 2005). However, the aerobic digestion will undergo additional respiration

process instead of fermentation process. Through this respiration, aerobic microorganism can further transform volatile fatty acids and other organics compound to bio-energy, which is required to produce more cells (Lehninger, 1973). This process is also referred as biosynthesis. Therefore, more cells are produced through aerobic digestion compared with through anaerobic digestion. As these new cells will also undergo fermentation and respiration, the digestion rate is also greater. This theory has been supported by Aivasidis and Diamantis (2010), as 30-50% of COD was converted to activated sludge in aerobic digestion and only 5% in anaerobic digestion.

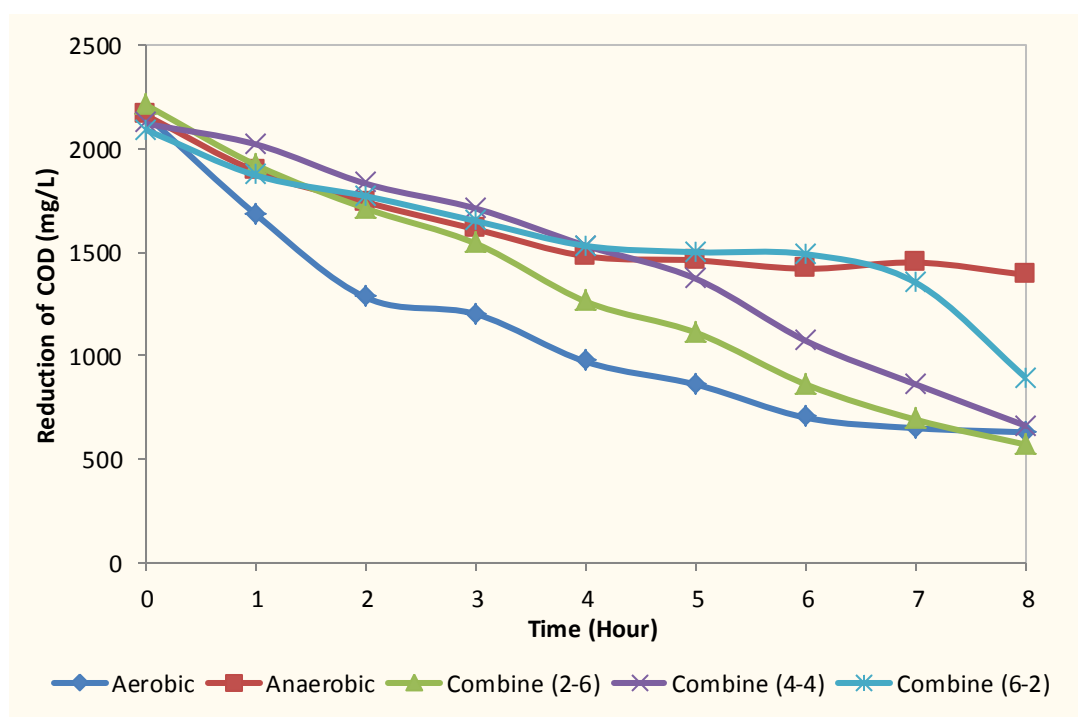


Figure 4.2: COD Concentration of Synthetic Wastewater for Three Systems

Table 4.1: COD Removal Rate and Efficiency for Three Systems

Treatment	Present Study		Leal (2010)*	
	Rate (mg/L-h)	Efficiency	Rate (mg/L-h)	Efficiency
Aerobic	191.3	70.83%	62.5	90%
Anaerobic	96.3	35.65%	33.4	59%
Combine (2-6)	205.0	74.21%		
Combine (4-4)	182.5	68.87%	58.4	89%
Combine (6-2)	150.0	57.42%		

*SBR and UASB operated at HRT 12 hours in treating grey water. Combine system consists of a sequence of UASB and SBR operated at HRT of 7 hours and 6 hours respectively and temperature of $32\pm 2^{\circ}\text{C}$.

In addition, anaerobic digestion achieved lower COD removal efficiency of 35.65% compared with aerobic digestion of 70.83%. As mentioned previously, the anaerobic is limited to fermentation activity, as nutrients (e.g. phosphorus and ammonia) are only consumed in the respiration process (Heijnen, 1991). Therefore, the effluent from the anaerobic digestion often contains ammonium ions (NH_4^+) and hydrogen sulphide (HS^-) which then contribute to the COD level. Although the concentration of ammonium ions was not measured in this experiment, this explanation has been practically proved by Leal (2010) and the result is attached in Appendices C. Based on this result, there is no reduction of ammonium ions in the effluent of the UASB reactor.

In combined anaerobic-aerobic system, the 2-6 combine system achieved the highest COD removal efficiency (74.21%), followed by 4-4 (68.87%) and 6-2 (57.42%) systems. This trend can be explained as the anaerobic digestion has lower digestion rate compared to the aerobic digestion rate. The COD removal rate dropped slowly when treated in anaerobic digester but dropped drastically after transferred to aerobic digester as shown Figure 4.2. Therefore, it can be concluded that the longer the synthetic wastewater was treated in the anaerobic digester the lower COD removal efficiency. In comparison with single digestion, the 6-2 combined system had the highest COD removal efficiency followed by aerobic digestion. This was probably due to the fact that the complex organic compounds were broken down to volatile fatty acids (VFA) which could be easily digested by subsequent aerobic

process (Gray, 2005). Furthermore, other combined systems also presented higher COD removal efficiency than anaerobic digestion.

According to Leal (2010), the COD removal rates were 62.5, 33.4 and 58.4 mg/L-h for aerobic, anaerobic and combined system, respectively. In comparison to this study, the removal rates reported by Leal (2010) were three times lower. This is because grey water contains large amount of colloidal COD as shown in Table 4.2. It is known that colloidal fraction of COD is poorly removed, especially in the UASB because it cannot be entrapped and flocculated in the sludge bed, and hence longer hydraulic retention time (HRT) is required to digest colloidal COD. This phenomenon was also supported by Elmitwali et al. (2000). However, the synthetic wastewater employed in this study did not contain colloidal COD. Thus, it is expected that the removal rate was quicker to digest the soluble COD. Despite the lower removal rate, the removal efficiency from Leal's study (2010) is higher than that in the present study. This could be due to the longer HRT (12 h) in Leal's study which was greater than the duration employed in this study. Nevertheless, both studies also showed that the combined system did not possess any advantages over aerobic digestion, if compared in term of removal efficiency and digestion rate. In fact, it should be highlighted that the combined system has advantages of methane and low sludge production.

