

**ANAEROBIC CO-DIGESTION OF ABATTOIR AND TEXTILE
INDUSTRY WASTEWATER IN A UASB REACTOR.**

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DECLARATION

I hereby certify that this work is my own, except where otherwise acknowledged, and that it has not been submitted previously for a degree at this or any other university.

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DEDICATION

This M-Tech dissertation is dedicated to my loving parents Richard and Sabina Ondari. May God bless them and keep them safe and healthy.

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I thank God in a very special way for being with me every step of the way. I wouldn't have come this far without His grace and guidance. I thank my parents too whose encouragements and efforts made me feel comfortable and settled throughout my stay in South Africa.

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ABSTRACT

Textile industry effluents are carcinogenic and highly recalcitrant hence difficult to degrade especially through biological methods. Abattoir effluents are classified under high-strength wastewaters because of their characteristic high organic load hence highly biodegradable. Anaerobic co-digestion is the concept of degrading two effluent streams with complementary characteristics in order to improve the substrate removal rate. The feasibility of co-digesting abattoir and textile wastewater in a UASB reactor was evaluated at mesophilic and ambient temperature conditions.

Preliminary experiments were conducted in 500 ml batch reactors to evaluate the optimum abattoir to textile synthetic wastewater ratio. The effect of COD, TVFA, alkalinity and pH on biogas yield was examined at both ambient and mesophilic temperatures. Anaerobic co-digestion of abattoir to textile wastewater in the ratio determined in the batch process was carried out in a 3 L UASB reactor by a continuous process. The continuous biodegradation process was executed at three different HRTs (22, 18 and 14 hrs) over a 60 day operation period. UASB reactor efficiency was achieved at organic loads ranging from 3.0 – 10.8 gCOD L⁻¹ day⁻¹. Continuous mode experiments were carried out at influent flow rates which corresponded to HRTs ranging between 1 to 8 days in order to evaluate the steady state operating parameters for the co-digestion process.

The abattoir to textile effluent ratio was found to be 60:40 respectively. The COD, TVFA, alkalinity and pH and biogas yield followed a similar pattern over time at both mesophilic and ambient temperature conditions. Experimental data adequately fit the Grau first order kinetic model and average COD removal efficiencies of 85% and BOD₅ of around 96% were achieved. The average biogas yield remained essentially constant, around 0.19 L/g COD_{removed}. The co-digested mixture was found to be biodegradable judging from the BOD:COD ratio of 0.53. TCOD removal efficiency decreased from 93% to 16% as HRT decreased from 8 days to 1 day. The kinetics of a UASB reactor co-digesting the mixture of synthetic abattoir and textile wastewater was evaluated in this study using Grau second order multicomponent substrate removal kinetic model. The Grau second order kinetic model, whose kinetic coefficient (k_s) was 0.389, was found to be suitable for predicting the performance of a lab-scale UASB reactor.

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LIST OF ACRONYMS

ADMI	American Dye Manufacturing Institute
APHA	American Public Health Association
AW	Abattoir Wastewater
AWWA	American Water Works Association
B. Alk.	Bicarbonate Alkalinity (equivalent calcium carbonate)
BNR	Biological Nutrient Removal
BOD ₅	5 day Biochemical Oxygen Demand (mg/L)
CMC	Carboxymethyl Cellulose (mg/L)
COD	Chemical Oxygen Demand (mg/L)
EPA	Environmental Protection Agency
FBR	Fluidized Bed Reactor
FVWs	Fruit and Vegetable Wastewaters
HRT	Hydraulic Retention Time (days)
LGE	London Garment Expo
NTU	Nephelometric Turbidity Units
OECD	Organization for Economic Co-operation and Development
OLR	Organic Loading Rate (kg m ⁻³ day ⁻¹)
POME	Palm Oil Mill Effluent
SCOD	Soluble Chemical Oxygen Demand (mg/L)
SLR	Sludge Loading Rate (kg m ⁻³ day ⁻¹)
TA	Total Alkalinity (g/L)
TAA	Total Aromatic Amines (mg benzidine/L)
TCOD	Total Chemical Oxygen Demand (mg/L)
TDS	Total Dissolved Solids (mg/L)
TMA	Textile Management Associates
TOC	Total Organic Carbon (g/L)
TS	Total Solids (mg/L)
TSS	Total Suspended Solids (mg/L)
TVFA	Total Volatile Fatty Acids (mg/L)
TW	Textile Wastewater
UASB	Upflow Anaerobic Sludge Blanket
UK	United Kingdom
UNO	United Nations Organization
US-EPA	United States-Environmental Production Agency
VS	Volatile Solids (mg/L)
VSS	Volatile Suspended Solids (mg/L)
WEF	Water Environment Federation

LIST OF SYMBOLS

μ	Maximum growth rate of microbes (g/L d)
Alk.	Alkalinity
CaCO_3	Calcium Carbonate
E	Fractional Removal Efficiency
eff	Effluent
H	Height (m)
I	Influent
k_s	Monod's constant
nd	not defined
P	TVFA/Alkalinity (equivalent acetic acid/equivalent calcium carbonate)
Q	Flow rate (L/d)
q_m	Methane gas per Litre of influent
Q_m	Methane gas per Litre of reactor
R^2	Correlation coefficient
REG	Regime
S	Substrate concentration (g COD/L)
t	reaction time (days)
V	Volume (m^3)
V_{OLR}	Volumetric Organic Loading Rate (g TCOD/L d)
V_{up}	Upflow velocity (L/d)
X	Biomass concentration (g/L)
Y	Biomass yield (g COD/L)

CHAPTER 1 . INTRODUCTION

1.1 Background information

Abattoir effluents are classified under high-strength wastewaters because of their characteristic high organic matter and remarkable environmental impact. Textile effluents on the other hand are classified under recalcitrant wastewaters because of the non-biodegradable nature of the constituent pollutants. Anaerobic wastewater treatment techniques are commonly utilized in degradation of abattoir wastewater due to its ability to degrade various types of organic pollutants and at the same time expend minimal energy while generating biogas which is a reliable source of green energy. Therefore, wastewater degradation in the absence of oxygen is regarded as one of the major sources of renewable energy. The breakdown of substrates in the absence of oxygen with the aid of acetogenic (hydrogen-producing) and methanogenic (methane-producing) bacteria converts complex organic compounds into methane, carbon dioxide and water. However, anaerobic treatment methods are most efficient when degrading nutrient rich wastewater but very inefficient when degrading nutrient deficient wastewaters. Abattoir and textile industry wastewater streams are examples of such nutrient rich and nutrient deficient wastewater respectively (Alrawi et al., 2011). Abattoir effluents are predominantly characterized by high quantities of nitrates, phosphates and lipids whereas textile effluents are predominantly characterized by dyes and sizing agents like starch and carboxymethyl cellulose (CMC). Textile industries are conventionally categorized among recalcitrant wastewaters owing to the low-biodegradability nature of its pollutants (Bouallagui et al., 2008).

Biological Nutrient Removal (BNR) entails an elaborate simultaneous nitrification and denitrification processes which require anaerobic and aerobic conditions, respectively. This process is cumbersome, expensive and technically demanding because aerobic and anaerobic microbes are antagonistic in nature which means that microbes thriving under anaerobic conditions will perish when introduced into an aerobic environment and vice versa (Bumpus et al., 1995). Anaerobic processes are driven by specialized microbes that breakdown complex organic compounds, under oxygen deficient conditions, into a gas cocktail comprising of hydrogen sulphide, carbon dioxide methane and water, conventionally referred to as biogas. The

microbes require nutrients to thrive; but as textile effluents have minimal traces of nutrients making them insufficient to guarantee efficient performance of the microbes in degrading complex and recalcitrant textile effluent. Anaerobic microbes are delicate and highly specialized, therefore, the digester conditions should be balanced appropriately in order to achieve the desired target (Kafle et al., 2014). The following factors are key in achieving a well-balanced digester; substrate dilution (volume of water used to dilute wastewater); optimum temperature ($37\text{ }^{\circ}\text{C} \pm 2$); substrate type (in order to achieve a suitable C:N ratio) and organic loading rate (overloading may lead to accumulation of volatile fatty acids). Sosnowski et al. (2003) pointed out that critical aspects as far as digester efficiencies are concerned are the buffer capacity and the Carbon/Nitrogen (C/N) ratio. Bouallagui et al. (2008) stated that abattoir effluent are characterized by high contents of nitrogen and consequently suggested that effluent of similar nature should preferably be co-digested with effluent that have high carbon content. This statement serves to justify the concept of co-digestion as viable and already in use. Consequently, an attempt is made in this study to co-digest abattoir and textile wastewater to ascertain the feasibility of anaerobic degradation. The discharge of these wastewaters into the environment irresponsibly causes odour nuisance, polluted groundwater, severe eutrophication, accumulation of carcinogenic compounds and breeding of deadly pathogens (Grygoruk et al., 2015).

Abattoir effluents are characterized by temporal loads (loads that vary over time) depending on the climatic and festive season of the year. On the same note, religious, cultural and medical reasons have also negatively influenced consumption of particular fractions of meat products which are predominantly fats and blood. This has led to the accumulation of lipids and nutrients in the abattoir effluent drains hence the need to improve their biodegradation strategy is crucial. Textile effluents exhibit low biodegradability because of various kinds of dyes it is composed of which are characterized by complex structures and high molecular weights. The low biodegradability is further aggravated by acute nutrients deficiency in textile effluent, thereby slowing down microbial activity. Two or more wastes with natural complementing characteristics can be combined and degraded together under anaerobic conditions, a process also known as anaerobic co-digestion. This also marks one of the milestones achieved by anaerobic technology as far as substrate degradation is concerned (Mahmood et al., 2015). Cuetos et al. (2008) observed that co-digestion steadied the bio-digester feed, hence upgrading

the C/N ratio by decreasing nitrogen concentration. The production of biogas is increased when co-substrates with low lipid and nitrogen waste content are degraded anaerobically due to the complementary of the two kinds of waste parameters, hence averting problems linked with the accumulation of high ammonia concentrations and intermediate volatile compounds (Castillo et al., 2006).

1.2 Kinetic Studies

In order to evaluate experimental hypotheses, examine the essence of relationships among variables, direct experimental design and interpret experimental results, mathematical models are applied in fundamental research of anaerobic technology. These models are also applied in predicting and controlling performance of the digester operation as well as optimizing the plant design over and above the scale-up pilot plant parameters. Presently, the models utilized in the industrial sector to evaluate kinetic constants are basic models that involve minimal parameters (Iza et al., 1991).

Anderson et al. (1996) stated that the kinetic models of the Monod type have been extensively applied in the description of anaerobic digesters process kinetics. Some scholars have found it difficult to use the Monod kinetic model even though some success has been reported in implementing it in the evaluation of anaerobic degradation. Isik et al. (2005) reported that the effluent residual organic load (COD) was independent of the feedstock substrate concentration in cases where pure varied cultures were utilized. Isik et al. (2005) postulated an expression that minimized the nutrient effect on the influent and effluent COD concentrations and further linked the phenomenon to biomass intensities. However, Grau et al. (1975) formulated a first and second order kinetic model centered on the linear removal concept of the elementary Monod expression. The model was verified experimentally and the chemical reaction kinetic constants were found to be three to five times higher than those of the substrate removal kinetics evaluated from the same data (Grau et al., 1975). Therefore, an attempt was made in this study to estimate UASB reactor efficiency from the Grau first and second order kinetics for the rate of substrate removal.

1.3 Purpose of Study

The viability of co-digesting two industrial effluent streams with complementary characteristics has been studied in the recent years with encouraging outcomes. However, no studies cited have adequately covered co-digestion of abattoir and textile effluents. Taking advantage of the complimentary characteristics of abattoir and textile industrial effluent streams, the purpose of this study is to establish the optimum operating parameters for efficient anaerobic co-digestion of nutrient rich abattoir effluent and recalcitrant textile industry effluent. The organic substrate removal rate will then be evaluated according to the Grau first and second order kinetic models.

1.4 Problem Statement

In practice, industrial effluent streams get discharged into the municipal sewerage system and mix up thoroughly before getting into the treatment plant. This results in the introduction of numerous pollutants, key of which are nutrients and non-biodegradable elements from recalcitrant effluents. The main problem with abattoir wastewaters is the treatment of blood which is a major source of organic load in the effluent. The organic load, mostly in the form of nutrients, cause severe cases of eutrophication in receiving waters, hence the need to reduce these organic pollutants before discharge is of paramount importance. Nutrients such as nitrates and phosphates can be removed by biological treatment or physiochemical methods, often within existing treatment plants. However, the use of BNR processes in treating abattoir wastewater is limited by technical setbacks and the high cost involved. Biological degradation of textile industry effluents on the other hand suffers major drawbacks owing to the recalcitrant nature of its constituent pollutants such as dyes and sizing reagents. Nonetheless, effluents have to meet globally accepted discharge limits while working within available resources (US-EPA. 2013).

1.5 Objectives

The main objective is to study the feasibility of anaerobic co-digestion in treating abattoir and textile wastewater in a UASB reactor in order to develop the synergy between nutrients removal in abattoir wastewater and the biodegradation of contaminants characterizing textile effluents.

The specific objectives of this research are to:

- a) Analyse and determine the raw abattoir and textile industry wastewater characteristics.
- b) Determine the optimum abattoir to textile wastewater ratio for efficient reactor biodegradation in terms of chemical oxygen demand (COD) removals and biogas yield.

- c) Analyze the substrate and dyes removal rate from the mixture in the anaerobic co-digestion process according to the Grau first order kinetic model.
- d) Evaluate the different operating parameters for steady state biodegradation processes using the Grau second-order multicomponent substrate removal kinetics for a UASB reactor.

1.6 Thesis Layout.

This dissertation reports on anaerobic co-digestion of abattoir and textile industry wastewater in an upflow anaerobic sludge blanket (UASB) reactor at mesophilic temperature conditions. Batch and continuous reactors were utilized in the process for preliminary investigation and subsequent organic degradation respectively. The thesis is comprised of 5 Chapters as follows: Chapter 1 is the Introduction. This Chapter introduces the anaerobic co-digestion topic, explaining precisely what was done and the reasons behind it. This Chapter also presents the Problem Statement and clearly stipulates the Objectives of this study, hence setting the background for scientific arguments and evaluation of the information and findings.

Chapter 2 is the Literature Review. This Chapter essentially identifies the research publications that have already been accomplished under anaerobic biodegradation and goes on to elaborate on the importance of synergy developed by co-digestion.

Chapter 3 presents the Methodology in terms of the methods used to gather information and data in this study in order to help answer the research questions. All experiments and related activities are presented in this Chapter.

Chapter 4 presents the final results of the research; experiments, analysis and discussions. The order and sequence of these results is based on the Specific Objectives (section 1.5). All conclusions are based on discussions of the results detailed here.

Chapter 5 is the Conclusion and Recommendations. This section summarizes the dissertation content and further recommends the possible application of the co-digestion ideology as well as the areas that may need further studies.

CHAPTER 2 . LITERATURE REVIEW

2.1 Background Information

The global issue on environmental integrity in all industries is the production of waste and particularly techniques of how to dispose of it safely. Environmental pollution is manifested in various ways some of which are; noise, air and water pollution among others. Water pollution is predominantly exhibited by wastewater generated from industries which eventually end up in critical sources of water like ground-water, springs, rivers and eventually dams as well as large water bodies. This poses a great risk to aquatic fauna and flora thereby extending to human beings and animals that depend on marine resources for nourishment. A large volume of industrial effluents calls for radical treatment measures before discharge into aquatic ecosystems. At the end of the 20th century, the quality of water deteriorated significantly and global warming escalated exponentially triggered by industrial development. Industrial development escalated population growth and hence elevated the standards of living which led to uneconomical food production practices and formulation of deplorable water management policies. The hasty urbanization, population growth and industrialization gave rise to amplified volumes of raw domestic and industrial effluent infiltrating into surface and ground water, hence, deteriorating the quality of accessible water. If the polluted water discharge into catchment areas is prolonged, it compromises the safety of drinking water thereby posing a serious health risk to both urban and rural residents. An inherent deficiency in policies governing the discharge of industrial effluents into receiving waters has negatively impacted the fauna and flora of marine environments, hence, degrading the human day to day livelihood support systems (Muhammad et al., 2011).

The necessity for provision of high drinking water standards is best displayed by the UNO Secretary General's Press Releases on World Water Day 2002. "An estimated 1.1 billion people lack access to safe drinking water, 2.5 billion people die each year from water related diseases – 10 times the number killed in wars, on average, each year. All too often, water is treated as an infinite free good. Yet even where supplies are sufficient or plentiful, they are increasingly at risk from pollution and rising demand. By 2025, two thirds of the world's population is likely to live in countries with moderate or severe water shortages." Indeed, water is an essential element for life yet fresh water comprises only 3% of the total water on earth. Out of this 3%, an

immense percentage, of 99.99%, is unsuitable for human consumption (Hinrichsan et al., 2002). This fact is exemplified by the deplorable state at which most of the accessible fresh water is in globally (Muhammad et al., 2011). Consequently, a high percentage of fresh water is available as wastewater which eventually finds its way to aquatic systems. Therefore, in order to make the wastewater available for safe consumption, economical wastewater treatment strategies have to be developed and relevant policies put in place to safe-guard appropriate disposal of wastewaters.

2.2 Wastewater Treatment

Only 20% of clean tap water is consumed, otherwise 80% of the fresh tap water flowing into homesteads is used up and discharged as wastewater forming part of the enormous volumes of sewage flowing into municipal treatment facilities (Liu et al., 2014). Industrial effluents also form a considerable fraction of the wastewater to be treated in the water recycling process. Different industries discharge wastewater with different characteristics depending on the products they produce. Therefore, the composition of wastewater dictates appropriate treatment procedures. Research and practice has established, over time that wastewaters with high organic content are conveniently degraded biologically (Sayed et al., 1987; Ruiz et al., 1997). However, there are a number of physical and mechanical filtering phases that the wastewater has to pass through in order to eliminate most of the solid objects suspended in the effluent liquor.

2.2.1 Pre-treatment procedure

This procedure removes large objects, suspended solids, grit, oil, fats, grease and plant and animal tissue that will endanger or obstruct further treatment operations of the effluent downstream. The preliminary treatment methods available for abattoir and textile industry effluents include screens, plain sedimentation and dissolved air floatation (Michael et al., 1998). Gravitational separation is another preliminary treatment procedure which is more effective than screens although it has a number of setbacks some of which are higher running cost and higher propensities to emit unnerving odours. Consequently, a combination of dissolved air floatation and screening technology is applied in place of gravitational separation (Edstrom et al., 2003).

2.2.2 Physicochemical treatment.

In order to remove proteins, fat emulsions and colloidal material from wastewater the physicochemical procedure is employed by regulating the pH and treating the effluent with

particular coagulants and flocculants, which precipitate and agglomerate the liquefied and finely distributed organic matter into larger particles (flocs). This procedure involves chemical coagulation and flocculation that reduce particle negative surface charge and overcome repulsive forces between the particles. The formed flocs are then removed through a physical process such as dissolved air floatation or settling.