Table 4.2: Characteristics of Grey Water (Reference: Leal, 2010)

	Concentration (mg/L)
COD _{total}	833
COD _{suspended}	411
COD _{colloidal}	204
COD _{soluble}	224
Anionic surfactants	
Total N	41.2
NH ₄ -N	1.0
NO ₃ -N	0.12
Total P	6.6

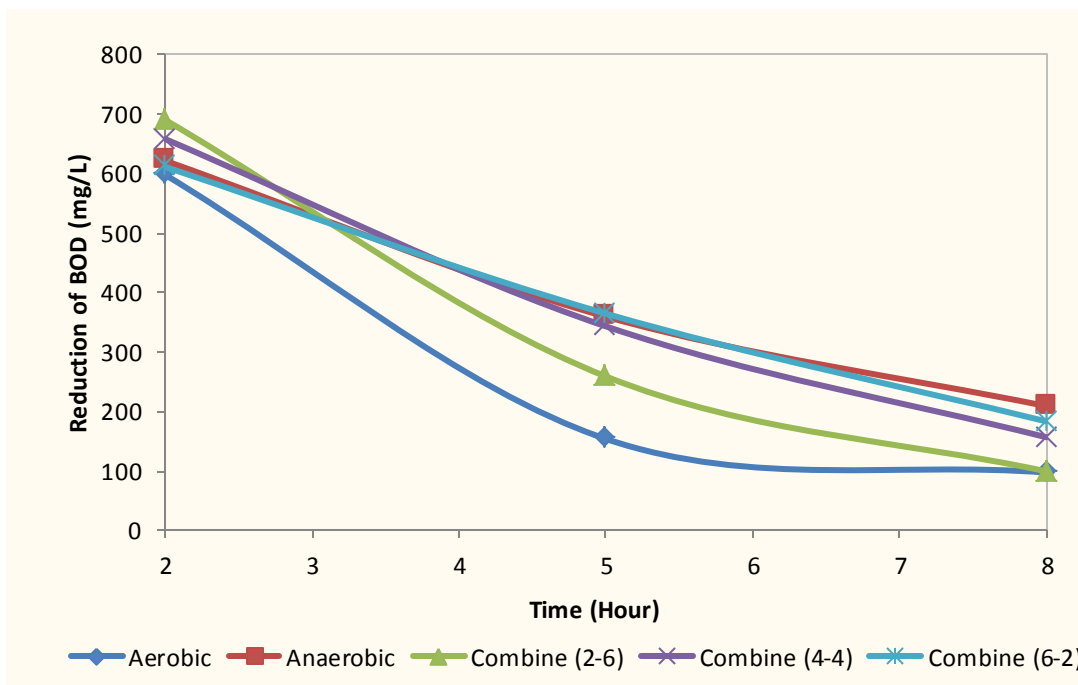


Figure 4.3: BOD₅ Concentration of Synthetic Wastewater for Three Systems

The BOD₅ removal depicted similar trend with COD removal (Figure 4.2). The BOD₅ concentration of aerobic digestion decreased rapidly and reached almost constant after five hours of digestion, while BOD₅ concentration in anaerobic digester decreased slowly and showed the highest BOD₅ concentration after eight hours of digestion in comparison with other digestion systems. The 2-6 combined system had the highest BOD removal efficiency of 85.59%, followed by aerobic digestion, 4-4 combined system, 6-2 combined system and anaerobic digestion, which were 83.70%, 76.17%, 69.99% and 66.35% respectively. The 2-6 combined system was found to have optimum removal efficiency among all the combined systems, and hence it was maintained for further study in section 4.3.

4.3 Effect of Initial COD Concentration in Three Systems

The initial COD concentration of wastewater was varied to give approximately 1420, 2160, 3330 and 4020 mg/L, and then treated in aerobic, anaerobic and 2-6 combine system. The COD concentration profiles of these three systems are shown in Figure 4.4 (a)-(c).

Figure 4.4 (a) revealed that the higher initial COD concentrations (4020, 3330 and 2160 mg/L) led to faster drop in the COD level in the aerobic digestion at the early stage. On the other hand, it took longer to degrade the COD when the initial COD concentration was 1420 mg/L. It was also found that the aerobic digestion could remove 70 – 80% of COD for different initial concentrations (Table 4.3). The COD reduction trend in Figure 4.4 (b) possessed the similar pattern as aerobic digestion; however, the COD removal efficiency in anaerobic digestion was 35 –50% only. Both of the results obtained for aerobic and anaerobic in this study were similar to the findings from Magnaye (2009), Ping Zhou (2004), and Miquesleto (2004). In the 2-6 combined system, the COD degraded slowly in anaerobic digester, but it degraded rapidly in aerobic digester as illustrated in Figure 4.4 (c). The removal efficiency was 60-78% in the 2-6 combined treatment.