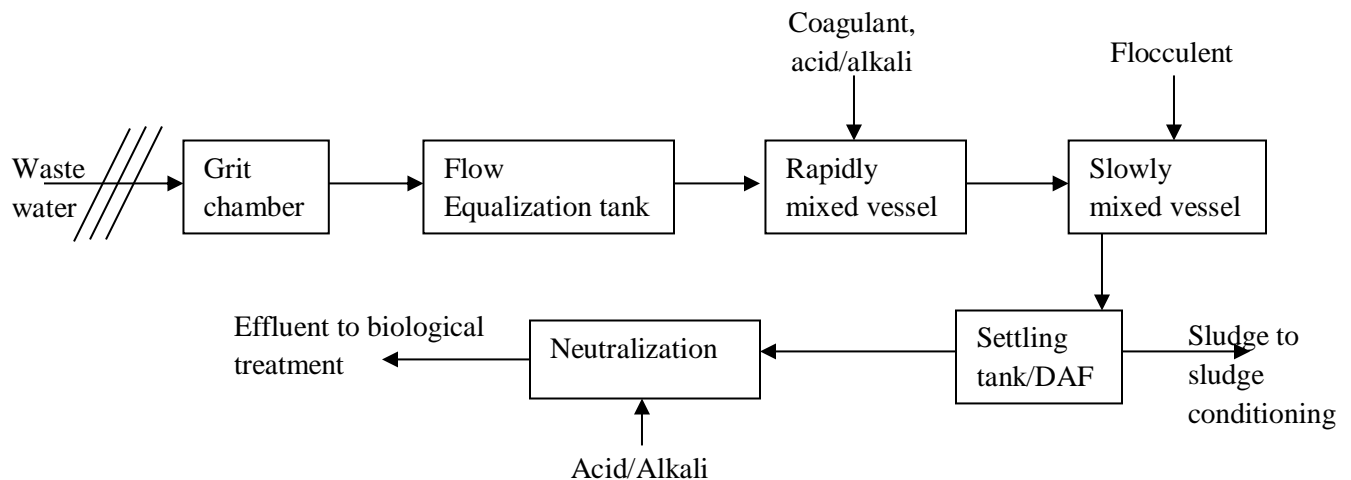


Figure 2.1: Unit operations in physicochemical treatment systems (Adopted from Yu et al., 2002).

2.2.3 Biological Treatment

This treatment processes involve the removal of pollutants from wastewaters biologically. They are more preferable than physicochemical processes in terms of environmental impacts, economy and operations. These procedures are more versatile and easily altered through changing the operating procedures to optimize current systems or developing new ones, extending the existing treatment works to purchasing new equipment, and using control systems to optimize treatment processes (Mittal, 2006). The predominant classification of biological processes are; anaerobic processes which operate in the absence of oxygen; aerobic which utilize oxygen and anoxic which is a blend of both. The structures are split into suspended growth processes best suited for the degradation of BOD, nitrification, de-nitrification, phosphorus and stabilization to reduce volume, improve sludge dewatering ability and produce usable methane gas (Metcalf and Eddy, 2003).

a) Aerobic Treatment

In aerobic treatment process, microorganisms degrade organics (BOD₅, Carbon and suspended solids) in the presence of oxygen. Hydrogen sulfide and ammonia are also oxidized to the less

harmful nitrates and sulphates. The process can also biologically remove nitrogen and phosphorus when coupled with a specialized anoxic treatment process. Aerobic procedures some of which include trickling filters, rotating biological contactors, activated sludge and aerated lagoons have been applied widely in the degradation of wastewater. The advantages of aerobic treatment plants are that they require smaller area for installation and have minimal odor nuisance. However, they have a number of disadvantages, key of them being the constant need for frequent routine care by a specialized operator and up to diurnal drainage of accumulated slurry. Another drawback is the piling up of huge amounts of sludge that have to be degraded appropriately before discarding (Masse et al., 2000). However, wastewater treatment could be further refined through aerobic systems following physico-chemical and anaerobic treatment procedures wherever abattoir plants need to treat their effluent to river discharge standards.

b) Anaerobic Treatment

This is a biological treatment technique where microbes degrade organic matter in the absence of oxygen. This treatment system is reliable and has a low retention time (Yu et al., 2002). The anaerobic systems have two main disadvantages. Foremost, it requires a larger area to install a running plant and a longer start-up time. Secondly, the process is renowned for the nuisance of flies due to the pungent odor it emits. Nonetheless, the advantages far outweigh the disadvantages some of which are;

- a) Production of usable energy in terms of biogas.
- b) High performance efficiency in the reduction of soluble and insoluble COD.
- c) No aeration energy requirement
- d) Minimum sludge production compared to aerobic systems (Speece et al., 1996)
- e) No need for chemical handling
- f) Anaerobic biomass can withstand lengthy starvation periods.

Seasonal wastewaters such as fish processing, abattoir and sugar refining industries are best treated anaerobically due to the fact that anaerobic biomass can remain inactive for several months (Omil et al., 1996).

2.2.4 Tertiary treatment

Further treatment of wastewater may be necessary after biological processes, to meet the effluent requirements for discharging to a river or for recycling and reuse purposes. For slaughterhouse

effluent, such treatment may include filtration, disinfection and cascade aeration (US-EPA, 2004). These polishing processes may attract extra costs in the overall treatment process hence they are rarely applied. Discharging biologically treated slaughterhouse effluent to a municipal sewer is a feasible option since it requires less treatment than that required for discharging to a river. However, the municipalities may impose surcharges for discharging to the sewers. Land application of biologically treated slaughterhouse effluent may be restricted by regulating bodies because it may degrade the quality of soils, destroy microorganisms within the soils, and increase odour problems. However, controlled application of the effluent may be useful in irrigated farming. Wetland systems may be used to polish the biologically treated effluent before discharging to a river. Constructed wetlands have been designed to include certain species for the removal of BOD, TSS, nutrients and heavy metals for optimal performance (Gonzalez, 1996). De-nitrification also occurs due to the anaerobic conditions in the water.

2.3 Environmental Impacts and Characterization of Wastewaters.

Domestic and industrial effluents vary depending on the quantity of pollutant parameters in strength and environmental impact. The characterization of the various effluents is critical in order to determine the type and intensity of treatment required. Characterization also helps determine whether further preliminary treatment is necessary because the toxic levels of some pollutants in wastewaters could hinder the biological process. The characteristics of effluents from various industries are distinctly different depending on;

- a. The type of industrial product
- b. The standards of hygiene required
- c. The nature of ingredients employed during the process
- d. The seasonality of the products produced. Some products are seasonal, hence the wastewater fluctuates from time to time.

Palm oil mill effluents (POME) are highly polluted and generally possess huge quantities of suspended colloidal particles, proteins and plant fibre components among other pollutants (Cheah et al., 1998). Generally speaking, industrial discharges that possess huge quantities of proteins and cellulose, like abattoir industry wastewater, have detrimental impacts on the ecosystem (Lettinga et al., 1997). The anaerobic process can be applied in the treatment of these organic pollutants because the biodegradable fractions are quite high over and above the fact that

they possess good buffering capacity. Michael et al. (1998) clearly stipulated the fact that discharging abattoir effluents without adhering to the pollution limit environmental regulations is detrimental to marine biospheres above interfering with water for irrigation.

Gonzalez (1996) stated that characterizing the negative impacts of organic matter, present in wastewater, can prove to be a mammoth task because it is tagged on a number of factors some of which include the rate of wastewater discharge, effluent potency and receiving water bodies engrossing capacity. Generally, UASB reactors were not utilized for treatment of wastewaters rich in nitrogenous compounds because the active biomass thickened during the degradation process. This phenomenon interfered with the granulation process drastically, thereby causing unprecedented loss of essential microorganisms in the reactor. However, Lattif et al. (2011) reported that the use of the UASB has been appropriate in the treatment of carbohydrate rich effluents.

2.3.1 Abattoir wastewater

Advanced technology in the 21st century rationalized the abattoir industry towards a trend of utilizing fewer, larger and more automated plants. Consequently, the environmental loadings have also increased in areas neighboring the abattoir factories. The primary environmental concern associated with abattoir industries is the generation of huge quantities of extremely contaminated liquid effluent (Britz et al., 2006; Durham et al., 2007). The primary contaminants in abattoir effluents are biodegradable organic matter, with soluble and insoluble fractions. Abattoir plants in general produce large amounts of highly polluted effluents predominantly from both the slaughtering line and guts cleaning point which greatly influences the concentration of organic matter in the final effluent (Torkian et al., 2003).

Abattoir effluents exhibit numerous shortcomings in comparison to other agro-processing industrial effluents with respect to biodegradation. Foremost, the high colloidal content in the effluent doesn't only accelerate the formation of scum, but also entraps biogas within the substrate hence reducing biogas yield significantly. Secondly, the nutrient content, colloidal matter and BOD concentration of receiving waters are increased considerably by abattoir effluents (Aguilar et al., 2002). Thirdly, disease causing pathogens thriving in abattoir wastes can easily be passed on to people through contaminated aquatic structures. Consequently, in order to avert water borne disasters, an effort should be made to meet environmental concerns and protect

public health by treating abattoir effluents effectively. The composition and volume of effluents depend on the type of cattle unit slaughtered, the nature and scale of operation employed and design of the plant used. The concentration of pollutants in abattoir effluents varies, depending on the efficiency of preliminary treatment giving pollutant parameter values of suspended solids (SS), chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) concentrations ranging from 250 – 5000 mg/L, 1000 – 20000 mg/L, 150 – 10000 mg/L and 22 – 217 mg/L, respectively (Masse et al., 2001).

Aerobic processes and physico-chemical treatment techniques have been implemented in the degradation of abattoir effluents (Sayed et al., 1988; Caixeta et al., 2002). However, these techniques have been rated inferior compared to anaerobic treatment procedures because of their characteristic unnerving stench and high maintenance cost with respect to aeration and floating sludge. Anaerobic treatment technology has proven to be a vital researchable area in organic waste management because it tends to offset the setbacks exhibited by both aerobic and physico-chemical methods. Anaerobic process aids the conversion of large fractions of degradable organic carbon in wastewater to potential energy in form of biogas, reduces pathogenic microorganisms, generates less sludge and also minimizes odours (Borja et al., 2005). Another advantage of anaerobic biodegradation technology is low maintenance cost because there is no cost incurred for aeration and hence, there is no provision for skilled expertise in the process.

Anaerobic degradation structures for academic study, simulation and all round applications with respect to abattoir effluent treatment have been reported since the 1950s (Dague et al., 1995). However, according to Fannin (1987), the early conventional anaerobic techniques had a number of shortcomings some of which include; delayed organic matter degradation, long hydraulic retention times, residual organic matter accumulation and the need for huge reactor capacities. Many of these previous setbacks have been offset by the application of advanced anaerobic digesters like UASB reactors (Lettinga et al., 1991). However, application of these advanced digesters in the treatment of wastewaters from abattoir industries is still incipient, owing to the shortcomings of insoluble organic material which result in biomass loss and consequently, a decline in the biogas yield. The prowess of the anaerobic system is hence pinned on a reliable elementary pretreatment method to eliminate the insoluble organic matter. Several researchers concur with the fact that the form and nature of contaminants in effluents does impact the

efficiency of advanced anaerobic digesters (Schmidt et al., 1993). Therefore, it has become routine to do away with suspended solids leaving behind minimal quantities of residual particles in the reactor without any major setbacks in performance (Fannin, 1987). Preliminary hydrolysis of biodegradable matter was reported (Del Borghi et al., 1999) as a way through which the efficiency of reactors treating bio-solids rich effluents can be improved. A number of abattoir wastewater preliminary treatment techniques have been reported in literature (Masse et al., 2002).

2.3.2 Textile Wastewater

The textile industrial effluent forms significant proportions of pollution loads present in catchment areas. In the manufacture of most textile goods, wet chemical procedures generate effluents whose pollution load come from impurities removed from raw materials as well as from residual chemical reagents used in the procedure (ADMI, 1973; OECD, 1981). The rate of consumption of process water is generally specific to the type of material or final product since this dictates the type of material or final transformation process. Large amounts of water are generally required for wet processing consequently, textile industry generates immense effluent volumes with profound variations in composition. Therefore, before appropriate pollution mitigation technologies can be considered, it is necessary to identify the generic types of wastes from the multiple processing operations employed by the industry as vast quantities of dyes are manufactured and applied in various industries every year (Zollinger, 1987; Meyer et al., 1992). Textile effluents fluctuate from time to time owing to the batchwise nature of the dyeing process which ends up making textile effluent characterization cumbersome (O'Neill et al., 1999). The general procedures in a typical textile mill are; desizing, scouring, bleaching, dyeing and printing (O'Neill et al., 2000 and Shaw et al., 2002). Synthetic dyes including azo dyes are used to colour natural textile fabrics, leather, plastics, paper, mineral oils, waxes, foodstuffs and cosmetics among other things (Carliell et al., 1995).

The textile industry accounts for two-thirds of the total dyestuff market (Riu et al., 1998), consuming a large proportion of reactive azo dyes due to the actual high demand for cotton fabrics with brilliant colours (Phillips, 1996). The concern for azo dyes in the degradation of textile wastewater arose because foremost; a little quantity of azo dye in water increases the turbidity significantly as reported by Wong et al. (1999) and secondly, aromatic amines resulting

from anaerobic degradation of azo dyes in the effluent are toxic to predominant microbes. The degradation of textile effluents before discharge is a major concern to environmentalists because synthetic dyes used are difficult to degrade using conventional wastewater treatment techniques based on adsorption and aerobic processes (Bumpus, 1995; Vandevivere et al., 1998; O'Neill et al., 1999). Although textile effluent has a low toxic effect on receiving waters, the dyes introduce an aesthetic menace with great impact on the public opinion and high turbidity shatters the confidence of water users downstream. Furthermore, studies have reported that the first step of azo dye degradation anaerobically begins by the reductive cleavage of the azo bond, thereby leading to formation of corresponding aromatic amines (Wuhrmann et al., 1980; Haug et al., 1991; Zissi et al., 1996). This step eliminates the colour from the textile effluent, however, it imposes serious health hazards because mineralization of aromatic amines is both carcinogenic and poisonous (Pasti-Grigsby et al., 1992; Carliell et al., 1995; Field et al., 1995). Therefore, it is important to radically treat textile wastewater before discharge into water bodies.

2.3.3 Effluent pre-treatment and synthesis

The pretreatment procedure is a critical step in biodegradation process that reduces fats and suspended solids in high strength effluents (Abelleira-Pereira et al., 2015). The application of anaerobic methods in degradation of wastewater discharged from abattoir industries is still incipient due to the setbacks posed by accumulation of floating lipids and suspended solids in the digester which leads to biomass washout and reduction in the biomass yield (Gannoun et al., 2009). Hence the success of anaerobic systems is pinned on an effective primary treatment to eliminate fats and suspended solids (Abelleira-Pereira et al., 2015). Numerous studies have demonstrated that the nature of pollutants (soluble or insoluble) in the effluent is a function of the reactor performance (Sayed et al., 1988). Therefore, removing total suspended solids (TSS) before degradation has become common practice such that only the soluble portion of effluents (i.e. with minimal residual solids) is fed into bioreactors without any issues related to clogging (Gannoun et al., 2009). Hamdi et al. (1992) reported that biodegradation done anaerobically significantly improved when the abattoir wastewater was pre-treated because the effluent got standardized and the TSS was solubilized into more soluble COD by the population of natural bacteria present in the wastewater without aeration at 30 °C. The study also observed that a maximum removal of TSS (upto 80%) into more soluble COD was achieved under stirred conditions.

The extreme diversity of pollutants in abattoir and textile industry effluents poses problems in assessing their characteristics and subsequently makes it very difficult to control some biodegradation conditions (Razaviarani et al., 2015). Therefore, based on the concept of pre-treatment, abattoir and textile effluent in this study were synthesized in order to achieve reasonable levels of homogeneity and reproducibility in order to necessitate continuous studies (Turgay et al., 2011). Synthesized effluents also make it easy to control certain parameters (TSS and pH) that would otherwise fluctuate considerably with every sample of raw industrial discharge collected (Wang et al., 2015). O'Neill et al. (1999) treated simulated textile industry wastewater under anoxic conditions (anaerobic-aerobic conditions). The simulated textile effluent (STE) used by O'Neill et al. (1999) contained; hydrolysed reactive azo-dye, modified starch, 0.15 g l^{-1} NaCl, 0.53 g l^{-1} acetic acid, trace elements and nutrients, $((\text{NH}_4)_2\text{SO}_4, 0.28 \text{ g l}^{-1}; \text{NH}_4\text{Cl}, 0.23 \text{ g l}^{-1}; \text{NaHPO}_4, 0.038 \text{ g l}^{-1})$. In the study, O'Neill et al. (1999) diluted the feed which was refrigerated as a 10-fold concentrate with tap water containing bicarbonate thereby bringing the final NaHCO_3 concentration to 2 g l^{-1} . O'Neill et al. (1999) observed efficient colour removal in a UASB reactor as well as upto 47% increase in the BOD:COD ratio.

Shaw et al. (2002) similarly treated coloured textile effluents under anaerobic/aerobic conditions using sequencing batch reactors. The study (Shaw et al., 2002) developed a six-phase anoxic sequencing laboratory scale batch reactor to treat synthetic textile effluent whose constituent components were starch, polyvinyl alcohol (PVOH), carboxymethyl cellulose (CMC), NaCl, Na_2CO_3 , NaOH, remazol black (reactive azo dye) and trace elements. Shaw et al. (2002) reported 66% removal of the applied total organic carbon compared to 76% from a control reactor without dye. Shaw et al. (2002) also reported 94% colour removal however, dye metabolised caused reactor instability. Similarly, the treatment of synthetic wastewater containing azo dyes was also carried out by Turgay et al. (2011) using anaerobic biological method and chemical oxidation. Turgay et al. (2011) prepared two different kinds of synthetic wastewater compositions. The first synthetic dye solution (ww 1) was prepared as a mixture of Reactive Black 5 and Procion Red MX-5B at equal concentrations of 200 mg/l each with an addition of 1 g/l yeast extract. The second synthetic dye solution (ww 2) which was more similar to real textile wastewater constituted 12 g NaCl , $0.049 \text{ g Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 0.024 g NaNO_3 , 0.255 g KHSO_4 , $200 \text{ mg Reactive Black 5 dye}$, $200 \text{ mg Procion Red MX 5B}$, the soap and washing solution from cotton, and 1 g of yeast for 1 L solution.

2.3.4 Mixing

Mixing provides good contact between microbes and substrates, reduces resistance to mass transfer, minimizes buildup of inhibitory intermediates and stabilizes environmental conditions (Grady et al., 1992). When mixing is inefficient, overall rate of process will be impaired by pockets of material at different stages of digestion, whereby every stage has a different pH and temperature (Stafford, 1982). Mixing can be accomplished through mechanical mixing, biogas recirculation or through slurry recirculation (Karim et al., 2005_a). Investigations have been done to observe the effects of mixing on the performance of digesters treating waste with higher concentration (Karim et al., 2005_b) while slurry recirculation showed better results compared to impeller and biogas recirculation mixing mode (Karim et al., 2005_c).

Mixing also improved the gas production as compared to unmixed digesters (Karim et al., 2005_b). Vigorous mixing has more setbacks compared to intermittent mixing (Kaparaju et al., 2008), where this has been adopted widely in large-scale municipal and farm waste digesters (Muhammad et al., 2011). Sludge granules are formed due to fluidization (Guiot et al., 1992). Fluidization is achieved by mixing of the sludge by the flow and gas release. Rapid mixing is not encouraged as methanogens can be less efficient in this mode of operation (Gerardi, 2003). However, Karim et al. (2005_b) mentioned that mixing during start-up is not beneficial due to the fact that the pH of the digester will be lowered, resulting in performance instability as well as leading to a prolonged start-up period. Mixing in palm oil mills which depend on biogas produced (Ma et al., 1985) is less efficient compared to mechanical mixing of more viscous substrate. Thus, mixing becomes the vital functional parameter for such cases.