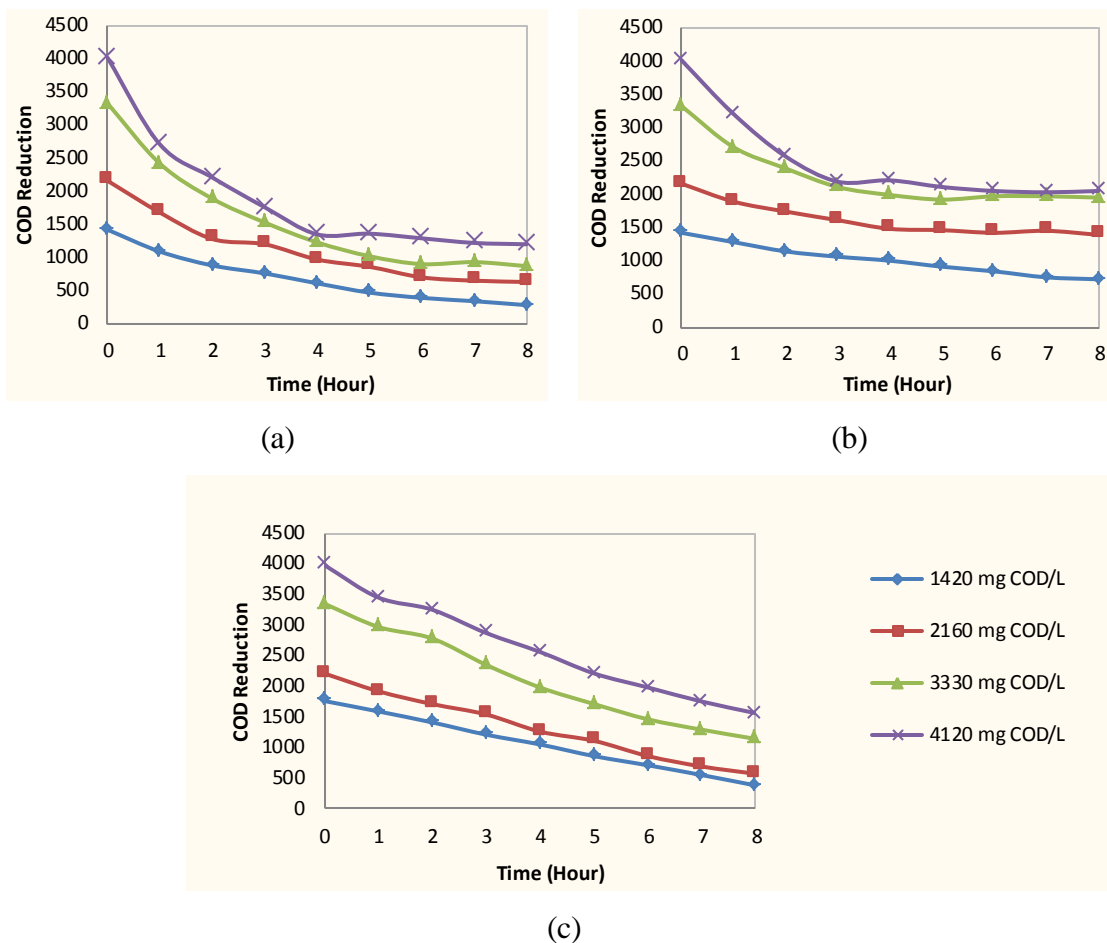


Figure 4.4: Effect of Initial COD Concentration in (a) Aerobic Digestion, (b) Anaerobic Digestion, (c) 2-6 Combined Digestion

Table 4.3: COD removal (%) for Different Initial Concentration in Three Systems

Initial COD concentration (mg/L)	COD removal (%)		
	Aerobic	Anaerobic	2-6 Combined
1420	80.28	49.30	78.41
2160	70.83	35.65	74.21
3330	73.87	41.44	65.97
4120	70.15	49.00	60.80

4.4 Kinetics Studies

4.4.1 Monod Model

The experimental values were used to determine the parameters and to verify the performance of the Monod model. Monod kinetic model is considered as the function relationship exists between the specific growth and the essential substrate. Plot of $(dC_s/dt)^{-1}$ versus $1/C_s$ for various initial COD concentration in different digestion systems are plotted in Figure 4.5.

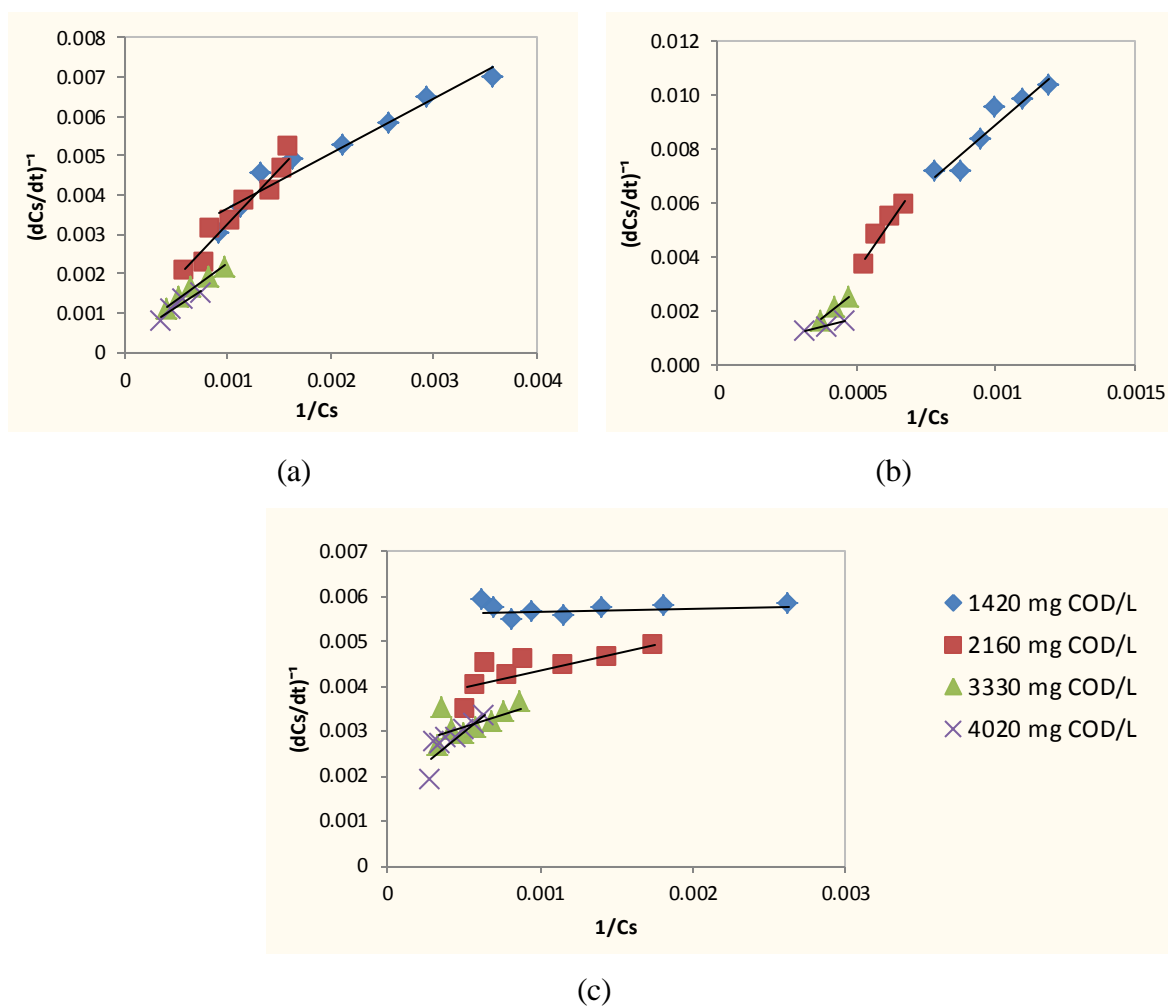


Figure 4.5: Monod Model in (a) Aerobic Digestion, (b) Anaerobic Digestion, (c) 2-6 Combined Digestion

Table 4.4: Kinetic Parameters for the Monod Model in Three Systems

Digestion Scheme		Initial COD concentration (mg/L)			
		1420	2160	3330	4020
Aerobic	K_I (mg COD/L h)	-500	-10000	-20000	1000
	K_s (mg COD/L)	-695.5	-28480	-36960	4863
	R^2	0.94	0.94	0.99	0.97
Anaerobic	K_I (mg COD/L h)	-100000	333.33	1000	-10000
	K_s (mg COD/L)	886100	-4906.7	-8020	27660
	R^2	0.90	0.95	0.98	0.96
2-6	K_I (mg COD/L h)	-200	-333.33	-500	-1000
Combined	K_s (mg COD/L)	12.4	259	509.5	2769
	R^2	0.09	0.61	0.37	0.69

Based on Table 4.3, the kinetic parameters, K_I and K_s , for aerobic and anaerobic digestions were inconsistent. Therefore, the operating conditions were unpredicted, even though the determination coefficient, R^2 , indicated value more than 0.9. The R^2 values for the 2-6 combined system were generally lower than 0.9, in other words, the experimental data obtained did not fit into the Monod kinetic model. In the combined system, the product of maximum specific degradation rate and biomass concentration, K_I , decreased as the initial COD concentration increased, while half saturated constant, K_s , increased as the initial COD concentration increased.

4.4.2 First Order Model

The First Order model was applied to the experimental data to verify the performance of the model. The results of $\ln(C_s/C_{s0})$ versus time were plotted for various initial substrate concentrations (Figure 4.6). It is found that the R^2 values larger than 0.9 for all cases. The values of rate constants in the First Order model were found to increase in general with the increase in the initial COD concentration for both aerobic and anaerobic digestion, except for initial COD concentration of 1420 mg/L in aerobic digestion. This was probably because the aerobic degradation rate was faster for initial COD concentration of 1420 mg/L if compared with initial COD concentration of 2160 mg/L. Nevertheless, the k_I value decreased as initial

COD concentration increased for 2-6 combined digestion. This was in agreement with the results of Saravanan and Lakshmanan (2008).

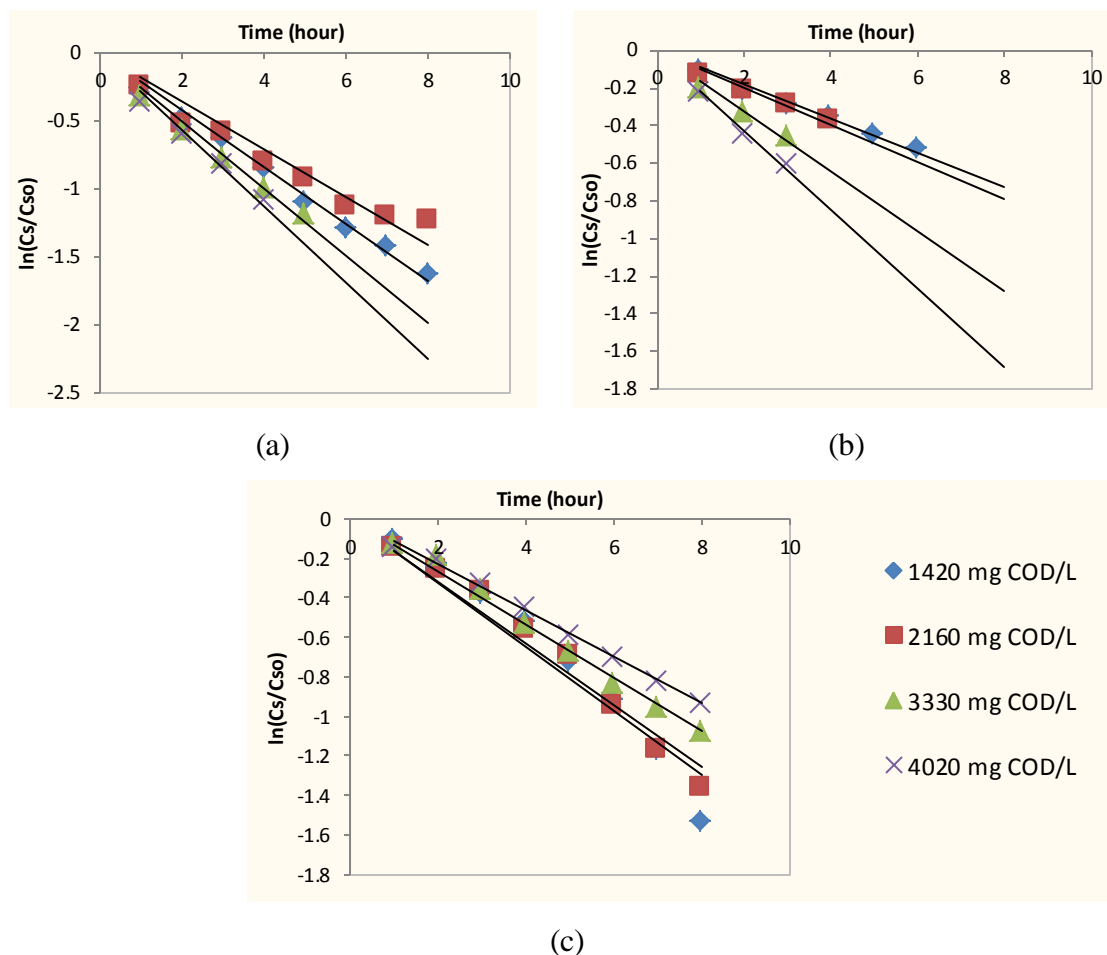


Figure 4.6: First Order Model in (a) Aerobic Digestion, (b) Anaerobic Digestion, (c) 2-6 Combined Digestion

Table 4.5: Kinetic Parameters for the First Order Model in Three Systems

Digestion Scheme		Initial COD concentration (mg/L)			
		1420	2160	3330	4020
Aerobic	k_I (h^{-1})	0.209	0.175	0.248	0.280
	R^2	0.99	0.90	0.97	0.96
Anaerobic	k_I (h^{-1})	0.09	0.098	0.159	0.210
	R^2	0.98	0.94	0.91	0.98
2-6 Combined	k_I (h^{-1})	0.163	0.157	0.134	0.116
	R^2	0.93	0.97	0.99	0.99

4.4.3 Diffusional Model

The experiment data were plotted for the Diffusional model (Figure 4.7). The values of the rate constant and R^2 values are presented in Table 4.6.