2.4 Anaerobic co-digestion

Anaerobic treatment methods are most applicable to nutrient rich wastewaters on account of the high biogas yield. Consequently, anaerobic treatment processes suffer major drawbacks with regards to limited microbial performance when degrading nutrient deficient wastewaters. The efficiency of a bioreactor is evaluated by the population of active microbes with respect to variations in the operational and environmental conditions within the bioreactor (Demirel et al., 2005). There are various techniques used in anaerobic biodegradation to improve the biogas yield. This is mainly achieved by adjusting the reactor conditions to suit the bacteria responsible for the conversion of organic substrates to biogas (acidogenic and methanogenic bacteria)

(Alrawi et al., 2011). In biodegradation, co-digestion is the term used to describe the combined treatment of several wastes with complementary characteristics, being one of the main advantages of anaerobic technology (Fonoll et al., 2015). Various interaction mechanisms are involved in the co-digestion mixture some of which include hydrophobic interactions, ionic, covalent and hydrogen bonding in aqueous media among others (Fonoll et al., 2015). These interaction mechanisms play a crucial role in as far as supernatant substrate removal efficiencies are concerned (Fonoll et al., 2015). Co-digestion is an excellent way of diluting toxicants and supplying missing nutrients at the same time (Buchanan et al., 2015). Studies have demonstrated that co-digestion of two or more organic substrates from individual industrial effluent streams improved the biogas yield significantly (Del Borghi et al., 1999). There is a high concentration of organic matter in abattoir wastewater, predominantly in the form of proteins, fats, adequate nitrogen, sufficient alkalinity and micronutrients for bacterial growth. Gannoun et al. (2007) mixed olive mill wastewater (OMW) with abattoir (AW) in order to reduce the toxicity of phenolic compounds and at the same time create provision for a source of nitrogen required to achieve balanced COD/N ratio. Preliminary studies done by Gannoun et al. (2005) on the co-digestion of OMW:AW under mesophilic conditions affirmed that the mixture reduced toxicity and improved the anaerobic process.

Anaerobic degradation of AW is delicate and the performance of bioreactors can be easily derailed (Wang et al., 2003). Literature has attributed this failure to a number of reasons, key of them being the accumulation of high levels of free ammonia resulting from the breakdown of nitrogen-rich protein compounds in blood (Alvarez et al., 2008). Most effluents with high quantities of nitrogen waste potentially inhibit methanogens because of the high presence of ammonia from the breakdown of proteins (Alvarez et al., 2008). The extent to which ammonia inhibits the biodegradation process fluctuates depending on the prevailing parameters such as substrate, inoculum, pH and temperature (Angelidaki et al., 1993). Koster et al. (1998) and Hashimoto (1986) suggested that the uncharged ammonia present in the supernatant was the major cause of ammonia inhibition. Alvarez et al. (2008) proposed that co-digestion of AW with complementary co-substrates was the remedy to ammonia problems because the nutrient content will be balanced thus, decreasing the negative effect of poisonous compounds on the biodegradation process. Murto et al. (2004) who co-digested AW, swine slurry, vegetable residue and various industrial effluents established a stable and well buffered system with biogas yield of

0.8 – 1 m³ kg⁻¹VS. Mixtures of abattoir remnants (stomach, rumen and intestinal content), food waste and liquefied manure were examined by Edstrom et al. (2003) under mesophilic conditions using a laboratory scale bioreactor. The process was stable at OLRs above 2.5 kg VS m⁻³d⁻¹ and HRT below 40 days resulting to effective biogas yields of 0.7 – 0.86 m³ kg⁻¹VS. Callaghan et al. (2002) examined continuous co-digestion of cattle manure with FVWs and poultry manure. Alvarez et al. (2008) co-digested pig manure and blood, both of which have high nutrient (Nitrogen and Phosphorus) content with fruit and vegetable wastes (FVWs) which have low nutrient content. A critical aspect for bioreactor performance is the buffering capacity and C/N ratio (Murto et al., 2004). The merits of co-digestion are; neutralization of potential poisonous compounds, balanced substrate concentration, enhanced synergy in microbes performance and hence, improved biogas yield. Sosnowski et al. (2003) also suggested hygienic stabilization and increased degradation rate as a critical advantage of co-digestion.

2.5 UASB Reactor Performance

The organic loading rate (OLR) is a critical process parameter in anaerobic treatment. In the case of a UASB reactor system, decreased hydraulic residence time may result in biomass washout, which inevitably leads to process failure (Chen et al., 1980). However, overloading may not necessarily be the result of residence time, but may also result from organic overload which eventually causes inhibition in microbial performance due to VFAs accumulation which goes hand in hand with a low buffering capacity. A UASB reactor operated under organic overload conditions in a study done by Borja et al. (1994) became unstable after 15 days operation period due to the high volatile fatty acid content of the reactant. Studies done to degrade palm oil mill effluent (POME) have reported that suspended and colloidal components of POME in the form of fat, protein and cellulose have adverse impacts on the performance of UASB reactors and can result in the deterioration of microbial activities and washout of the active biomass (Borja et al., 1994; Torkian et al., 2003). In a study by Haroun et al. (2009), the COD, BOD and color removal efficiency in simulated textile wastewater was investigated in a fluidized bed reactor (FBR) with activated carbon as support material. The effect of operational conditions such as organic loading rate (OLR), hydraulic retention time (HRT) and influence of glucose concentration as substrate additives on the maximum colour removal in the reactor was examined. Results pointed out that anaerobic treatment of textile wastewater was possible with the supplementation of substrate additives as external carbon sources such as glucose. A further increase in the external carbon

source added to textile wastewater did not improve the color removal efficiency of the anaerobic reactor.

The optimum pH for a majority of microbial to thrive is between 6.8 and 7.2 whereas the pH values less than 4 and more than 9.5 are intolerable (Gerardi et al., 2006). Quite a number of reactor failure cases have been reported in various studies of wastewater treatment due to the accumulation of volatile fatty acids concentration, resulting in a drop in pH which inhibited methanogenesis (Patel et al., 2002; Parawira et al., 2006). Consequently, the concentration of fatty acids is a vital parameter to monitor in order to guarantee reactor performance (Buyukkamaci et al., 2004). Similar results were observed by Hamdi et al. (1992), where biogas production was improved by increase of the OLR until 4.5 g COD/Ld; it averaged from 0.24 (77% of methane) to 1.1 L/Ld (68% of methane). However, the biogas production declined from 0.30 to 0.15 L/g COD removed. Tritt et al. (1992) on the other hand reported that a decrease of COD removal from 80% to 30% when the OLR was increased from 2.5 to 18 g TCOD/Ld in an anaerobic filter treating raw abattoir wastewater. Anaerobic digestion of the same wastewater after 2 h settling period improved COD reduction by additional 10% – 15%. These results supported the pretreatment step and showed a significant improvement in process efficiency as measured by COD removal, and eventual biogas yield. At an OLR of 6 g COD/Ld, the UAF performance declined. Consequently, a decrease of biogas production was observed (0.20 – 0.15 L biogas/g COD removed) and the COD removal efficiency ranged between 77% and 80%. The reason of the low biogas production was due to washout of bacterial biomass at low HRT. It seems that the protein hydrolysis and the ammonification rates were higher than the methanogenic bacteria activity.

Mirbagheri et al. (2012) optimized HRT and OLR in a UASB reactor at various operational temperatures. The study (Mirbagheri et al., 2012) worked on a 5 L UASB reactor which had an effective height of 160 cm and 5 cm diameter treating fortified municipal wastewater at volumetric organic loadings of 3.6, 7.2, 10.8 and 14.4 kg m⁻³d⁻¹ at 30 °C and 20 °C temperatures and pH values ranging from 7.6 – 8.4. The pH value was regulated by adding NaHCO₃ and K₂HPO₄ into the wastewater. Mirbagheri et al. (2012) reported an optimum of organic loading range between 7.2 and 10.8 kg m⁻³d⁻¹ at all temperature conditions with COD removal efficiency of about of 85% and 73% in UASB reactor at 30 °C and low temperature about 20 °C.

Mirbagheri et al. (2012) further reported an optimum HRT of 4 hours for influent COD concentration of 1200 mg/L and a nitrate removal efficiency of about 80% at optimized organic loading range.

2.6 Kinetics Models

Bhunias et al. (2008) reported that bacterial growth kinetics are based on two fundamental relationships, i.e., growth and substrate utilization rate. Various kinetic models predominantly based on Monod's equation or its modifications are reported in literature (Castillo et al., 1999 and Isik et al., 2005 and Bhunias et al., 2008). A review of literature revealed that most of the kinetic models are non-linear in nature (Tassou et al., 2014 and Mailier et al., 2011).

2.6.1 Substrate removal kinetics for single components.

Equation (2.1) is a Monod expression which is used to describe the transportation of single substrates into a cell. The Monod expression (Grau et al., 1975) can also be used to describe the rate of substrate removal when translated into a differential equation:

$$-\frac{dS}{dt} = \frac{\mu X}{Y} \times \left[\frac{S}{k_s + S} \right] \quad (2.1)$$

where: S is the substrate concentration, k_s is Monod's constant, X is the biomass concentration, μ is the maximum growth rate of microorganisms, Y is the biomass yield and t is the reaction time.

Integration of equation (2.1) results into two formulas depending on the potency of the biomass activity (X) also referred to as biomass concentration. Grau et al. (1975) proved that the substrate removal rate remains constant if the initial specific substrate concentration S_0/k_0 is less than 2.

Consequently, equation (2.1) integrates into:

$$k_s \ln \left(\frac{S_0}{S} \right) + S_0 - S = \frac{\mu X}{Y} t \quad (2.2)$$

where: S_0 is the initial substrate concentration.

Grau et al. (1975) went on to show that for low values of k_s in relation to S, equation (2.2) translates into a zero order kinetic since the logarithmic expression becomes negligible when it is multiplied by the low value of k_s .

2.6.2 Substrate removal kinetics for multicomponents.

Substrates are eliminated from multicomponent solutions and absorbed into cells simultaneously. Cultures that are homogenous and heterogeneous have been described with sequential growth as well as sequential removal (Grau et al., 1975). According to Grau et al. (1975), a broken line was used to characterize the removal of individual substrates from a mixture when a graph of total substrate concentration against time was plotted. The depletion of one component from the mixture was denoted by each breakpoint.

2.6.3 Multicomponents kinetic model.

Studies have proven that residual single substrates are related to the rate of instantaneous removal for multiple substrates. In order to consider the initial rate, Grau et al. (1975) expressed the rate as a function of the quantity of residual substrates.

$$V = f\left(\frac{m}{M}\right) \quad (2.3)$$

where; V is the relative rate of removal; M is the original number of components present; and m is quantity of residual components.

A review of common substrate utilization kinetic models for anaerobic systems was carried out by Malta-Alarez et al. (1990). The Monod model is widely used for UASB reactors and for industrial effluents (Castillo et al., 1999). However, in a study by Isik et al. (2005), it was established that the Monod model was not appropriate for interpreting the kinetic data of a UASB reactor treating simulated textile wastewater. The K_S values estimated in the study from the Monod model are very large, k_{max} and Y values were acceptable as 0.125 mg VSS mg COD⁻¹ 0.84 per day, respectively. k_{max} , Y and K_S values were 0.77 – 6.67 mg COD (mg VSS⁻¹ per day), 0.40 – 0.11 mg VSS mg COD⁻¹, and 105 – 3180 mg COD l⁻¹, respectively, for anaerobic oxidation of long chain fatty acids (Pavlostathis et al., 1991). The models applied in Isik et al., 2005 were also evaluated by comparing the predicted COD values obtained from this continuous operation of lab-scale UASB reactor. The COD values predicted with the Stover-Kincannon, Grau second order and Contois models gave a high correlation (97%) with actual COD concentrations measured from the UASB reactor. Therefore, a first order model was unsuitable for predicting the COD values compared to the other investigated models.

A kinetic model for multicomponent substrate removal by activated sludge was developed by Grau et al. (1975). The model was based on the linear removal concept which is a special case of the broader Monod equation. Both the simultaneous and sequential removals were considered in the Kinetic Model. The Model maintained that the “order of reaction” analogical to chemical reaction kinetics, which in their study (Grau et al., 1975) simulated random and gradual diminution with time of individual components. The model was verified experimentally and it was found that the variation coefficients of the substrate removal kinetics constants were 3 – 5 times lower than those of the chemical reaction kinetics constants, calculated from the same data.

Studies undertaken by Bhunia et al. (2008) to explore the applicability of different kinetic models for the performance appraisals of UASB reactors treating wastewater in the range of 300-4000 mg COD/L investigated three predominant kinetic models namely, Monod, Grau second-order and Haldane model. Both linear and non-linear regressions were performed on the models in the study by Bhunia et al. (2008) and Grau second-order model was found to be the class of fit for the wide range of data sets in the UASB reactor. Several studies relevant to anaerobic degradation of some industrial wastewaters have similarly been reported in literature (Pavlostathis et al., 1991 and Esquerre et al., 2015). However, none of the studies contained a kinetic study relevant to anaerobic reactors co-digesting a mixture of abattoir and textile industry wastewater.

2.7 Current trends in Literature

Anaerobic wastewater treatment at mesophilic conditions is more preferred in literature over aerobic treatment because of the generation of renewable biogas energy and minimal running cost. The performance of UASB reactors in literature is satisfactory depending on the prevailing parameters and type of effluent degraded. Studies have reported success in the application of UASB reactors in degrading high strength wastewaters. Abattoir effluents contain high quantities of organic matter thus anaerobic treatment techniques are effective as long as the Organic Loading Rate (OLR) is optimized. Textile effluents on the other hand are recalcitrant and toxic making it difficult to degrade through anaerobic techniques. Furthermore, literature has reported that anaerobic degradation of textile wastewater yields aromatic amines as by-products which are evidently more destructive than the dyes present in raw textile effluents. Aromatic amines are reported to be carcinogenic, poisonous and non-biodegradable. However, anaerobic co-digestion

postulates the concept of digesting two industrial effluent streams with complementary characteristics. Abattoir effluent is high in nutrient content while textile industry effluent is nutrient deficient hence this study tends to examine the synergy that may be developed while co-digesting the two effluent streams together. According to literature, anaerobic co-digestion improved biogas generation and substrate removal rate through stabilization of the reactant and optimization of the Carbon/Nitrogen ratio. Although anaerobic co-digestion has been successful in treating most high-strength wastewaters, limited information cited covered the co-digestion of textile and abattoir effluents.

CHAPTER 3 . METHODOLOGY

Wastewater and inoculum sampling was critical because the specimen collected varied from time to time depending on the peak hours of the abattoir plant. Similarly, the characterization of raw abattoir wastewater dictated the concentration of the synthetic abattoir wastewater ingredients. The ingredient components used to synthesize both textile and abattoir wastewaters were adopted from studies that dealt with similar industrial effluent streams. The batch and UASB reactors schematic diagrams represented were used for batch and continuous anaerobic degradation, respectively. Preliminary experiments run in batch mode were the basis for continuous anaerobic digestion since they established the optimum biodegradation working parameters. Well acclimatized inoculum accelerated the start-up process thereby improving the wastewater substrate removal rate at mesophilic and ambient temperature conditions. The rate of substrate removal was evaluated through Grau first and second order kinetic model. Statistical analysis of wastewater quality parameters were measured using Standard Methods of Water and Wastewater Analysis.

3.1 Wastewater sampling

3.1.1 Abattoir wastewater

The Abattoir Wastewater was sampled from an abattoir factory in Parys, South Africa. The major pollutants in the abattoir effluent were pieces of skin, meat, blood and excrement which originated from various phases of the abattoir plant. The organic load concentration varied since the abattoir wastewater got mixed with fluctuating volumes of water from routine cleaning of premises and equipment. However, in order to achieve effluent reproducibility, the abattoir wastewater used in this study was synthesized to simulate industrial standards based on the raw effluent characterization. Table 3.1 shows the ingredient components used to synthesize the abattoir effluent in this study adopted from Bergamo et al. (2009).

The raw and synthetic abattoir effluents were both characterized according to the standards of wastewater treatment described in APHA-AWWA-WEF 2005.

3.1.2 Textile wastewater.

Similarly, to achieve effluent reproducibility, the textile wastewater was also synthesized to simulate industrial textile wastewater characteristics. The composition of synthetic textile

effluent studied in this work was prepared based on the scouring, desizing, dyeing, printing and bleaching processes in a typical cotton textile industrial effluent.

Table 3.1: Composition of the synthetic abattoir effluent in this study.

COMPONENT	CONCENTRATION (mg/L)
Carbohydrates	
Sucrose	323
Starch	187
Cellulose	330
Proteins (Abattoir Blood extract)	4735
Lipids	
Oleic acid	26
Stearic acid	26
Metal traces	
NaCl	215
MgCl ₂ .6H ₂ O	13
CaCl ₂ .2H ₂ O	10
pH Buffer (NaHCO₃)	170

Table 3.2 shows the ingredients used to produce the synthetic textile wastewater used in this study adopted from O’neill et al. (1999) and Shaw et al. (2002).

Table 3.2: Composition of the synthetic Textile effluent in this study.

Component used	Concentrations (mg/L)
Acetic acid	150
Na ₂ CO ₃	300
Carboxymethyl Cellulose (CMC)	45
Azo dyes	
Reactive Black	10
Congo Red	10
Chlorazol Black	7.5
NaOH	200
NaHCO₃	600
K₂HPO₄	6
Starch	450
KH₂PO₄	7.5
NH₄Cl	12
Glucose	310
NaCl	150
Micronutrients	
CaCl ₂	6
MgCl ₂ .H ₂ O	15
FeCl ₃	6
ZnCl ₂	1.5
MnCl ₂ .4H ₂ O	1.5
CuCl ₂ .2H ₂ O	1.5
Na ₂ MoO ₄ .2H ₂ O	0.6
AlCl ₃	0.6

The simulated textile wastewater was also characterized according to the standards of wastewater treatment described in APHA-AWWA-WEF 2005.

3.2 Wastewater Pre-treatment Procedure

The abattoir wastewater for the present study collected from Parys had already undergone pre-treatment on an in-situ stirred anaerobic tank reactor. However, the wastewater collected was still filtered in order to eliminate suspended solids less than 1 mm in diameter. The fraction of blood extracts constituting the abattoir synthetic effluent in this study was derived from the pre-treated raw abattoir effluent. On the other hand, the textile effluent used in this study was synthesized to simulate the industrial effluent. This makes it easy to achieve reproducibility for continuous studies.

3.3 Experimental Unit

3.3.1 Preliminary Batch reactors

The preliminary anaerobic degradation was run in 500 ml bottles made of glass and tightly fastened by use of plastic caps. These plastic caps had provision through which two pipes were fitted. One pipe conveyed the effluent sample in and out of the reactor, whereas the other pipe collected biogas by under-water displacement method. The digesters were mechanically mixed by agitating it manually an hour prior to sampling and recording of the biogas volume. Mixing was not critical in this study because the process was slow and hence not limited to mass transfer. The batch digesters (shown in Figure 3.1) were utilized in all preliminary biodegradation process.

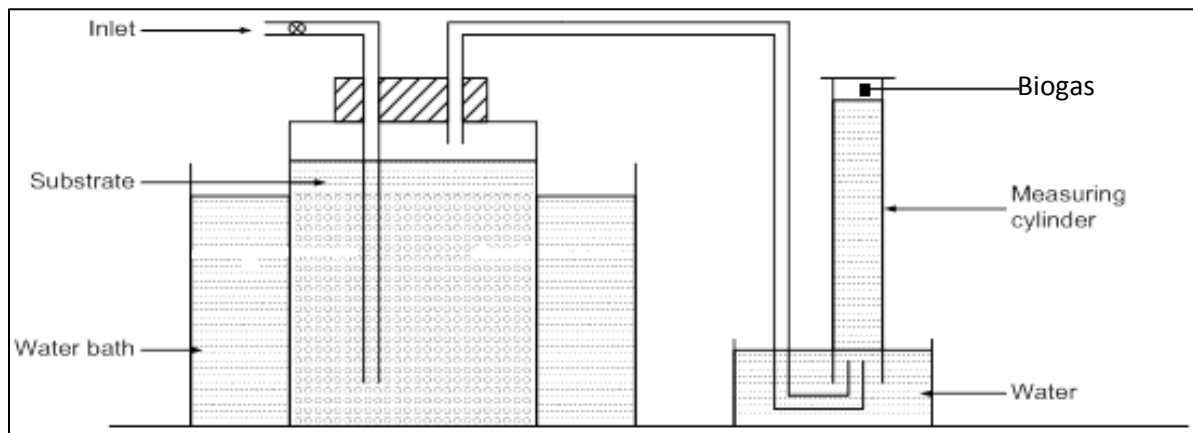


Figure 3.1: Schematic diagram of the batch reactor.

3.3.2 UASB reactor

Continuous anaerobic degradation was run in 3 L lab-scale upflow anaerobic sludge blanket (UASB) reactor. The reactor was made of a 10 mm thick cylindrical Perspex flask whose external diameter was 0.15 m and total height was 0.3 m (Appendix A). The inflow, recirculation and outflow of the reactant were regulated by intermittent pumping at certain intervals. The feedstock was stored in a refrigerator that was maintained at 4° C. The temperature of the reactor was regulated using a thermostatic water bath heater. Biogas production was collected and measured by the water displacement method.

3.4 Inoculum Preparation Process

Granular sludge from the secondary digester of a municipal sewage treatment plant was used to inoculate the UASB reactor. The sludge was first acclimatized to the abattoir wastewater inside a 5 L reactor operated batch-wise per day at mesophilic conditions (37 ± 1 °C) for a period not less than 90 days. The proportion of raw influent abattoir wastewater was increased slowly until it occupied 100% of the supernatant during this period. The parameters examined were COD removal efficiencies, biogas yield and pH. The inoculum was maintained at mesophilic conditions until the production of biogas ceased.

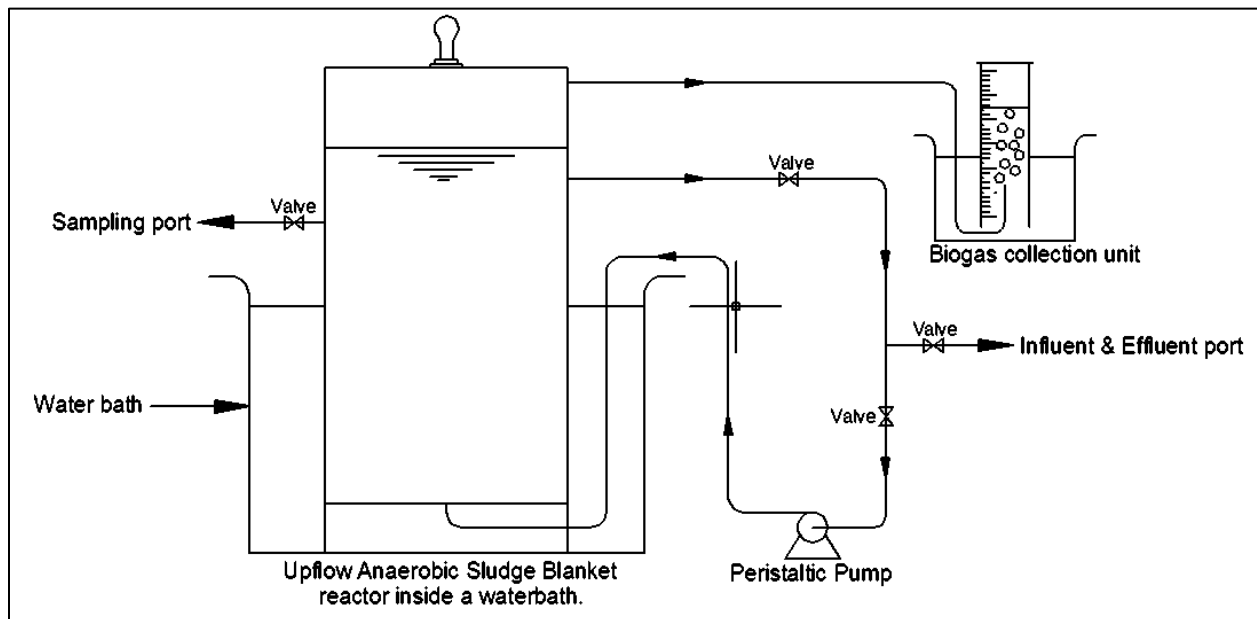


Figure 3.2: Schematic diagram of a setup of the continuous bioreactor.

3.5 Anaerobic Co-digestion Start-up Process

3.5.1 Inoculum

A sludge wet weight of 0.8 kg was added into the reactor and left to stabilize for 27 hours after which 1.5 L (50% of the residual reactor volume) of the synthetic effluent was added into the reactor. This was also left undisturbed for another 24 hours. The supernatant volume was collected and analysed then as soon as 97% of the substrate removal efficiency was achieved, the UASB reactor was entirely filled-up with the effluent. Similarly, the supernatant samples were analysed only after achieving 91 % COD removal and continuous feeding began 24 hours later, a procedure adopted from Caixeta et al. (2002).

3.5.2 Preliminary treatment process

(a) Determination of the optimum abattoir to textile wastewater ratio

The 500 ml anaerobic batch reactors were used to investigate the optimum mixing ratio of abattoir to textile wastewater. Various proportions of AW: TW (v/v) (20:80; 40:60; 60:40; 80:20) were degraded in 0.5 L batch reactors and the biodegradability and toxicity of the wastes under mesophilic conditions evaluated (37 ± 1 °C). The wastewater was added batch-wise daily for 11 days and the prevailing parameters investigated (COD, BOD₅ pH and methane yield). In order to simulate a continuous process, 50 ml of the supernatant volume was sampled daily, from which the wastewater was analyzed then a fresh wastewater sample of equal volume was replaced throughout the whole operation period.

(b) Effect of reaction temperature and initial influent concentration.

In this batch experiment, there were five runs at both mesophilic and ambient temperature conditions. The 500 ml anaerobic batch reactors were similarly utilized in this experiment. A ratio of 1:3 of inoculum to effluent was used to load each reactor. The experimental runs are described in Table 3.3 in which letters ‘M’ and ‘A’ denoted ‘mesophilic’ and ‘ambient’ temperature conditions respectively. An initial organic load (S_0) volume of 300 ml was added into the batch reactor and then topped up with distilled water (75 ml) up to the 500 ml mark for each experimental run.

The digesters were sampled daily during the operation period. Sampling was terminated when less than 30% variation in COD and cumulative biogas production was observed.

Table 3.3: Description of the experimental runs at various initial substrate concentrations.

Experiment run	S ₀ (mg COD/L)	Temperature (°C)
M1	3622	37
A1	3622	Ambient
M2	2766	37
A2	2766	Ambient
M3	1725	37
A3	1725	Ambient
M4	1109	37
A4	1109	Ambient
M5	674	37
A5	674	Ambient

M – Mesophilic Temperature **1** – 3622 g COD/L initial substrate concentration
A – Ambient Temperature **2** – 2766 g COD/L initial substrate concentration
 3 – 1725 g COD/L initial substrate concentration
 4 – 1109 g COD/L initial substrate concentration
 5 – 674 g COD/L initial substrate concentration

Kinetic evaluation

A first-order model (Eqn. 3.1) postulated by Grau et al. (1975) was applied in kinetic characterization of the experimental runs in order to evaluate the influence of influent organic load and temperature variation on the anaerobic process kinetics.

$$S/S_0 = \exp - (k_1 X_0 t / S_0) \quad (3.1)$$

where: S is the residual substrate concentration (g COD/L), S₀ is the initial substrate concentration (g COD/L), k₁ is a kinetic constant linked with Grau’s first-order kinetic model (g COD/L day), X₀ biomass concentration (VSS)/L.

If X₀ was a constant in the UASB reactor, the term k₁X₀ also becomes a constant, hence equation (3.1) is simplified to equation (3.2).

$$S/S_0 = \exp - (k'_1 t / S_0) \quad (3.2)$$

For purposes of evaluating the kinetic constant of the first-order model, equation (3.2) is further simplified to equation (3.3):

$$-\ln(S/S_0) = pt \quad (3.3)$$

where p is equal to k'₁/S₀.

A plot of ‘-Ln(S/S₀)’ on the ordinate against ‘t’ on the abscissa yields a linear trend. Therefore, experimental data was fit to the linear function using the least-squares method and the gradient

(p) of the graph worked out. Eventually, the value of k'_1 was calculated through the following expression:

$$k'_1 = pS_0 \quad (3.4)$$

3.5.3 Continuous biodegradation process.

(a) Pretreated raw abattoir effluent characterization and anaerobic degradation

In this experiment, the raw abattoir wastewater that was pretreated was degraded continuously in the UASB reactor. Sludge equivalent to 50% of the reactor volume was fed into the reactor followed by pretreated abattoir wastewater after 27 hours rest period. The mixture was then left to stabilize for a day. The supernatant was then sampled and analyzed regularly and as soon as COD removal efficiency reached 91%, continuous feeding commenced. The UASB reactor was run at HRTs of 22, 18 and 14 hours between days 0 to 21, 21 to 39 and 39 to 60 respectively. The OLR was varied in the course of degradation ranging between 2700 to 1082 g COD L⁻¹. The influent pH was corrected to 7.0 in the first regime by adding sodium bicarbonate. However, the feedstock was fed without pH correction in the two subsequent regimes.

(b) Evaluation of continuous co-digestion feasibility for synthetic effluent streams.

After determining the optimum Abattoir: Textile effluent ratio in the batch process, a comparison of the three synthetic wastewater streams (abattoir, textile and optimum mixture) was done. The anaerobic degradation efficiencies of the three effluent streams were examined in a continuous UASB reactor process. The results were then evaluated to establish the synergy developed in the anaerobic co-digestion process degrading a mixture of abattoir and textile industry synthetic effluent. The OLR in terms of COD was raised gradually by increasing the feed rate during the start-up period while keeping the influent COD constant. The temperature was maintained at the optimal mesophilic temperature range of 37±1°C.

(c) Steady state operation parameters in an UASB reactor.

In this experiment, the synthetic mixture of abattoir to textile wastewater was degraded anaerobically until steady state parameters were achieved. Half (50%) of the reactor volume was filled-up with inoculum followed by distilled water until the full operational capacity of the reactor was occupied. At this point, the feedstock was then pumped continuously at a flow rate of 0.375 L/d (equivalent to 8 day HRT). Once steady state conditions were achieved, continuous mode experimental runs were done at influent flow rates of 0.375, 0.5, 0.6, 0.75, 1.0, 1.5 and 3.0

L/d, which corresponded to HRT values of 8, 6, 4, 3, 2 and 1 days, respectively. As the influent flow rate increased, the HRT decreased at constant influent concentration. The reactor was operated at mesophilic temperature conditions throughout the digestion period.

3.6 Analytical Methods

The UASB reactor was sampled daily and the residual COD determined. The influent and effluent flow rates and the biogas production were monitored daily. The temperature, pH, Total and soluble COD, alkalinity, volatile fatty acids/total alkalinity (VFA/TA), proteins, ammonium, phosphates, VSS and total suspended solids (TSS) were measured in the influent and effluent, and the biogas composition was also determined. Analyses of COD, BOD₅, Total solids (TS), TSS, were done according to the procedure standards methods (APHA, 1998). The pH was determined immediately after sampling to avoid any change due to CO₂ evolution using a pH meter (WWT pH 330). Total volatile fatty acid (TVFA) and bicarbonate alkalinity (B. Alk.) concentrations in the effluent of were measured using the titrimetric method described by Anderson et al. (1992). Total Aromatic Amines (TAAs) were determined colorimetrically at 440 nm after reacting with 4-dimethylamino benzaldehyde-HCl (Oren et al., 1991). TAAs released from anaerobic, and chemical reduction were quantified using benzidine as a standard solution/reagent at absorbance maxima of 440 nm. Concentration of the gases in the biogas (CH₄ and CO₂) was also analyzed by gas chromatography, using the same chromatograph equipped with thermal conductivity detector. Carrier and make-up gas were helium and nitrogen, respectively. Column, injector and detector temperatures were 35, 60 and 160°C, respectively, and the sample volume collected was 1 mL.

3.7 Statistical Analysis

The analyses of the different parameters during the anaerobic process were done in triplicate at steady-state. Steady-state conditions were assumed when the coefficient of variation for measured parameters was less than 10%. Ms Excel was used to compute the data illustrated in this study. Error bars were also produced by Ms Excel from the mean and standard deviation of the data. The values given in figures are mean \pm standard deviation (SD) and n is the numbers of samples. Regression analysis between y and x variables was performed using the EXCEL in Microsoft WindowsTM.

The linear correlation was assessed with r^2 value as the correlation coefficient and reflects statistical significance between dependent and independent variables. Average steady-state data discussed in this study were calculated as mean values.

The data were analyzed using ANOVA with statistically significant differences for $p < 0.05$. The statistical program used was STATA 11. The ANOVA analysis was performed in order to evaluate the influence of the operating conditions during the pretreatment and anaerobic co-digestion.

CHAPTER 4 . RESULTS AND DISCUSSION

4.1 Characterization of Wastewater

Raw abattoir wastewater sampled was characterized and the results obtained were used to ascertain the range of synthetic abattoir effluent parameters. The characteristics of the raw abattoir effluent are shown in Table 4.1.

4.1.1 Abattoir wastewater

Abattoir industry wastewater falls under the category of high-strength wastewater. Raw abattoir wastewater collected from Parys was characterized according to the Standard Methods of wastewater treatment (APHA-AWWA-WEF 2005). The range of parameter values measured is displayed in Table 4.1. The high COD, BOD and TSS exhibit the high presence of organic matter characteristic of most abattoir effluents. The pollutants of abattoir effluents vary from time to time depending on the time of the day, day of the week or season of the year, hence, it is highly unlikely that samples of wastewater collected from the same abattoir plant at different times yield similar results. The abattoir plant from which the abattoir wastewater was sampled from was predominantly dealing with beef and pork. The plant operated for 6 days of the week, from Monday to Saturday. Pigs (110 pigs per week) were slaughtered on Fridays whereas the cattle (15 cows per day) were slaughtered on the rest of the days. The number of animal units slaughtered per day influenced the quality and quantity of effluent generated which partly accounts for the variation of parameters measured from the abattoir plant.

Table 4.1: Characteristics of raw abattoir effluent.

Parameter	Minimum and maximum values
Biochemical oxygen demand (mg l ⁻¹)	476 – 3850
pH	6.85 – 8.19
Chemical oxygen demand (mg l ⁻¹)	935 – 6600
Total suspended solids (mg l ⁻¹)	750 – 4400
Phosphates (mg l ⁻¹)	7 – 68
Turbidity (NTU) ^a	90 – 1680
Nitrates (mg l ⁻¹)	24 – 250
Fats and Oils (mg l ⁻¹)	40 – 600
Volatile suspended solids (mg l ⁻¹)	660 – 5250

However, there was need to control the organic loading rate of the feedstock into the reactor in this study. Hence an effort was made to keep the abattoir wastewater organic load as constant as possible. Therefore, to achieve some degree of uniformity and homogeneity of the effluent mixture, the abattoir effluent used in this study was synthesized to simulate real industrial

effluent. This ensured that the effluent parameters were kept as constant as possible in order to investigate the steady state operation parameters. The characterization of the abattoir wastewater synthesized from the components displayed in Table 3.1 is shown in Table 4.2.

Table 4.2: Parameters of the synthetic abattoir wastewater.

Parameter	Mean values
pH	7.81 ± 0.33
Chemical oxygen demand (mg l ⁻¹)	6445 ± 141
Biochemical oxygen demand (mg l ⁻¹)	3435 ± 65
Turbidity (NTU) ^a	1226 ± 27
Total suspended solids (mg l ⁻¹)	425 ± 9.3
Nitrates (mg l ⁻¹)	20.3 ± 0.4
Phosphates (mg l ⁻¹)	52 ± 2.1

The presence of nitrates and phosphates in the synthetic abattoir wastewater, despite the fact that there was no nitrate or phosphate containing salt in the ingredients shown in Table 3.1, is attributed to pretreated raw abattoir wastewater added as part of the ingredients as a source of blood and proteins.

4.1.2 Textile wastewater

Due to the fluctuating characteristics exhibited by textile effluents, the wastewater used in this study was synthesized in order to achieve some degree of homogeneity. The characterization of simulated textile wastewater is shown in Table 4.3.

Table 4.3: Synthetic textile wastewater parameters.

Parameter	Mean values
pH	8.65 ± 0.14
Chemical oxygen demand (mg l ⁻¹)	2407 ± 53
Biochemical Oxygen Demand, BOD ₅ (mg l ⁻¹)	449 ± 11
Turbidity (NTU) ^a	942 ± 27

^a NTU = Nephelometric turbidity units

4.2 Optimum Co-digestion Ratio

4.2.1 Performance of the preliminary anaerobic batch Reactors.

The co-digestion of abattoir and textile wastewater was investigated at various percentage proportions of abattoir to textile wastewater. The AW:TW percentage proportions were 80:20; 60:40; 40:60; 20:80 as well the controls, 0:100 and 100:0 percent of the abattoir to textile wastewater, respectively. The respective COD values at various ratios are shown in Table 4.4. The interaction mechanisms discussed under section 2.4 improved the quality of wastewater

mixture at all abattoir to textile effluent proportions on account of the settlement of precipitated suspended solids. Anaerobic biodegradation results from the batch reactors suggested that percentage COD removal and biogas production increased with decreasing content of abattoir wastewater up to 60:40 and 40:60 abattoir:textile effluent percentage ratio respectively, after which both parameters decreased.

Table 4.4: Batch reactor performance at different effluent proportions after 11 day operation period.

PARAMETERS	ABATTOIR:TEXTILE WASTEWATER RATIO					
	100:0	80:20	60:40	40:60	20:80	0:100
pH	7.55±0.34	7.66±0.33	7.61±0.26	7.63±0.22	7.76±0.21	8.02±0.24
COD Before (mg/L)	6418±104	5276±97	3622±84	2963±72	2635±78	2464±53
BOD₅/COD Ratio	0.76±0.07	0.64±0.06	0.55±0.06	0.43±0.04	0.37±0.05	0.24±0.03
Biogas (L/gCOD_{REM})	0.0747 ± 0.009	0.0579 ± 0.008	0.1268 ± 0.018	0.1126 ± 0.013	0.0436 ± 0.005	0.0338 ± 0.003
Turbidity	350.7±89	398.8±35	369.3±34	320.9±58	262.2±65	218.2±98

The abattoir and textile effluent mixture stabilized the anaerobic co-digestion process because of the synergy created from neutralization of the toxic and recalcitrant properties of TW. Therefore, in the subsequent co-digestion process, the mixture used was in the ratio of 60:40 of abattoir to textile wastewater. The better performance with the 60:40 ratio was further justified by the biodegradability of the effluent which was 0.55 as opposed to 0.43 BOD:COD ratio for the 40:60 mix ratio. A BOD:COD ratio higher than 0.5 conventionally depicts an effluent that can be degraded biologically and the higher the value, the more biodegradable it becomes (Sharma et al., 1996). The turbidity parameter value was an average of 350 NTU for 100% abattoir wastewater after 11 days of operation from an initial value of 1226 NTU (Table 4.2). This owes to the fact that the microbes had formed floccules

This experiment was executed in order to determine the optimum abattoir to textile wastewater mix ratio for the co-digestion anaerobic degradation. The optimum abattoir:textile wastewater percentage ratio was 60:40 for which the COD was 3622 mg/L. This mixture was subsequently used in 3 L UASB reactor for the anaerobic co-digestion process.

4.3 Evaluation of Substrate and Dye Removal Efficiencies.

4.3.1 The effect of temperature on biodegradation.

The initial concentration (S_0) for experimental run M1 was 3622 mg COD/L at mesophilic and ambient conditions and the effect of temperature on biodegradation is shown in Figures 4.1 and 4.2. The concentration of TVFAs in Figure 4.1 and Figure 4.2 decreased throughout the co-digestion process. However, the pH remained fairly constant because TVFAs were neutralized with the gradual increase in alkalinity. COD removal, TVFA removal and biogas yield were more enhanced in run M1 compared to A1. The COD removal efficiencies observed for experimental runs M1 and A1 were 98% and 92%, respectively. Similarly, the biogas yield in experimental run M1 was 23.4% higher than that in run A1.