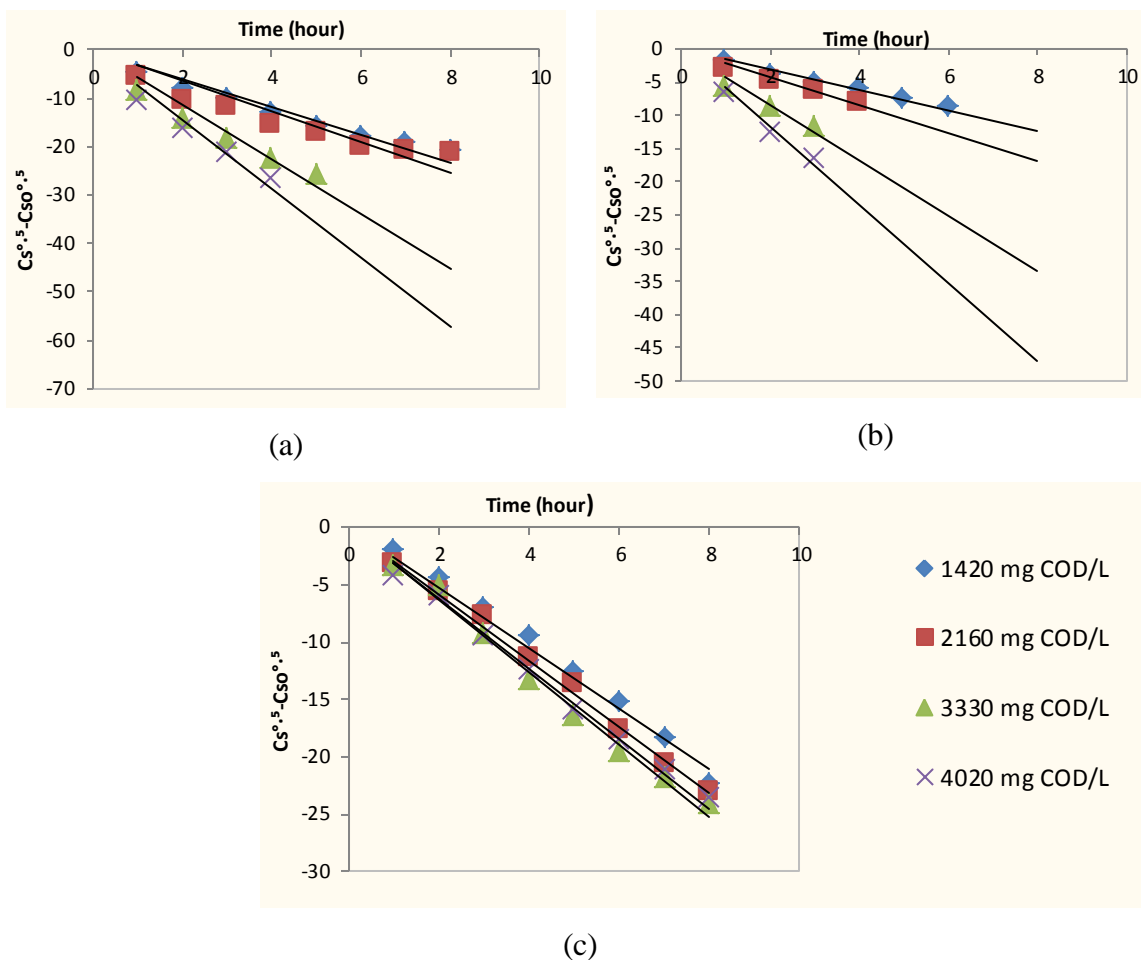


Figure 4.7: Diffusional Model in (a) Aerobic Digestion, (b) Anaerobic Digestion, (c) 2-6 Combined Digestion

Table 4.6: Kinetic Parameters for the Diffusional Model in Three Systems

Digestion Scheme		Initial COD concentration (mg/L)			
		1420	2160	3330	4020
Aerobic	k_D (mg COD ^{0.5} /L ^{0.5} h)	-2.906	-3.149	-5.575	-7.148
	R^2	0.91	0.84	0.79	0.85
Anaerobic	k_D (mg COD ^{0.5} /L ^{0.5} h)	-1.529	-2.135	-4.185	-5.855
	R^2	0.95	0.88	0.84	0.95
2-6 Combined	k_D (mg COD ^{0.5} /L ^{0.5} h)	-2.621	-2.886	-3.061	-3.151
	R^2	0.99	0.99	0.99	0.99

The Diffusional model failed miserably in representing both aerobic and anaerobic digestion of synthetic wastewater due to poor R^2 value obtained. However, the COD reduction profile in combined digestion was well explained by the Diffusional model with high values of R^2 (0.99) for all initial COD concentrations. It was also found that the diffusional constant, k_D , decreased as initial COD concentration increased.

4.4.4 Singh Model

The experimental data were plotted for Singh model and are shown in Figure 4.8. From the best-fit lines, the value of rate constant and R^2 were found and they are listed in Table 4.7. Both aerobic and anaerobic digestions were considered to satisfy the Singh model with R^2 approximately to 0.9. The rate constants for both digestions were found to be increased as initial COD concentration increased; except for 1420 mg/L as shown in Table 4.7. This is probably due to greater concentration of biomass inside digester while performing this experiment hence degradation rate was faster in comparison with 2160 mg/L. In addition, low R^2 value shows that inability of this model in describing degradation of synthetic wastewater in combined digestion system.