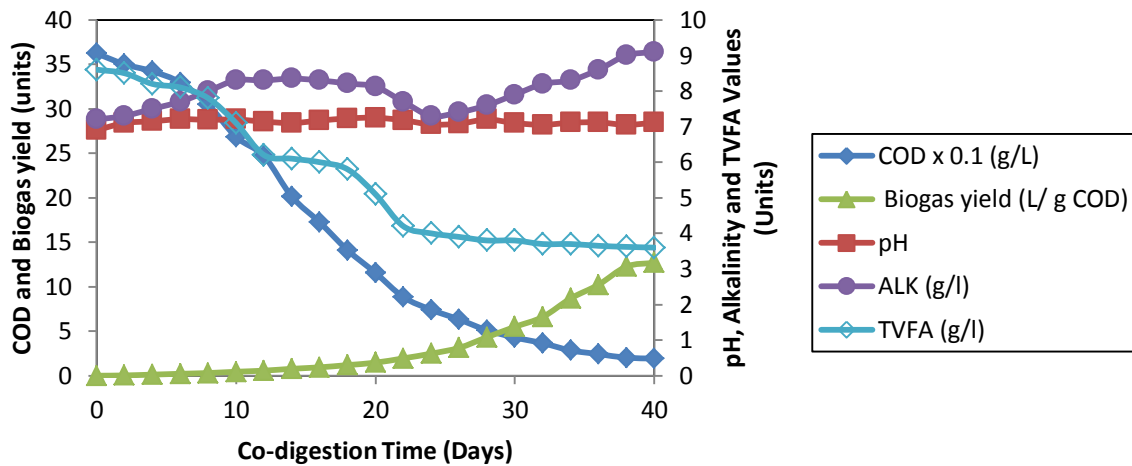


Figure 4.1: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run M1.

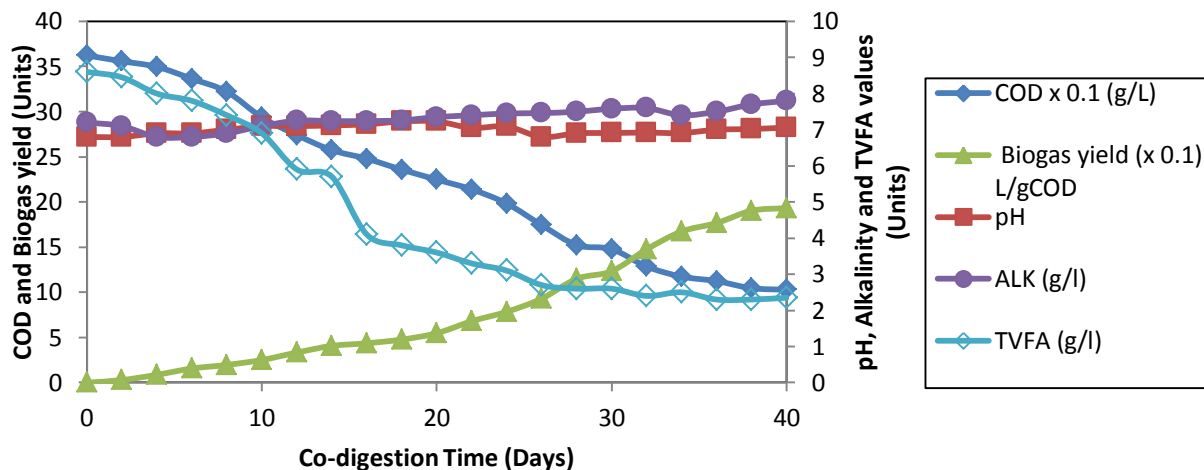


Figure 4.2: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run A1.

The changes of operational parameters in the third experimental run (run 3) whose initial concentration (S_0) was 2766 mg COD/L is shown in Figures 4.3 and 4.4 at mesophilic and ambient temperatures respectively. A 12.6% reduction in removal efficiency resulted from the initial substrate concentration (S_0) decrease in run 2 compared to run 1. A COD removal efficiency of 93% and 87% for Experiment M2 and A2 respectively, was also observed. The biogas yield in run 1 was 1.4 times that observed in run 2 and 22% lower in Experiment A2 than M2.

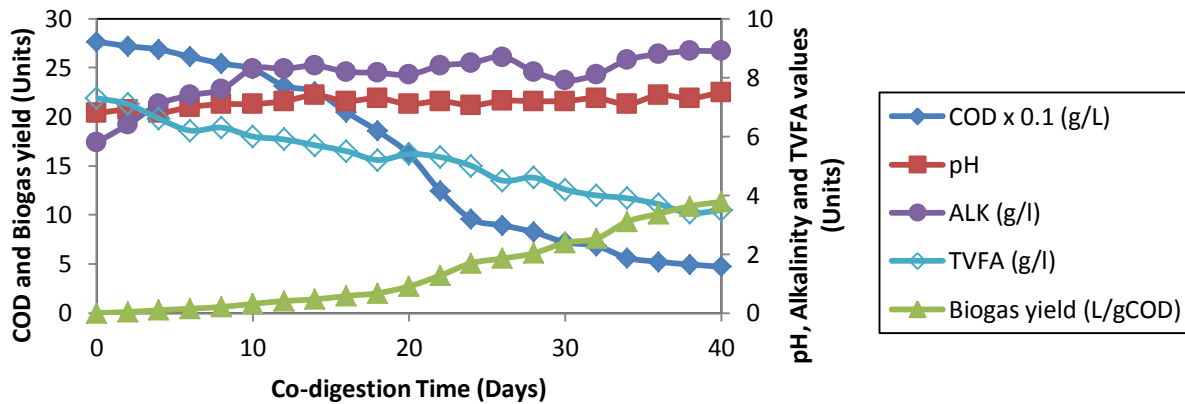


Figure 4.3: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run M2.

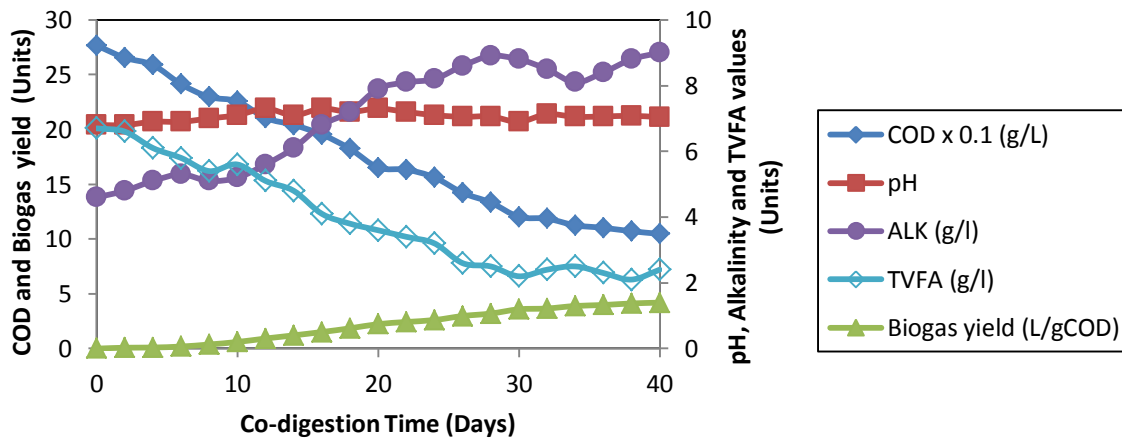


Figure 4.4: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run A2.

The third experimental run (run 3) whose initial substrate concentration (S_o) was 1725 mg COD/L is represented in Figures 4.5 and 4.6. A drop in COD removal efficiency was observed with further decrease of the influent organic load (S_o) by approximately 3% and 5% for experiments M3 and A3 respectively. The COD removal efficiencies observed were 90% and 82% for experimental runs M3 and A3 respectively. The biogas yield was 13.4% lower in experiment A3 compared to M3, an occurrence which can be explained by the reduced organic load in experiment A3 compared to M3.

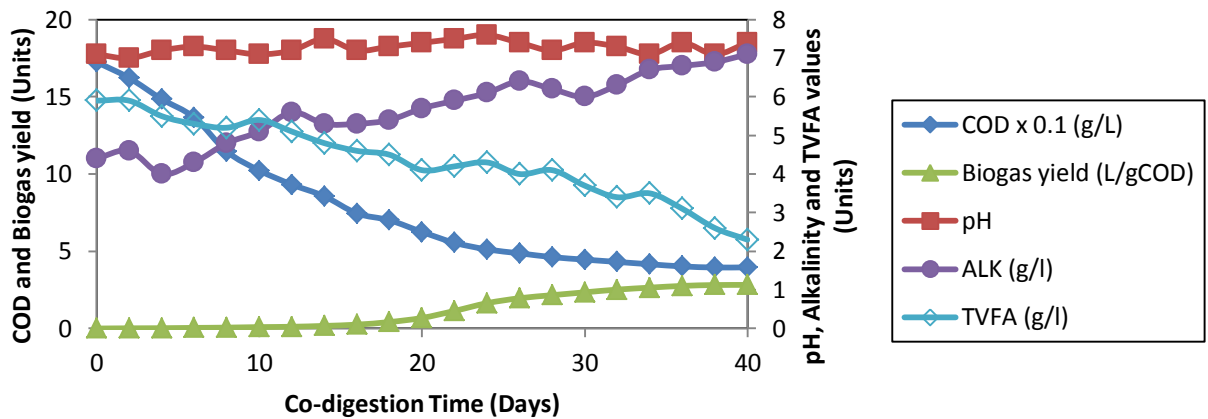


Figure 4.5: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run M3.

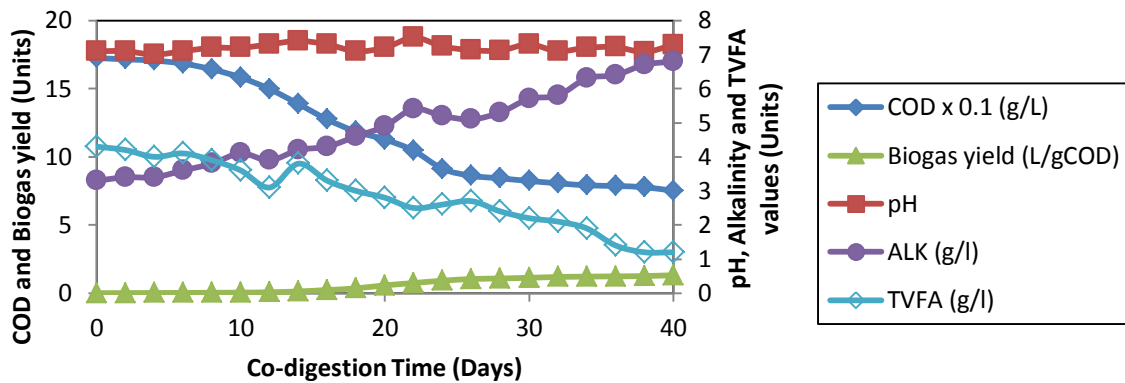


Figure 4.6: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run A3.

The COD removal efficiency for the fourth experimental run (run 4) was 36% and 35% for runs M4 and A4 respectively, whose initial concentration (S_0) was 1109 mg COD/L as shown in Figures 4.7 and 4.8. The COD degradation efficiency decreased with decrease in initial substrate concentration. The slight difference in COD removal efficiency observed was because of the minimal initial substrate concentration which led to microbial strain in the scramble for food during the organic matter breakdown process. The biogas yield was 23% higher in experiment run M4 than in A4.

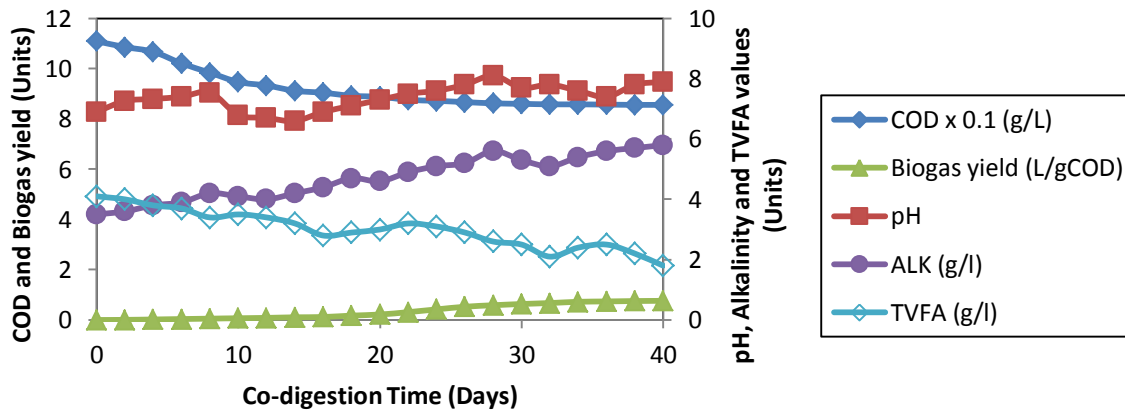


Figure 4.7: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run M4.

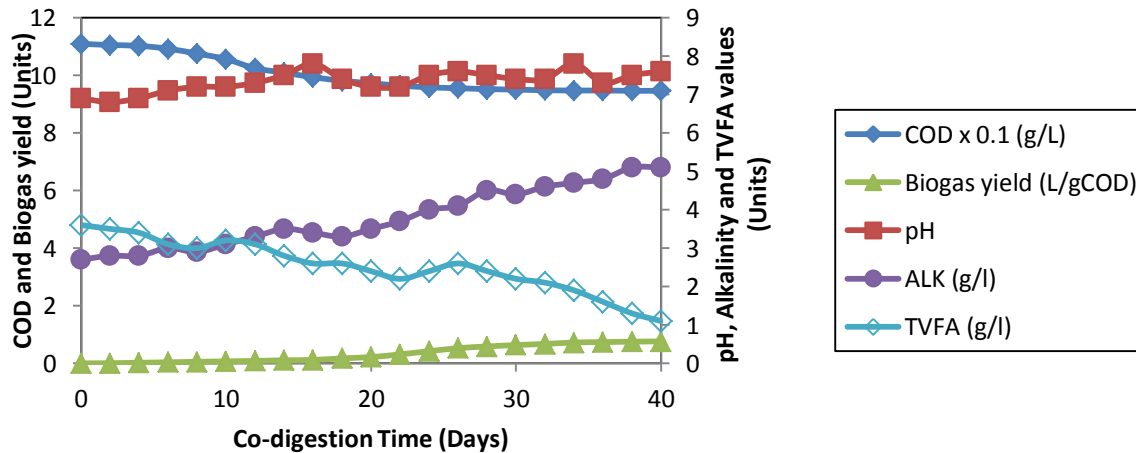


Figure 4.8: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run A4.

The TVFA parameter value decreased during the operation period of experiment M4 and A4, however, the ultimate TVFA values were distinctly lower than those recorded in run 3. The pH values on the other hand were lower throughout the co-digestion period.

Experimental run 5 is shown in Figures 4.9 and 4.10 with an initial influent concentration of 674 mg COD/L. The COD removal efficiencies were 23% and 17% for experimental runs M5 and A5, respectively. The predominant disparity in COD removal efficiencies between digestion M and A resulted to a biogas yield that was 24.8% higher in experiment M5 than A5. The variations of all control parameters against operation period were comparable to those observed in preceding experimental runs. On the contrary, alkalinity and TVFA values were higher in preceding experimental runs than in the last run (run 5).

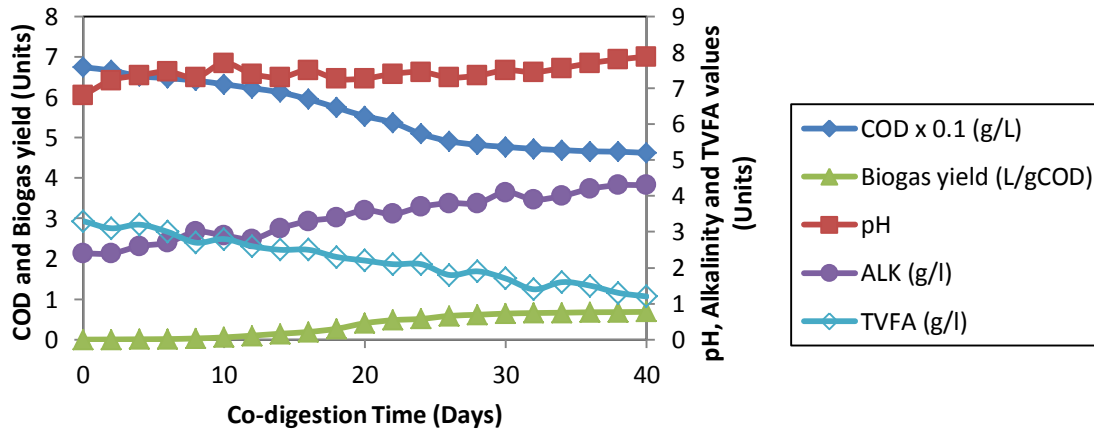


Figure 4.9: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run M5.

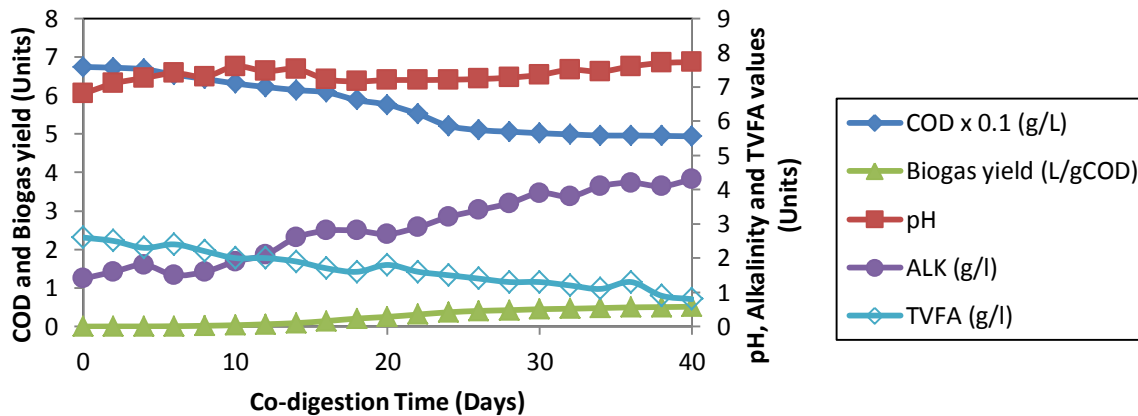


Figure 4.10: The effect of initial organic load, pH, alkalinity and TVFA on biogas yield for experimental run A5.

Comparing the two individual runs (M5 and A5) under run 5, a higher value of pH and alkalinity was observed in run M5 compared to run A5 whereas the TVFA parameter is also higher in run

M5 than in run A5. Evaluating all the experimental runs, an inference can be made that a decrease in the initial substrate concentration resulted to a reduction in the COD degradation efficiency as well as a decrease of the biogas yield. On the contrary, Sanchez et al. (2001) reported a reduction in COD removal efficiency and an increase in biogas yield with increase in the initial substrate concentration. The disparity in this study was explained by the presence of azo dyes in the co-digestion mixture whose cleavage disintegration generated aromatic amines whose toxicity dominated with every decrease in the initial substrate concentration, a phenomenon also observed by Isik et al. (2005). A decrease in the influent organic load (S_o), decreased the substrate removal efficiency under both mesophilic and ambient conditions. Furthermore, the decrease in initial substrate (S_o) also decreased the concentration of TVFA and alkalinity thereby raising the pH value.

The COD removal efficiency was a function of the operating temperature and initial substrate concentration. The concentration trend of TVFA and alkalinity generally decreased when the influent concentration decreased from 3622 to 674 mg COD/L (Figures 4.1 to 4.10). The concentration of TVFA was generally higher in digesters operating at mesophilic temperature while the pH values were lower than those observed at mesophilic temperature.

4.3.2 Batch experiment kinetic evaluation

The experiments were characterized Grau's first-order kinetic model described in section 3.5.2(b). The gradient (p) values and first-order kinetic constant values (k'_1) are shown in Tables 4.5 and 4.6.

Table 4.5: Gradient (p) values evaluated using Grau's first-order kinetic model.

Run	S_o (mg COD/L)	Slope values (p , in days ⁻¹)			
		A (35 °C)		B (ambient temperature)	
		P value	VC* (%)	P value	VC* (%)
1	3622	0.0826	81.6	0.0345	76.8
2	2766	0.0518	88.8	0.0264	66.4
3	1725	0.0401	56.4	0.0253	76.0
4	1109	0.0062	45.4	0.0046	58.3
5	674	0.0112	70.9	0.0095	70.8

*VC, variance coefficients.

Table 4.6: Kinetic constant (k'_1) values evaluated using Grau's first-order kinetic model.

Run	S_o (mg COD/L)	Values of k'_1 (g COD/L day)			
		A (35 °C)		B (ambient temperature)	
		k'_1	VC* (%)	k'_1	VC* (%)
1	3622	0.2992	81.6	0.1250	76.8
2	2766	0.1433	88.8	0.0730	66.4
3	1725	0.0692	56.4	0.0436	76.0
4	1109	0.0069	45.4	0.0051	58.3
5	674	0.0075	70.9	0.0064	70.8

*VC, variance coefficients.

The values of k'_1 were significantly lower for the degradation at ambient conditions compared to the degradation at mesophilic conditions. A decrease of k'_1 values was observed when the influent organic load decreased from 3622 to 2766 mg COD/L/day for both reactor conditions (mesophilic and ambient). A similar observation was made by Sanchez et al. (2001) apart from the fact that lower differences of the k'_1 values were noted at higher influent organic load. The expression representing reaction rate, $-dS/dt = k'_1 S/S_o$ (Grau et al., 1975), was immensely affected by the influent organic load range. Consequently, a decrease in the influent organic load derailed the rate of substrate removal. The value of k_s varies greatly with a decrease in S_o because of the unpredictability nature of a pseudo-steady reactor state.

4.3.3 Total Aromatic Amines removal efficiency and Methane yield

The effect of varying organic substrate initial concentration at mesophilic and ambient temperature conditions on the COD removal efficiencies and TAA concentrations are shown in Fig. 4.11. The COD was reduced effectively during the first 3 experimental runs (1 to 3) for both mesophilic and ambient temperature conditions. The average concentration of total aromatic amines (TAA) was arguably high in the first 2 runs (1 and 2), affirming the fact that the bonds of azo dyes present in the mixture were undergoing cleavage at a higher rate compared to the rest of the runs thereby producing higher concentrations of TAA.

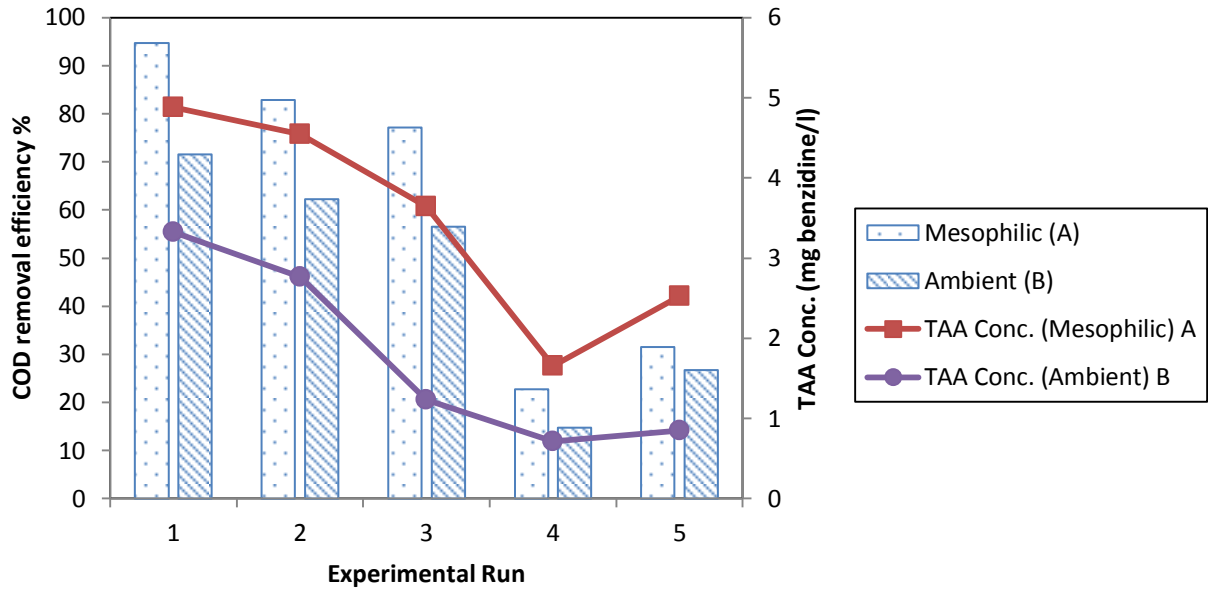


Figure 4.11: Effect of substrate concentration on the COD removal efficiency and TAA concentration in UASB reactor.

As operating temperature was lowered, the biogas yield increased, which explained why the trend of biogas yield at mesophilic temperature conditions is lower than the biogas yield recorded at ambient conditions as shown in Fig. 4.12. The insolubility of Hydrogen and Carbon dioxide decreased with increasing temperature. Therefore, the higher presence of these gases in aqueous form promoted better biogas yield. A similar observation was made by Masse et al., (2001). In another study by Kotsyurbenko et al. (1993), higher formation of acetate from Hydrogen and Carbon dioxide at lower temperatures was observed. The concentration of CO₂ was predicted from calculations based on the percentage saturation of CO₂ at various temperatures as reported in literature.

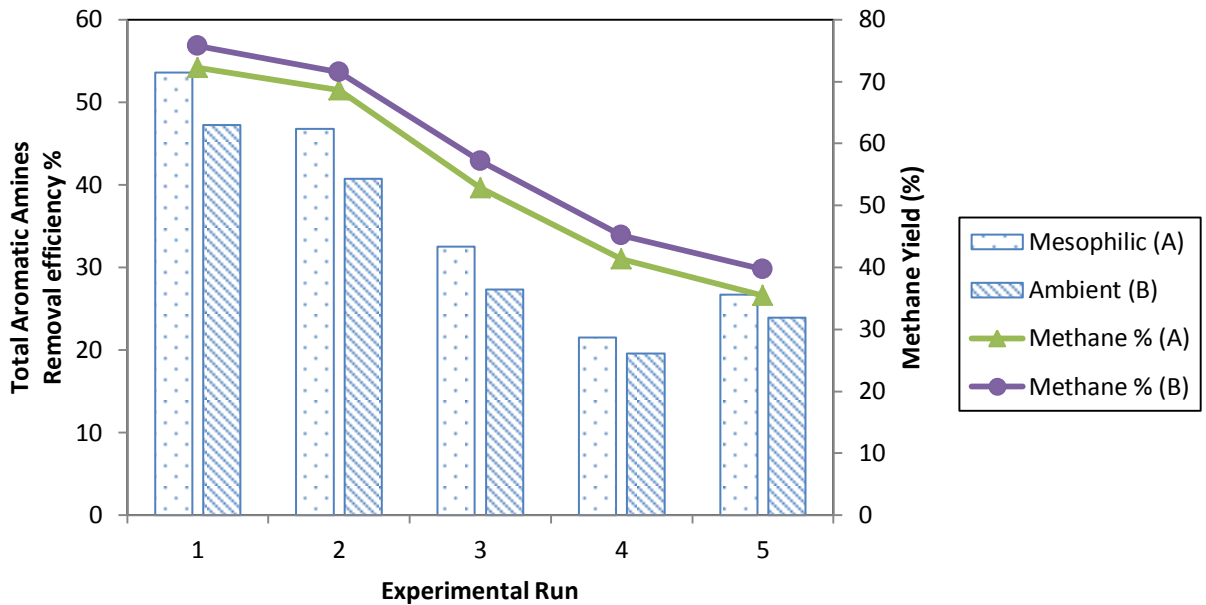


Figure 4.12: Effect of substrate concentration on TAA percentage removal and biogas yield.

a) Mesophilic temperature conditions

The COD removal efficiencies decreased from 94.7% to 22.8% at mesophilic temperature conditions as the initial substrate concentration decreased from 3622 to 674 mg COD/L as shown in Fig. 4.11. The COD removal efficiency decreased with decrease in initial substrate concentration because at lower initial substrate concentration, the microbial replication was lower compared to microbial replication at higher initial substrate concentration. The toxicity effect of TAA was inherent in all experimental runs. However, at higher initial organic substrate the high microbial replication meant that there were still sufficient microorganisms present to breakdown the organic substrate, whereas at lower initial substrate concentrations (S_0), most of the microorganisms perished, leaving fewer microorganisms to assimilate the organic substrate.

This fact can also be explained in terms of low substrate concentration because it is often a limiting factor because methanogenic bacteria are characterized by low growth rates, thus, their metabolism is often considered rate limiting under anaerobic conditions. Literature has reported on similar phenomenon in the recent past (Bras et al., 2001; Beydilli et al., 1998; Lun et al., 1995). When the substrate was not a limiting factor (3622 mg COD/L), high COD removal efficiencies (98%) were obtained agreeing with what Isik et al. (2003) reported. In runs 4 and 5 (initial organic substrate concentration of 1109 and 674 mg COD/L respectively), low COD

removal efficiencies (22.8% and 31.5%, respectively) was associated to the inert COD emanating from azo dyes, also concluded by Germirli et al. (1991). According to Fig. 4.12, the percentage methane content decreased from 72 to 35% when the initial substrate concentration was decreased from 3622 to 674 mg COD/L.

Biogas yield decreased with a decrease in the initial substrate concentration fed, from an average value of $72.2 \pm 1.89\%$ in run 1 to $35.4 \pm 0.82\%$ in run 5. Conclusively, biogas production was significantly dependent on COD. Isik et al. (2005) reported on how biogas yield was statistically dependent on COD. TAA concentrations ranged between 4.9 ± 0.08 and 1.7 ± 0.03 mg benzidine/L at influent organic loads of 3622 and 1109 mg COD/L, respectively. The existence of TAA affirmed the degradation of azo dyes during the anaerobic process. The color removal in the mixture can be attributed to the electrons produced from the TAAs. Razo-Flores et al. (1997) also observed that electrons released from azo bond cleavage provided a reducing suitable environment.

The TAA removal efficiencies were $54 \pm 0.67\%$ and $22 \pm 0.76\%$ in runs 1 and 4, respectively, affirming the reduction of benzidine as shown in Fig. 4.12. Studies suggested that aromatic amines could be mineralized further when degraded in the absence of oxygen (Kalyuzhnyi et al., 2000 and Razo-Flores et al., 1997). On the contrary, Brown et al. (1987) stated that TAAs cannot be broken down in the absence of oxygen. In as much as there was a distinct relationship between the TAA removal efficiencies and COD removal efficiencies, further studies should be conducted to establish the relationship between TAA and COD concentrations in the co-digestion of synthetic abattoir and textile industrial effluents.

b) Ambient temperature conditions

The COD removal efficiencies decreased from 71.6% to 14.7% at ambient temperature conditions as the initial substrate concentration decreased from 3622 to 674 mg COD/L as shown in Fig. 4.11. Similarly, this can be attributed to a low substrate concentration as well as the drop in temperature conditions. Low COD removal efficiencies amounting to 14.7% and 26.7% were recorded in runs 4 and 5 with initial organic concentration of 1109 and 674 mg COD/L respectively.

According to Fig. 4.12, the percentage methane content decreased from 76 to 40% while the initial substrate concentration was decreased from 3622 to 674 mg COD/L. The proportion of methane in biogas increased as the operating temperature was lowered (Fig. 4.12). These results also indicated that the proportion of CO₂ increased concurrently in the process. Masse et al. (2000) observed an improved biogas yield with every drop in temperature. However, the biogas production under mesophilic conditions was higher than the biogas produced under ambient conditions. The percentage proportion of methane in biogas was higher in ambient conditions, but the percentage proportion of methane in terms of volume was higher at mesophilic conditions than ambient conditions. Generally, the trend of all parameters under ambient conditions followed a similar pattern as those in mesophilic conditions.

4.4 Continuous Anaerobic Degradation of Pretreated Raw Abattoir Effluent.

The sampled effluent showed minimal COD variation as represented in Figure 4.13. Moreover, the COD removal efficiency decreased with decrease in HRT from 18 to 14 hours. The decreased COD removal efficiency depicted a reduction in biodegradation process because the contact time between microbes and organic matter was reduced. HRTs of 22, 18 and 14 hours exhibited average COD removal efficiencies of 85%, 83% and 80% respectively.

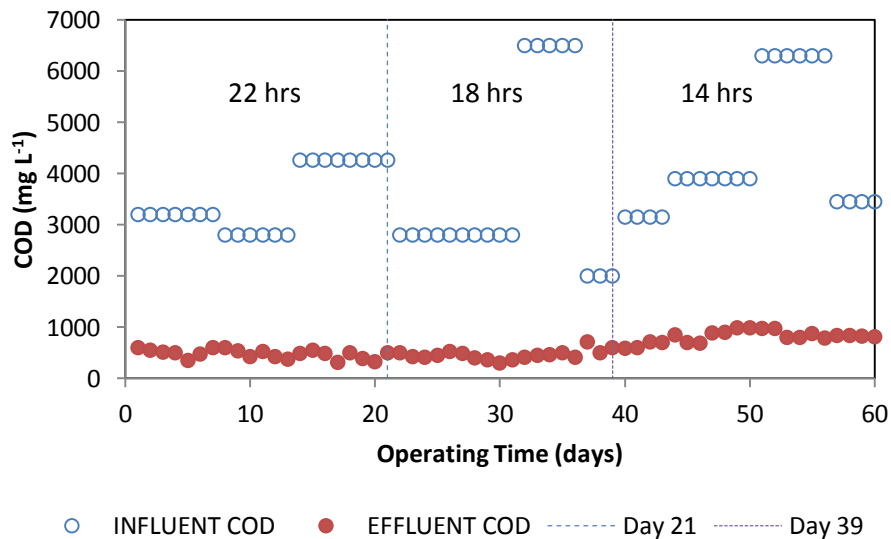


Figure 4.13: Influent and effluent COD dynamics throughout the operation period.

Biogas production for different HRT applied for different organic loads are presented in Figure 4.14. The biogas production fluctuated significantly in the first regime (22 h HRT) which then

steadied as biodegradation progressed. A mean biogas yield of 0.19 L/g COD_{removed} was maintained irrespective of the initial substrate concentration. The fluctuation observed in the biogas yield was attributed to variations in the reactant's pH conditions during the biodegradation process as well as microbes overpopulation. There was a notable decrease in biogas yield between days 28 to 36 because the high OLR caused a drastic increase in the population of microbes which, consequently, depleted the nutrients rapidly then the microbes were left competing for the nutrient traces left, thus causing a strain in reactor performance which significantly lowered the biogas yield. The other reason behind biogas yield decline was the long duration it took microbes to acclimatize to the organic shock load.

Figure 4.14 shows the trend of biogas production and the COD removal efficiency. The trend clearly exhibited the fact that an increase in substrate removal resulted in an increase in the biogas production. At the initial stages of the experiment, the biogas production was relatively low but the biogas yield improved as the experiment progressed and stabilized from day 13. The highest substrate removal and biogas yield was achieved between days 28 and 36 which indicated that the microbes were conveniently acclimatized to the organic loading rate. The highest drop in biogas yield was witnessed between day 48 and 49. This was elucidated by the organic shock loading on day 44 which was maintained for 7 days. This sudden increase in OLR may have provided sufficient nutrients to accelerate microbial replication exponentially which led to microbe strain (competing for food) when the substrate quantity reduced, thereby triggering a reactor slow down. However, the reactor picked up its performance after natural selection eliminated the weak microbes.

The pH remained constant throughout the biodegradation period ranging from 7.5 to 8.7 with a mean of 8.1. The buffering capacity of the supernatant was sufficient as Fig. 4.15 illustrates. Similarly, Caixeta et al. (2002) suggested that high acidity levels were neutralized by alkalinity inherent from the feedstock as well as alkalinity generated in the course of anaerobic degradation.

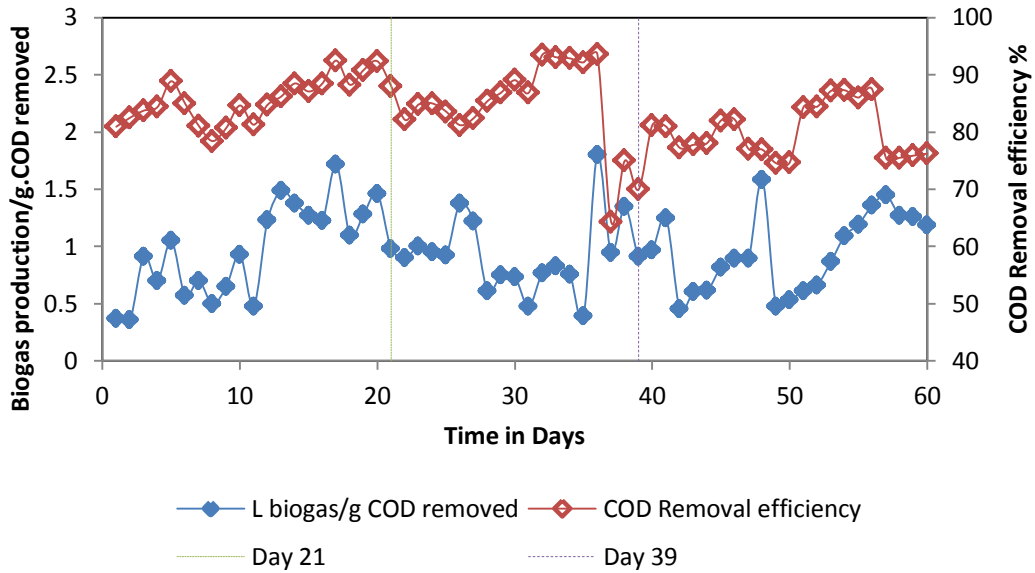


Figure 4.14: Biogas yield and COD removal efficiency (%) for different operational periods.

The average biochemical oxygen demand (BOD₅) removal efficiency was 96% for all three regimes shown in Table 4.7 which illustrates the anaerobic degradation process parameters of the UASB reactor.

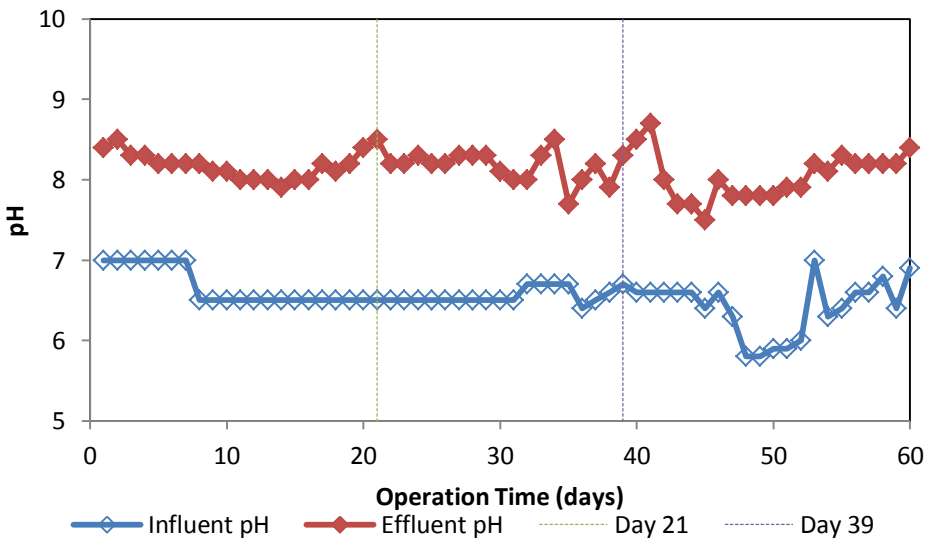


Figure 4.15: Variation of the influent and effluent pH with reaction time.