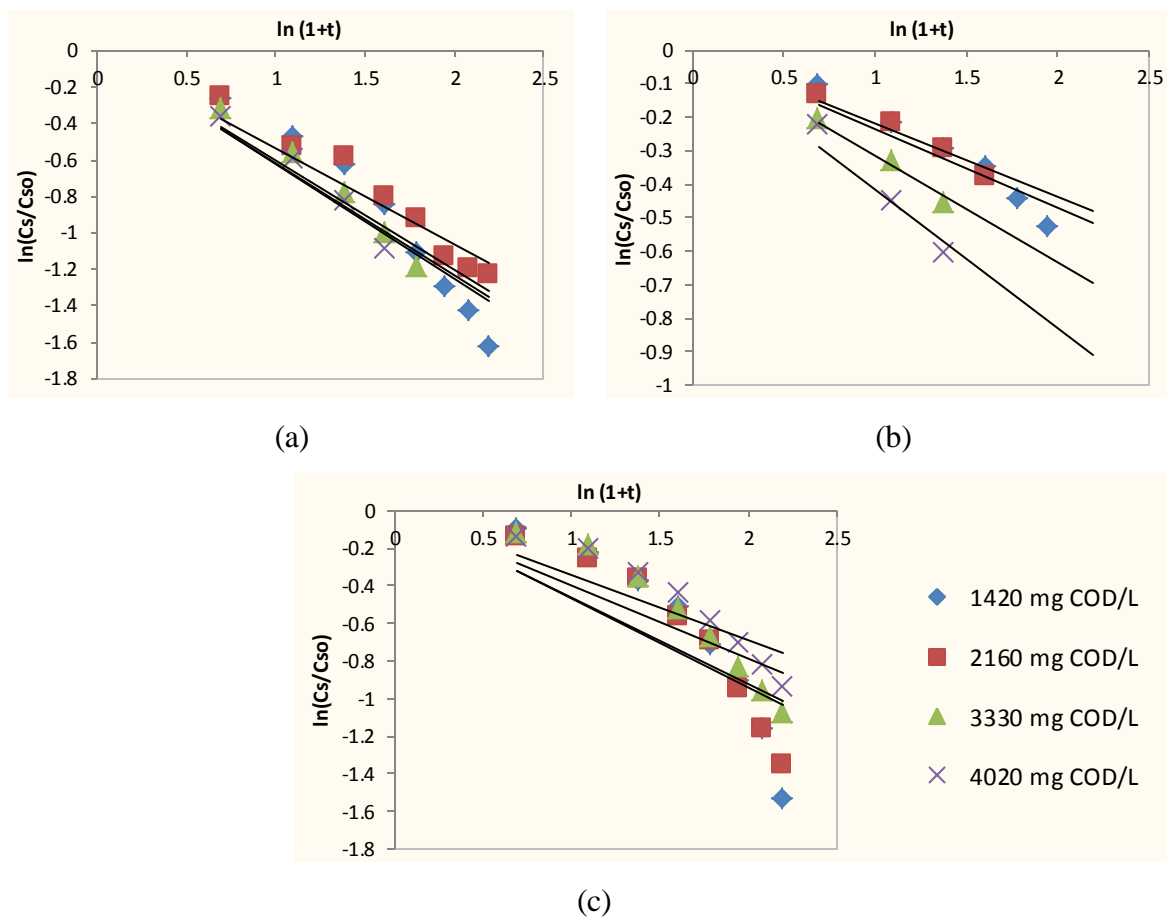


Figure 4.8: Singh Model in (a) Aerobic Digestion, (b) Anaerobic Digestion, (c) 2-6 Combined Digestion

Table 4.7: Kinetic Parameters for the Singh Model in Three Systems

Digestion Scheme		Initial COD concentration (mg/L)			
		1420	2160	3330	4020
Aerobic	k_{sj} (h^{-1})	0.625	0.526	0.587	0.615
	R^2	0.85	0.90	0.95	0.93
Anaerobic	k_{sj} (h^{-1})	0.235	0.219	0.315	0.412
	R^2	0.89	0.97	0.98	0.93
2-6 Combined	k_{sj} (h^{-1})	0.470	0.459	0.394	0.343
	R^2	0.66	0.72	0.77	0.79

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the experiments performed in three different biodegradation schemes, the following conclusions were established:

- a) The pH in aerobic digester was more alkaline than anaerobic digester after 8 hours of digestion process as CO₂ produced was stripped by aeration in aerobic digester, while anaerobic digestion was essentially stopped at acetogenesis and acidogenesis processes, whereby volatile fatty acids (VFA) was produced without being consumed by methanogenic bacteria. The study on pH and DO profiles would be related in aerobic digestion due to nitrification and denitrification activities.
- b) The 2-6 combined system achieved the highest COD and BOD efficiencies because VFA produced in anaerobic digestion could be easily digested by the subsequent aerobic digestion. Aerobic digestion had higher COD and BOD removal efficiencies and rates if compared with anaerobic digestion as anaerobic process underwent fermentation activity only instead of respiration activity. However, other combined scheme had lower COD and BOD removal efficiencies and rates than aerobic digestion owing to slow degradation rate occurred in anaerobic digestion as pre-treatment.

- c) Aerobic digestion had 70 – 80% of COD removal efficiency when treated with various initial COD concentrations of synthetic wastewater, while anaerobic digestion achieved 35 – 50% and 2-6 combined schemes achieved 60 – 78%. Consequently, it can be concluded that the combined system did not possess any advantage over aerobic digestion in terms of COD removal.
- d) Three of the digestion schemes did not fit with the Monod Kinetics Model. However, both aerobic and anaerobic fitted well with the First Kinetics Model and Singh Model, while the 2-6 combined schemes would be described nicely using Diffusional Model and Singh Model.

5.2 Recommendations and Future Studies

There are three criteria to be compared in three digestion systems, which are COD removal efficiency, sludge yield and bio-gas production. In fact, sludge yield and bio-gas production were unable to be measured in this study due to limitation setup of existing apparatus. Therefore, it is proposed that further investigation of these two criteria can be carried out in anaerobic digestion by using fluidised reactor (e.g. UASB) instead of the fixed bed reactor that used in this study. A well-mixed wastewater that contains sludge can be obtained from UASB, and hence total suspended solids (TSS) or volatile suspended solid (VSS) test can be performed. Biogas can be collected and analysed, thus the recovery can be compared in terms of anaerobic digestion and combined anaerobic-aerobic digestion.

In addition, other analysis tests are suggested to be performed throughout the digestion process such as total kjhedal nitrogen (TKN), ammonia-chloride (NH_4Cl), orthophosphate, and alkali metals (e.g. Na, K, Ca, Mg). Therefore, a complete nutrient degradation profiles can be obtained and studied. These analysis tests are very important when comparing the performance and operating conditions (pH and DO) in aerobic and anaerobic digestions.

Furthermore, the study on different operating conditions can be performed. For example, different operating temperatures will cause different COD degradation rates, efficiencies and biological activities. The operation temperature level can be divided into Psychrophilic ($< 20^{\circ}\text{C}$), Mesophilic ($20 - 50^{\circ}\text{C}$) and Thermophilic ($50 - 70^{\circ}\text{C}$). In fact, each temperature level is used to serve for different purposes. Thermophilic temperature may pasteurize the biomass reducing the content of pathogenic organisms (Drier and Obma, 1963) and better effluent quality, while Mesophilic temperature tends to provide better operational control and lower energy is required for heating. Therefore, it is suggested that optimum temperature level can be investigated when treating with synthetic wastewater. Other operating parameters include pH, alkalinity, oxidation rate and retention time can be varied in order to obtain optimum operating conditions.

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APPENDICES

APPENDIX A: MSDS Sheet

Chemical Safety Data: Potassium dichromate



Common synonyms	None
Formula	$K_2Cr_2O_7$
Physical properties	Form: orange-red crystalline solid Stability: Stable Melting point: 398 C Boiling point: 500 C Specific gravity: 2.68
Principal hazards	<ul style="list-style-type: none"> • Potassium dichromate is toxic if swallowed, inhaled or absorbed through the skin. It is corrosive and may produce severe eye damage. • Chromium (VI) compounds are carcinogens. • Potassium dichromate may act as a sensitizer. • This material is a strong oxidizing agent and reacts vigorously or explosively with a wide variety of reducing agents.
Safe handling	Wear safety glasses and gloves. Work in a well ventilated area, preferably using a fume cupboard. Ensure that any spills are cleaned up without delay. "Chromic acid" baths, which were once widely used for cleaning glassware, should not be used unless (a) there is no alternative available for cleaning, and (b) a suitable procedure has been determined BEFORE work starts for disposing of waste. Note that, since chromium (VI) is a carcinogen, used chromic acid cannot be disposed of down the drains. Chromic acid is, in any case, a very dangerous material and should not be used unless it is absolutely necessary.
Emergency	<p>Eye contact: Immediately flush the eye with water. Call for medical help.</p> <p>Skin contact: Wash off with soap and water.</p> <p>If swallowed: Call for medical help.</p>
Disposal	Store for later disposal as solid waste. Ensure that the container is marked both with the name of the chemical and a statement that it is a strong oxidizer and a carcinogen.
Protective equipment	Safety glasses, gloves.