Numerous studies have reported on successful performance of UASB reactors treating abattoir wastewater. Sayed et al. (1987) achieved COD removal efficiencies of up to 85% with 0.5 to 0.6 days (HRT) and volumetric OLRs 11 kg COD m⁻³. Dague et al. (1992) achieved 90% BOD₅

removal efficiencies at 5.8 day HRT and OLR of 0.33 kg BOD₅ m⁻³day⁻¹ as well as a biogas yield of 0.51 m³ kg⁻¹ COD_{removed}.

Table 4.7: Upflow anaerobic sludge blanket (UASB) degradation process parameters (mean±std).

HRT (h)	Flow (l day ⁻¹)	Organic Load (kg m ⁻³ day ⁻¹)	COD _I (kg m ⁻¹)	COD _E (kg m ⁻¹)	Removal efficiency (%)	Biogas production (ml day ⁻¹)	L biogas/g COD removed
22 (1 st reg.)	3.8 ± 0.4	3.0 ± 0.2	2.8 ± 81.2	0.485 ± 84	82.7 ± 3.0	400 ± 132	0.172 ± 0.052
		3.5 ± 0.3	3.2 ± 187	0.519 ± 87	83.8 ± 2.7	332 ± 103	0.124 ± 0.038
		4.4 ± 0.2	4.26 ± 151	0.447 ± 89	89.5 ± 2.1	569 ± 83	0.149 ± 0.024
18(2 nd reg.)	4.9 ± 0.6	2.7 ± 0.1	2.0 ± 47	0.605 ± 107	69.8 ± 5.3	633 ± 72	0.456 ± 0.066
		4.0 ± 0.2	2.8 ± 88	0.427 ± 69	84.7 ± 2.5	395 ± 173	0.168 ± 0.078
		8.7 ± 0.5	6.5 ± 272	0.452 ± 37	93.1 ± 0.6	400 ± 207	0.066 ± 0.034
14(3 rd reg.)	6.4 ± 0.65	6.0 ± 0.2	3.45 ± 91	0.836 ± 12	75.8 ± 0.4	1081 ± 105	0.414 ± 0.042
		6.7 ± 0.3	3.9 ± 87	0.861 ± 121	77.9 ± 3.1	707 ± 334	0.233 ± 0.112
		10.8 ± 0.4	6.3 ± 144	0.874 ± 90	86.1 ± 0.4	825 ± 206	0.152 ± 0.037

I = Influent, E = Effluent, nd = Not determined, REG = Regime (treatment phase).

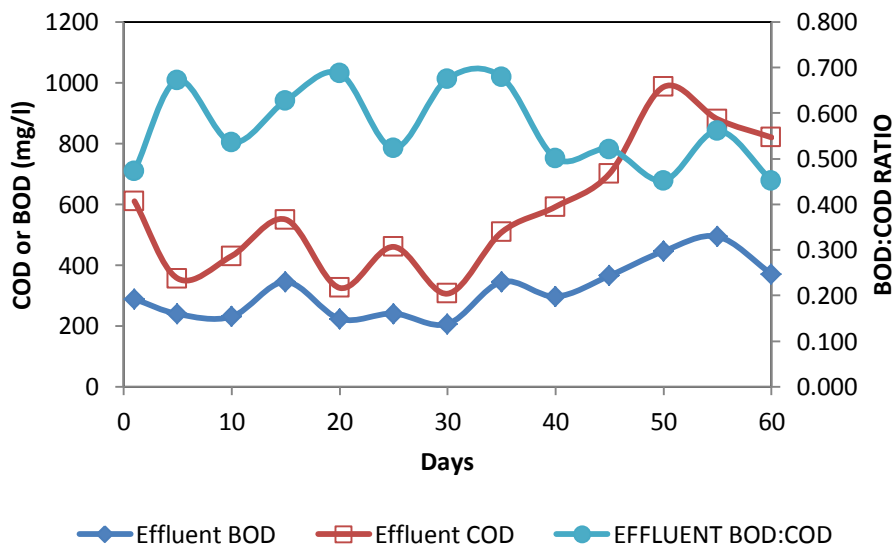


Figure 4.16: The effluent COD and BOD₅ (mg/l) and the BOD:COD ratio of the effluent from the reactor.

In this study, the BOD/COD ratio was 0.566 ± 0.09. The highest value of 0.687 was recorded on the 20th day and the lowest value of 0.452 was recorded on the 50th and 60th days as depicted in Figure 4.16. The trend of effluent BOD₅ correlated with the trend of effluent COD throughout the biodegradation process.

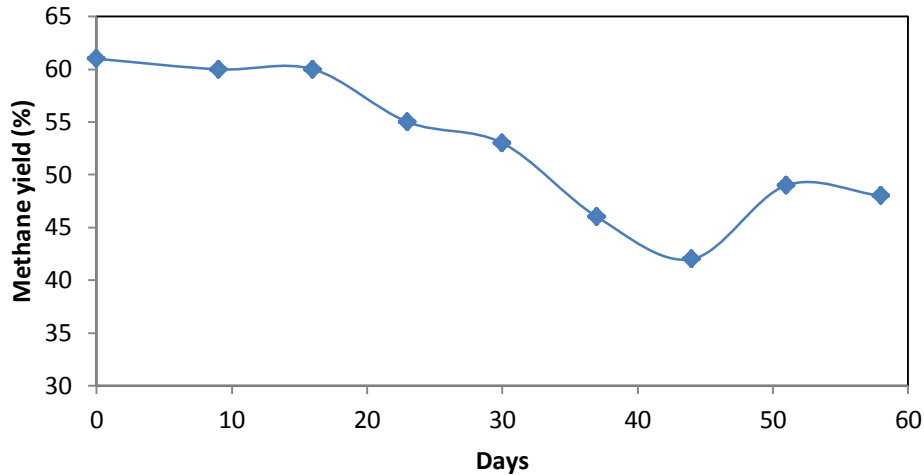


Figure 4.17: The methane yield (%) of the biogas.

At intermediate loading rates in this work, there was a consistent increase in biogas yield up to a particular organic load, as shown in Fig. 4.17, after which the biogas yield began dropping gradually. The drop signified the commencement of functional stress in the microbes and further increase in organic load resulted to a sharp decrease in biogas yield. Edstrom et al. (2003) similarly demonstrated difficulties in stable operation of a UASB reactor at loading rates above 1 kg of VS m⁻³d⁻¹.

The methane production in this study was in the same range as those reported for anaerobic degradation of slaughterhouse materials (Ruiz et al., 1997; Masse et al., 2003; Sayed et al., 1988). However, the biogas yield (52.7% ± 6.86%) was somewhat lower than what was previously reported. In a study by Masse et al. (2003), an average increase of biogas yield was reported with every drop in temperature from 20 °C (75.5%) to 10 °C (81.3%). Masse et al. (2000) suggested that a decrease in acidogenesis, due to a reduction in the hydrolysis of complex organics at lower temperature, leads to a drop in the proportion of carbon dioxide in the biogas. Additionally, the generation of acetate from carbon dioxide in the presence of hydrogen by homoacetogens also reduced the amount of carbon dioxide in biogas with every drop in temperature (Kotsyurbenko et al., 1993). Consequently, the biogas yield increased when the resulting acetate reduced. This study was performed at mesophilic conditions (37±1 °C), hence the insolubility of CO₂ and H₂ gases at this temperature accounts for the reduction in biogas yield.

4.5 Evaluation of anaerobic co-digestion feasibility in a continuous process.

4.5.1 COD and BOD₅ removal rate.

The COD and BOD₅ against co-digestion time for the mixture of abattoir and textile synthetic effluent shows a consistent COD_{out} decrease with increasing reaction time as shown in Figure 4.18. However, this decrease was consistent up to the 36th day where a steep increase was observed before the effluent COD adopted a rather gradual increase as recorded from day 43 to day 50.

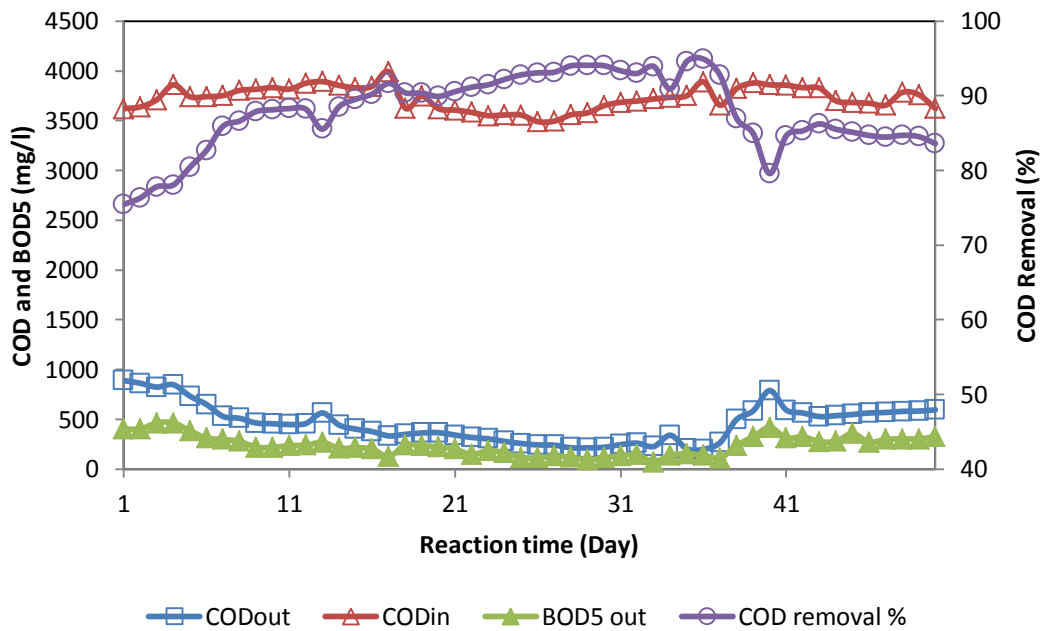


Figure 4.18: COD_{in}, COD_{out}, BOD_{5(out)} and COD removal efficiency against operation time for synthetic abattoir and textile wastewater mixture.

The effluent COD decreased consistently with increasing operation period up to the 36th day where it increased steeply before adopting a gradual ascent as depicted from day 43 to day 50. An attempt was made to keep the influent COD as constant as possible but there were fluctuations recorded depending on the synthetic wastewater preservation conditions. The average influent COD for the co-digestion reactor (Fig. 4.18) was 3726.18 ± 118.83 mg/L and the average effluent COD was 454.48 ± 89 mg/L. The effluent BOD₅ generally exhibited a trend similar to the effluent COD. Average COD removal efficiencies of 88 ± 5 % and an average effluent BOD₅ value of 227.2 ± 35.6 mg/L were achieved in this reactor, yielding average BOD₅:COD ratio of 0.53 ± 0.08 .

These results show that the reactor was stable, because the effluent COD and BOD₅ values maintained a relatively consistent trend in spite of the increasing organic loading rate (OLR). A BOD₅:COD ratio of 0.53 ± 0.08 indicated good biodegradability. The sharp increase in the effluent COD on day 37 – 40 can be explained by the high OLR of 6.855 gCOD/L.d fed into the reactor which was the highest OLR fed into the reactor throughout the digestion period as shown in Fig. 4.23. Consequently, there was a sharp decrease in the COD removal efficiency from the 37th – 40th day after which the COD removal efficiency improved rapidly and then adopted a relatively gradual ascent. Literature has shown that high organic load decreases the COD percentage reduction in UASB reactor systems (Patel et al., 2002; Torkian et al., 2003; Sanchez et al., 2005). The increase in organic load (Fig. 4.23) resulted into biomass washout and VFA accumulation, hence reducing the COD removal efficiency because the microbial environment tended towards low pH which had a negative effect on the biodegradation process and biogas production.

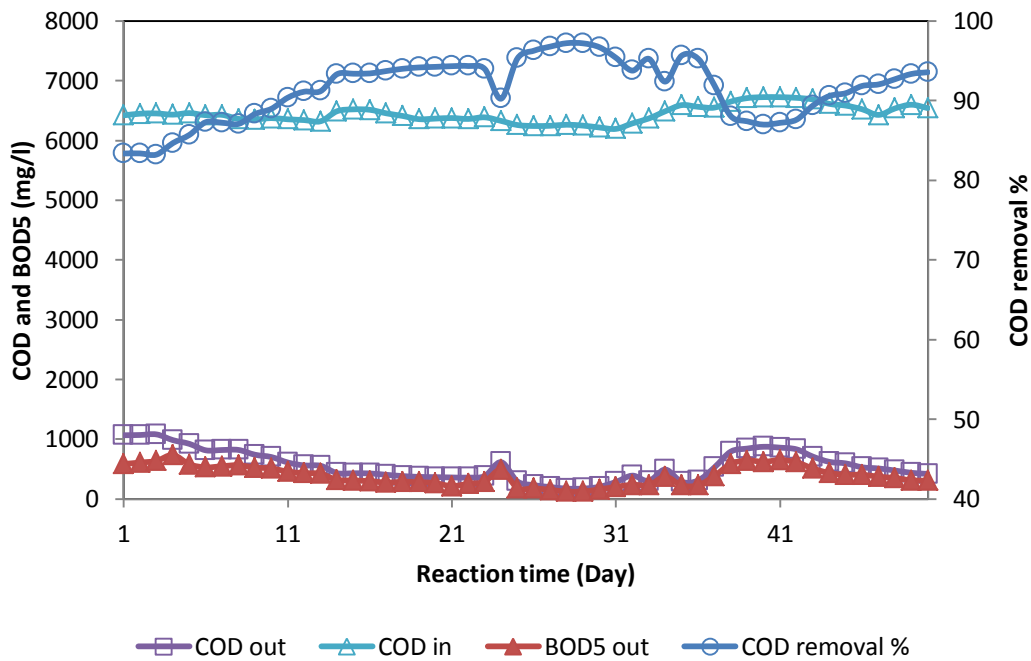


Figure 4.19: COD_{in}, COD_{out}, BOD_{5(out)} and COD removal efficiency against operation time for synthetic abattoir wastewater only.

The effluent COD similarly decreased with time upto the 36th day when it increased sharply and then began decreasing gradually upto the 50th day. The influent COD was also relatively constant with an average value of 6445 ± 141 mg/L and the effluent COD average value was $554.53 \pm$

71.49. The effluent BOD₅ average value was 390.4 ± 55.5 mg/L exhibiting a trend that was very similar to that of the effluent COD. The average COD removal efficiencies achieved in this reactor was 91.43 ± 3.82 and the average BOD₅:COD ratio achieved was 0.72 ± 0.06 .

Similarly, the results displayed in Fig. 4.19 show that synthetic abattoir effluent is readily biodegradable compared to the co-digestion mixture (Fig. 4.18). A mean BOD₅: COD ratio of 0.75 was achieved which depicts a readily biodegradable effluent. Conventionally, a value above 0.6 often indicates that biological treatment method is more preferable than a physico-chemical method (Lettinga et al., 1991). The reactor performance was generally stable since the effluent COD variations were less than 7.2% throughout the increasing OLRs. The highest COD removal efficiencies occurred between days 25 – 31 at an OLR of 5.942 kgCOD/m³d with the maximum percentage removal being 97.21% on the 28th day. Similarly, Soto et al. (1997) observed high degradation efficiency and excellent reactor stability at low HRTs. Meat processing plant effluent treated by Sayed et al. (1997) in a UASB reactor at HRTs between 0.5 and 0.6 days achieved 85% COD percentage reduction at volumetric loading rate of 11 kgCOD m⁻³ d⁻¹.

The effluent COD of synthetic abattoir exhibited a similar pattern as the reactor co-digesting abattoir and textile wastewater mixture excluding the values between days 41 to 50. The COD trend decreased gradually after the sharp increase between days 37 – 40. This resulted from high levels of organic nitrogen converted into ammonia at high organic loading, a phenomenon also observed by Caixeta et al. (2002). High alkalinity was induced in the reactor because of the high concentration of free ammonia. However, the rate of production of TVFAs was somewhat lower than the ammonification process, a phenomenon distinctly displayed by the pH pattern shown in Fig. 4.20. These resulted to a gradual pH increase from day 39 to day 48 as opposed to the co-digested mixture and textile wastewater.

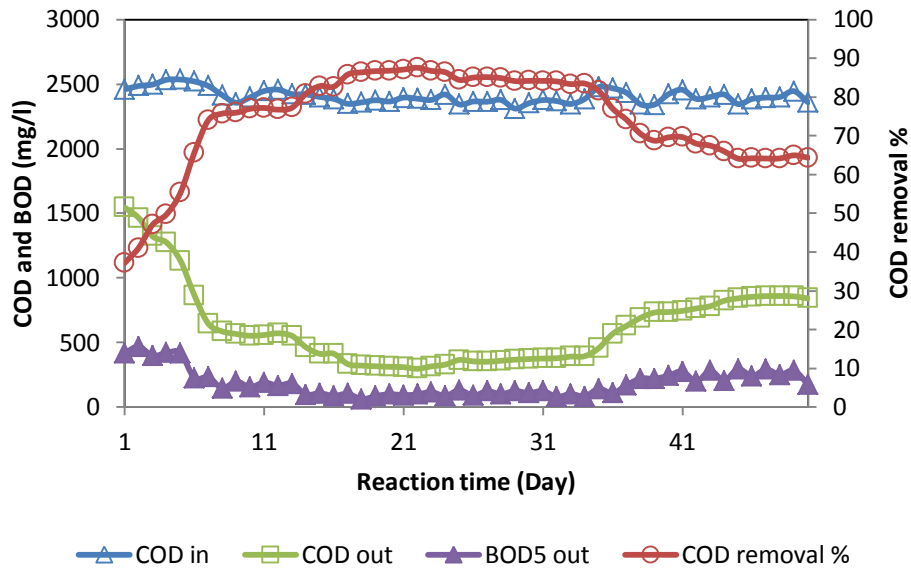


Figure 4.20: COD_{in}, COD_{out}, BOD_{5(out)} and COD removal efficiency against operation time for synthetic textile wastewater only.

The effluent COD decreased sharply with the operation period upto the 7th day when the COD stabilized and began decreasing gradually. This was elucidated by the rapid degradation of glucose present in the simulated mixture as a carbon source and as soon as most of it was degraded, the COD trend became more gradual and stable. The highest percentage COD removal was achieved between day 17 and 33 with the highest percentage removed being 87%. The effluent COD then increased sharply from day 35 to day 38 then adopted a more gradual ascent upto the 50th day. The influent COD was relatively constant in the course of the operation, with an average value of 2407 ± 53 mg/L. The average effluent COD was 623.94 ± 89.62 mg/L with average removal efficiencies of 74 ± 8 %. The BOD₅ values were way lower than the COD values compared to the reactors digesting the mixture as well as the abattoir wastewater. The average effluent BOD₅ value was 186.2 ± 13.7 mg/L yielding an average BOD₅: COD value of 0.29 ± 0.05 .