APPENDIX B: Sample Calculations

1. BOD Concentration (mg/L)**Table 1: Dissolve Oxygen (DO) in Aerobic Digestion**

Time (h)	Sample Wastewater Volume (mL)	DO _f (mg/L)	DO _i (mg/L)	BOD ₅ (mg/L)	Average (mg/L)
	0.5	7.35	8.06	424.56	
2	1	5.72	7.88	648.52	597.92
	2	3.02	7.82	720.68	
	1	7.49	7.78	87.02	
5	2	7.29	8.02	109.89	154.15
	5	3.29	7.72	265.56	
	2	7.23	7.88	96.78	
8	5	6.46	8.24	106.56	97.59
	10	5.12	8.10	89.45	

By referring to the column of 2 hours and sample wastewater of 0.5 mL:

$$\begin{aligned}
 BOD_5 &= \frac{DO_i - DO_f}{\frac{\text{Sample wastewater volume}}{\text{Total volume}}} \quad , \text{ where} \\
 &= \frac{8.06 \text{ mg/L} - 7.35 \text{ mg/L}}{\frac{0.5 \text{ mL}}{300 \text{ mL}}} \quad DO_i = \text{Initial Dissolve Oxygen} \\
 &= 424.56 \text{ mg/L} \quad DO_f = \text{Dissolve Oxygen after 5 days}
 \end{aligned}$$

Average of BOD₅ for 2 hours of digestion in aerobic:

$$\begin{aligned}
 BOD_5 &= \frac{424.56 + 648.52 + 720.68}{3} \\
 &= 597.92 \text{ mg/L}
 \end{aligned}$$

2. COD Removal Efficiency (%) and Rate (mg/L-h)

Table 2: COD Reduction for Three Digestion System

Hour	COD (mg/L)		
	Aerobic	Anaerobic	Combine (2-6)
0	2160	2160	2210
1	1680	1890	1920
2	1280	1740	1710
3	1200	1610	1540
4	970	1480	1260
5	860	1460	1110
6	700	1420	860
7	650	1450	690
8	630	1390	570

By referring to Aerobic Digestion:

$$\begin{aligned}
 \text{COD Removal Efficiency} &= \frac{COD_{t_o} - COD_{t_f}}{COD_{t_o}} \times 100\% && , \text{ where} \\
 &= \frac{2160 \text{ mg/L} - 630 \text{ mg/L}}{2160 \text{ mg/L}} \times 100\% && COD_{t_o} = \text{Initial COD concentration} \\
 &= 70.83\% && COD_{t_f} = \text{Final COD concentration}
 \end{aligned}$$

$$\begin{aligned}
 \text{COD Removal Rate} &= \frac{COD_{t_o} - COD_{t_f}}{t} && , \text{ where} \\
 &= \frac{2160 \text{ mg/L} - 630 \text{ mg/L}}{8 \text{ h}} && t = \text{Time for digestion} \\
 &= 191.3 \text{ mg/L} \cdot \text{h}
 \end{aligned}$$

APPENDIX C: Results of Grey Wastewater Treatment (Reference: Leal, 2010)

Table 3.3: Operation and performance of biological reactors for grey water treatment.

	SBR 12 (aerobic system)	SBR6	UASB12 (anaerobic system)	UASB7	UASB7 + SBR6 (anaerobic-aerobic system)
HRT (h)	11.7 ± 1.1	6.1 ± 0.8	12.3 ± 1.8	7.0 ± 2.0	13.17 ± 2.03
VLR (kg CODm ³ d ⁻¹)	1.6 ± 0.5	1.9 ± 0.4	1.7 ± 0.4	2.7 ± 0.8	1.5 ± 0.6
COD removal rate (kg CODm ³ d ⁻¹)	1.5 ± 0.4	1.5 ± 0.4	0.8 ± 0.3	1.1 ± 0.6	1.4 ± 0.5
SLR (kg COD (kg VSS) ⁻¹ d ⁻¹)	0.29 ± 0.07	0.6 ± 0.3	0.12 ± 0.04	0.23 ± 0.08	**
Sludge concentration (g VSSL ⁻¹)	5.5 ± 1.1	3.3 ± 1.1	12.5 ± 2.4	12.7 ± 4.3	**
SRT (d)	15	379	392	97	**
Yield (kg VSS(kg COD) ⁻¹)	0.12	0.06	0.08	0.18	0.18
COD removal (%)	90 ± 7	82 ± 06	51 ± 13	39 ± 15	89 ± 3
COD effluent (mgL ⁻¹)	82 ± 47	100 ± 33	392 ± 85	528 ± 180	100 ± 33
Anionic surfactants (mgL ⁻¹)	1.4 ± 1.2	1.3 ± 1.5	33.4 ± 4.1	35.9 ± 5.3	1.3 ± 1.5
Effluent total N (mgL ⁻¹)	31 ± 20	26 ± 13	34 ± 17	32 ± 10	26 ± 13
Effluent NH4-N (mgL ⁻¹)	0.35 ± 0.20	0.4 ± 0.1	4.7 ± 2.1	5.4 ± 2.4	0.4 ± 0.1
Effluent NO3-N (mgL ⁻¹)	1.5 ± 1.4	22.6 ± 13.5	0.2 ± 0.1	0.2 ± 0.1	22.6 ± 13.5
Effluent total P (mgL ⁻¹)	4.4 ± 2.4	5.8 ± 1.7	5.3 ± 1.5	6.1 ± 1.7	5.8 ± 1.7
Effluent VSS (mgL ⁻¹)	45 ± 61	30 ± 26	7 ± 9	21 ± 23	30 ± 26
Removal total N (%)	35 ± 37	26 ± 27	15 ± 33	-1 ± 63	2 ± 56
NH4-N removal (%)	51 ± 47	92 ± 4	*	*	7 ± 86
Total P removal (%)	28 ± 50	31 ± 11	11 ± 28	1 ± 36	3 ± 44
Methane flow (NL d ⁻¹)	**	**	0.76	0.8	0.8
Methane production (NL m ⁻³)	**	**	123	71.5	71.5

* No ammonium removal

** Not applicable

APPENDIX D: Review on Anaerobic-aerobic Digestion using High Rate Reactor

(Reference: Chan et al., 2009)

No	Type ^a	Type of wastewater ^b	Influent COD (mg/L)	OLR ^c (kg COD/m ³ ·d)	Total COD removal (%)	Anaerobic COD removal (%)	Aerobic COD removal (%)	Total HRT ^d (h or d)	Anaerobic HRT ^d (h or d)	HRT ^d (h or d)
1	UASB + CSTR	Wool acid dyeing ww	499 -2000	-	83-97	51-84	-	3.3 d	17 h	-
2	UASB + CSTR	Cotton textile mill ww	604 -1038	-	40-85	9-51	-	5.75 d	30 h	4.5 d
3	UASB + CSTR	Simulated textile ww	4214	1.01-15.84	91-97	-	-	19.17-122 d	-	-
4	2 UASBs + CSTR	Food solid waste leachate	5400 -20000	4.3-16	96-98	58-79	85-89	5.75 d	1.25 d	4.5 d
5	UASB + CSTR	Pulp and paper industry effluent	5500 -6600	16	91	85	-	11.54 h	5 h	6.54 h
6	UASB + CSTR	Pharmaceutical industry ww	3000	3.6	97	68-89	71-85	-	-	-
7	UASB + AS	Olive mill ww + municipal ww	1800 -4400	3-7	95-96	70-90	>60	28.3 h	14.7 h	13.6 h
8	UASB + AS	Starch Industry ww	20000	15	-	77-93	64	5 d	1 d	4 d
9	UASB + AS	Municipal ww	386 -958	-	85-93	69-84	43-56	6.8 h	4 h	2.8 h
10	UASB + AFB	Synthetic textile ww	2000 -3000	-	-	-	-	2.7-32.7 h	1.4-20 h	1.3-12.7 h
11	UASB + AFB	Synthetic textile ww	2700	4.8	80	50	60	20 h	10 h	10 h
12	RBC + SBR	Mixture of cheese whey and dairy manure	37400 -65700	5.2-14.1	99	46.3-62.6	93-95	-	2-5 d	-
13	RBC + SBR	Screened dairy manure	39000 -40100	8.2-26.8	98	18.7-29	86-87	-	1-4 d	-
14	FFB + FFB	Slaughter house ww	400 -1600	0.39	92	-	-	4.7-7.3 d	1.2 d	3.5-6.1 d
15	EGSB + Aerobic biofilm reactor	POME	35000	10	95.6	93	22	-	3 d	-
16	UBF + MBR	Synthetic ww	6000 -14500	7.2	99	98	-	1 d	-	-
17	UASB + Aerobic solid contact system	Municipal ww	341	2.6	-	34	-	3.53-6.2 h	3.2 h	0.33-3 h
18	UASB + RBC	Domestic sewage	640	-	84-95	35-47	52-56	6-13.5 h	3-6 h	3-7.5 h
19	CSTR + Activated sludge	Green olive debittering ww	23500	0.47	83.5	37.4-48.9	73.6	55 d	50 d	5 d

APPENDIX E: Setup of This Study



Figure 1: Aerobic Digester



Figure 2: Anaerobic Digester

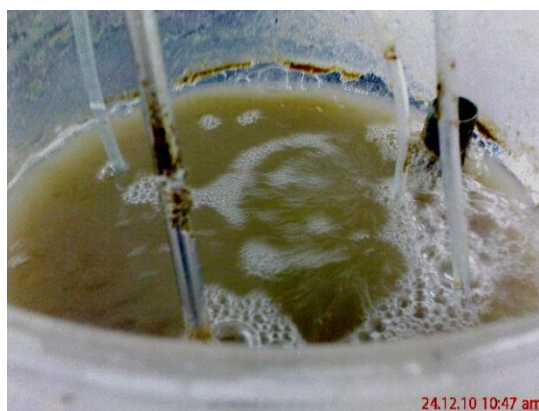


Figure 3: Aerobic Digestion



Figure 4: Anaerobic Digestion



Figure 5: Bio Balls Seeded with Anaerobic Sludge

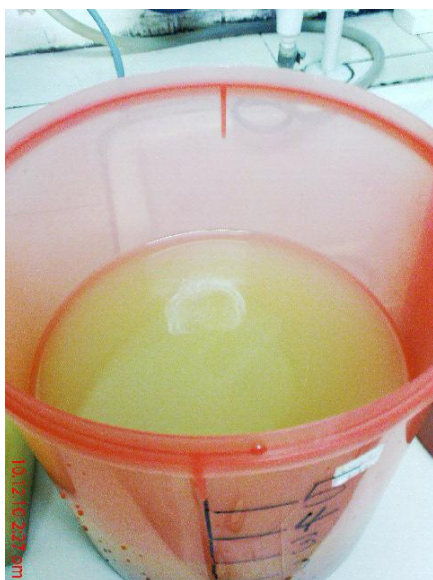


Figure 6: Aerobic Treated Wastewater



Figure 7: Anaerobic Treated Wastewater



Figure 8: Comparison between Aerobic and Anaerobic Treated Wastewater

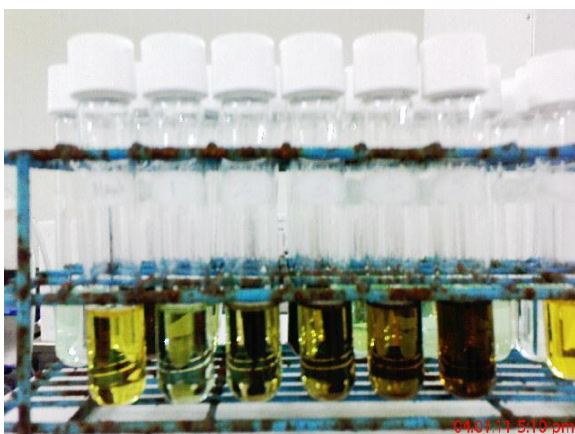


Figure 9: COD Analysis Tests

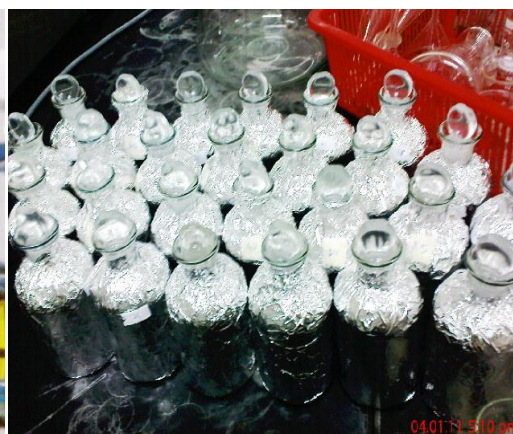


Figure 10: BOD Analysis Tests