Average COD removal of 74% indicated the presence of biological activity in the reactor. However the biodegradability of the reactant was very low indicated by a BOD₅: COD ratio of 0.29. The low biodegradability suggests that textile wastewater treatment requires a more physio-chemical treatment than a biological one, a fact also pointed out by Lettinga et al. (1991). The effluent COD displayed a pattern similar to that shown by Haroun et al. (2009).

4.5.2 pH

The pH variations for all the wastewater streams are represented in Fig. 4.21. Generally, all reactors demonstrated well buffered processes because the pH values were maintained between 7.1 and 8.4. The pH values of the feedstock were corrected to between 7.06 and 7.18 (Table 3.1 and Table 3.2) but the pH had little variation owing to the bacteria forming acid as well as the ammonification process (Bergamo et al., 2009). The average pH values for the mixture, abattoir and textile wastewater were 7.85 ± 0.39 , 7.81 ± 0.33 and 7.76 ± 0.28 , respectively. The trend of all reactors exhibited similar patterns throughout the process. The initial pH values were around 7.1 at day 1 but soon after, the pH values increased steeply upto day 8. These can be explained by the ammonification process, which increased alkalinity in the reactor. However, from day 8 upto day 21, the pH trend was basically constant which indicated that the alkalinity was neutralized by the increasing production of VFAs in the acidogenesis process. It also indicated that the rate of ammonia production was equal to the rate of VFA production. After day 21, the pH values began decreasing which indicated that the rate of VFA production was higher than the rate of ammonia production. However, the pH of the system was still within allowable limits for anaerobic biodegradation. At stable pH, the value of VFA production is equal to the rate at which it is utilized in methane (CH_4) production (Buyukkamaci et al., 2004).

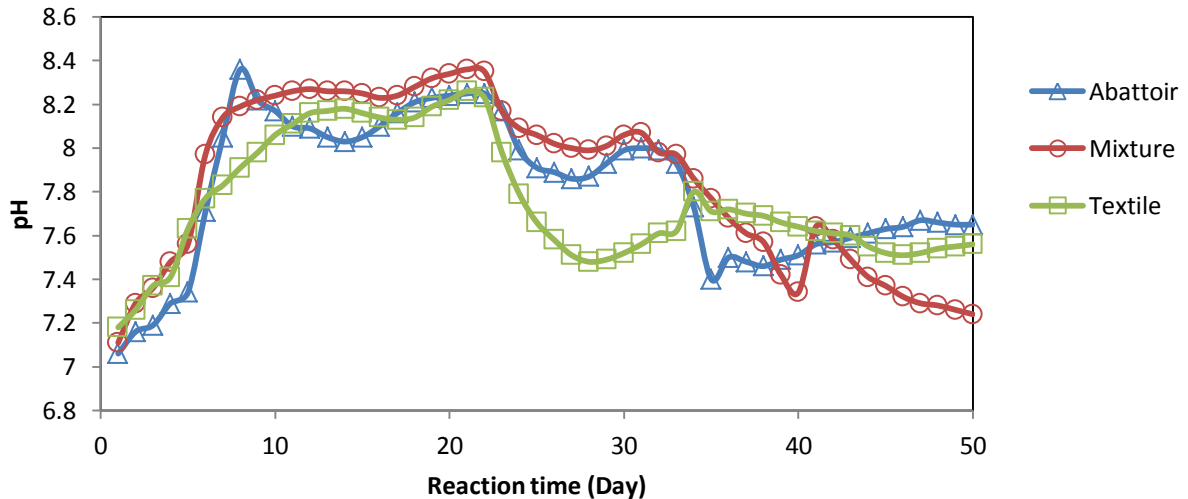


Figure 4.21: Variation of the pH with the digestion time for all the three reactors.

The pH observed in this process was predominantly within tolerable limits. This corresponded with the steady biogas production as shown in Fig. 4.22 which indicated no inhibition of the methanogenesis process.

4.5.3 Biogas production process

The biogas production throughout the operation period is shown in Fig. 4.22, while Fig. 4.23 shows the biogas yield of the co-digested mixture.

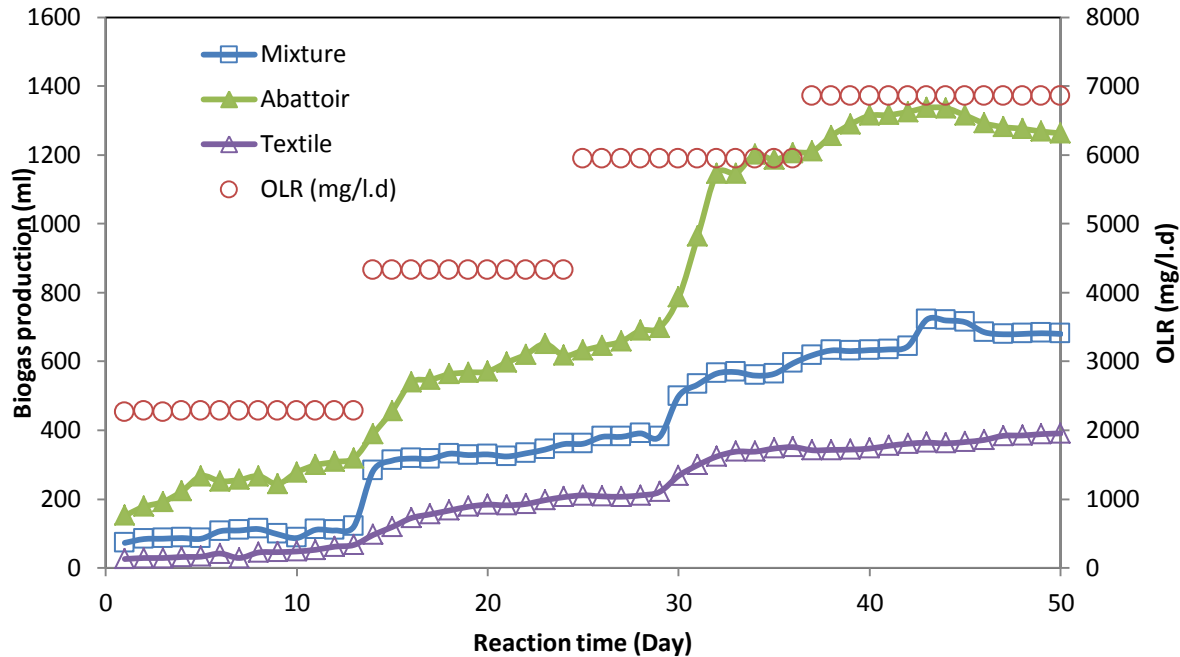


Figure 4.22: Variation of biogas production at different OLRs with the digestion time for all three reactors.

An increase in influent organic load increased the biogas yield until 6.855 kg COD/m³d beyond which a drop was observed in the two reactors digesting abattoir, and the co-digestion mixture. The abattoir effluent had the highest biogas yield whereas textile wastewater had the lowest biogas yield. The decrease in biogas yield beyond 6.855 kg COD/m³d organic load was caused by low pH (high acidity) due to the accumulation of VFAs at high OLRs. The low pH derailed normal operation of methanogenic bacteria coupled with biomass washout. The biogas production averaged from 0.031 (54% of methane) to 0.221 L/g.COD_{removed} (71% of methane) in the co-digestion mixture. Studies done by Hamdi et al. (1992) and Tritt et al. (1992) both agree with the fact that biomass production increases with increasing OLR upto a certain concentration beyond which the reactor fails due to accumulation of VFAs and eventual biomass washout.

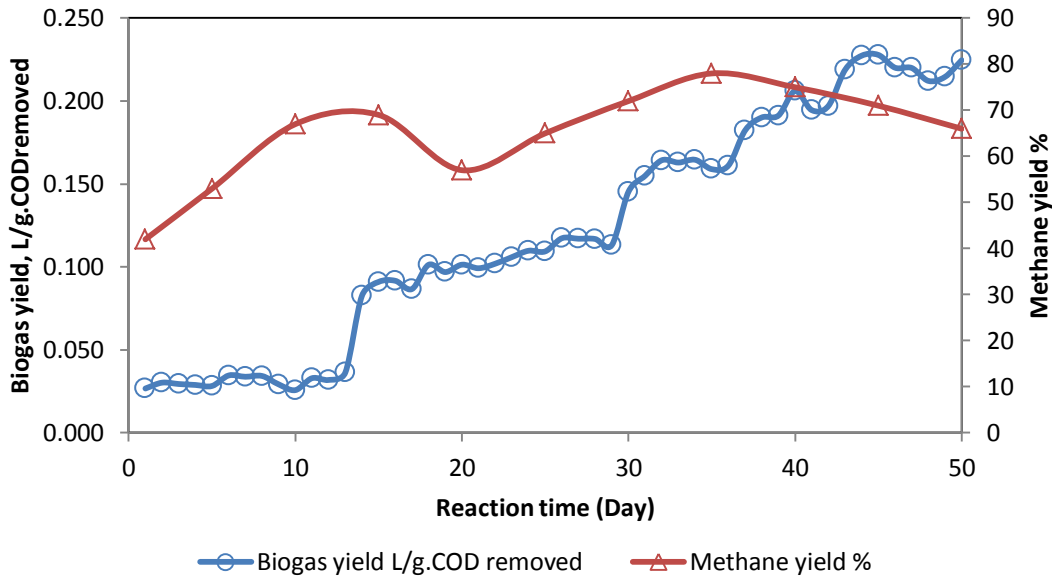


Figure 4.23: Variation of biogas production and percentage methane yield with digestion time for the co-digestion reactor.

4.6 Evaluation of the Operating Parameters for Steady State Co-digestion Process in the UASB

The UASB reactor achieved steady state after 24 days as shown in Fig 4.24 while being fed continuously at a flow rate of 0.375 L/d (8 day HRT). The flow rate of the reactor was then increased gradually up to 3 L/d (1 day HRT) and the various steady state parameter values are shown in Table 4.8.

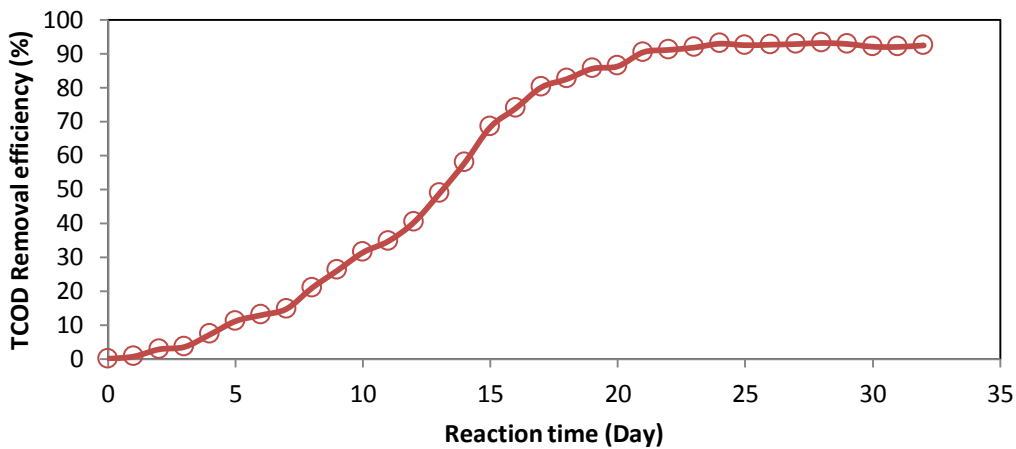


Figure 4.24: Effect of reaction time on TCOD removal efficiency at 0.375 L/d flow rate.

4.6.1 Effect of OLR, HRT and flow rate on substrate removal

The percentage reduction of SCOD, VSS, TCOD and TSS was caused by the increase in volumetric organic loading rate (V_{OLR}) at constant initial TCOD. At a V_{OLR} of 1.81 g TCOD/L d, an abrupt drop in percentage reduction was observed. An increase in TVFA/Alkalinity ratio (P) was responsible for this drop in TCOD because the TVFA increased whereas alkalinity decreased which collectively resulted to a drop in the pH value. The biogas quality was highly influenced by the P ratio such that an increase in P resulted in an increase in CO_2 concentration on all the experimental runs examined. The effect of HRT on the P ratio is illustrated in Fig.4.25.

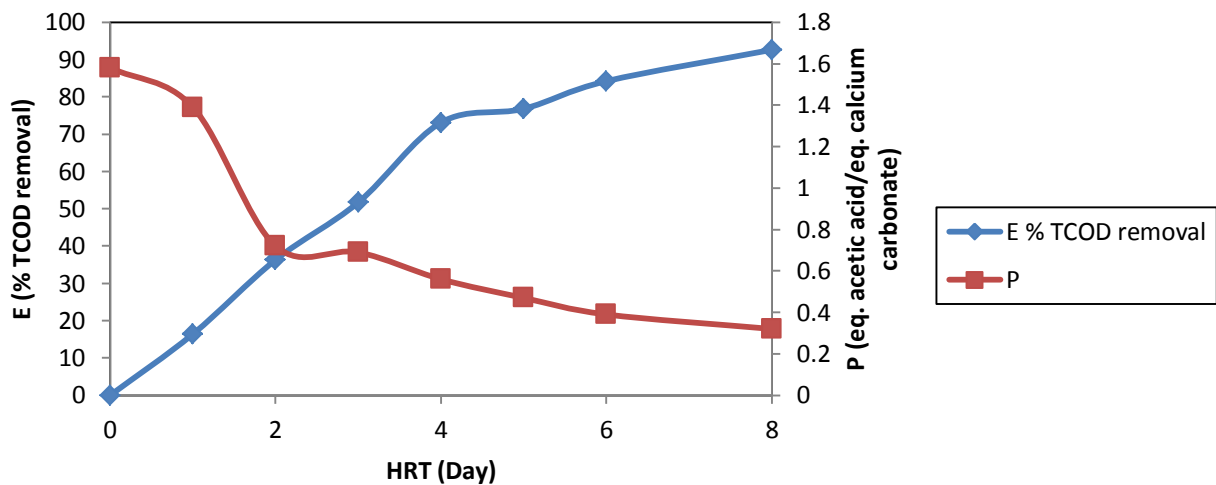


Figure 4.25: The effect of HRT variation on TCOD percentage reduction and TVFA/alkalinity ratio (P).

The steady state parameter values achieved under the various experimental conditions examined are shown in Table 4.8. As HRT increased, the value of P decreased. However, when the $VOLR$ was more than or equal to 1.81 g TCOD/L d, the percentage reduction dropped abruptly thereby increasing the TVFA/Alkalinity ratio beyond 0.7 which consequently destabilized the anaerobic degradation conditions. The TVFA/Alkalinity ratio (P) increased from 0.3 to 0.7 when the concentration of Carbon dioxide increased as shown in Fig. 4.26. At high P values, Carbon dioxide concentration remained rather constant. A similar trend was observed by Sanchez et al. (2005) and Yu et al. (2002). However, the CO_2 concentration increased when the value of P went up from 0.3 to 0.7 and remained practically constant at higher P values.

Table 4.8: Steady state parameters at various hydraulic retention times (HRTs)^A.

Flow Rates (L/d)	0.375		0.5		0.6		0.75		1		1.5		3		
HRT (d)	8		6		5		4		3		2		1		
V _{OLR} (g TCOD/L d)	0.45		0.6		0.72		0.91		1.21		1.81		3.62		
Parameter	Influent	Effluent	E (%)	Effluent	E (%)	Effluent	E (%)	Effluent	E (%)	Effluent	E (%)	Effluent	E (%)	Effluent	E (%)
TCOD	3622	268.028	92.6	572.276	84.2	840.304	76.8	974.318	73.1	1749.426	51.7	2307.214	36.3	3027.992	16.4
SCOD	2493	144.594	94.2	483.642	80.6	655.659	73.7	775.323	68.9	1161.738	53.4	1455.912	41.6	2041.767	18.1
TSS	697	46.002	93.4	116.399	83.3	237.677	65.9	273.224	60.8	368.016	47.2	432.14	38	520.659	25.3
VSS	506	44.022	91.3	94.116	81.4	131.054	74.1	145.728	71.2	203.412	59.8	225.676	55.4	301.07	40.5
TVFA	740	213		224		287		315		332		336		481	
Alkalinity	567	794		688		737		667		578		558		416	
p^b	1.58	0.32		0.39		0.47		0.56		0.69		0.72		1.39	
pH	6.7	7.3		7.4		7.4		7.3		7.2		7.2		6.9	
Q (l/l w d)		4.1		3.2		2.6		2.1		2		1.2		1	
CH₄		64.3		61.6		54.5		51.6		49.8		34.4		28.4	
CO₂		35.4		37.8		44.8		47.1		48.4		62.1		65.7	
q_M (L/L w d)		2.59		1.96		1.46		1.44		1.41		1.16		0.97	
Q_M (L/L r d)		0.17		0.19		0.22		0.29		0.38		0.49		0.64	

^a Values are averages of 50 determinations taken over seven weeks after the steady-state conditions had been reached. The differences between the observed values were less than 3.7% in all cases.

^b TVFA/alkalinity ratio is expressed in equivalents of acetic acid/equivalents of calcium carbonate.

A similar trend was observed by Sanchez et al. (2005) in the study of anaerobic digestion of piggery wastewater and similarly in the acidogenesis of dairy and gelatin-rich wastewaters using upflow anaerobic reactors (Yu et al., 2002).

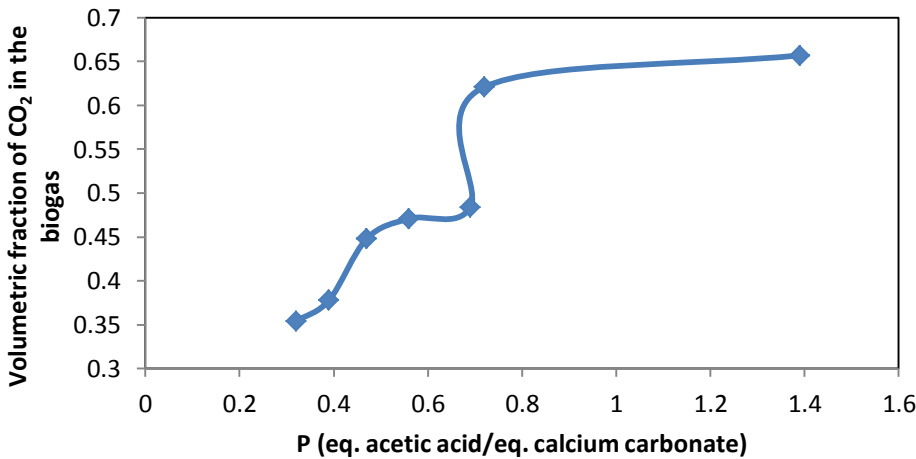


Figure 4.26: Volumetric proportion of carbon dioxide (CO₂) against the TVFA/alkalinity (*P*) ratio.

A decrease in HRT increased the residual substrate concentration indicating a slow-down in the degradation process which resulted to the increase of TVFA concentration and consequently the *P* ratio (Figure 4.26). This resulted into a linear function equation (4.1);

$$\mathbf{P = 0.564(S) + 0.115} \quad \mathbf{(4.1)}$$

The regression coefficient value (r^2) was 0.94, which was in the same range with the regression coefficient obtained in literature (Sanchez et al., 2005). Equation (4.1) demonstrates the anaerobic co-digestion stability and also ascertains the influence of substrate concentration on reactor performance. The degradation process of this study was favourable between *P* values of 0.5 and 0.65. However, when the value went beyond 0.65 the process became unstable, thereby slowing the degradation process. This was mainly observed when substrate concentrations exceeded 1.05 g SCOD/L. The good performance was because of the synergy achieved in the co-digestion mixture. Fannin (1987) elucidated how the TVFA/alkalinity ratio (*P*) was used as a measure of process stability in the sense that, when the ratio is less than 0.4, the process is considered to be operating favourably without the risk of acidification. The mineral acids and aromatic compounds present in the supernatant were associated with the ordinate value which consequently exhibited a profound influence on the *P*-value.

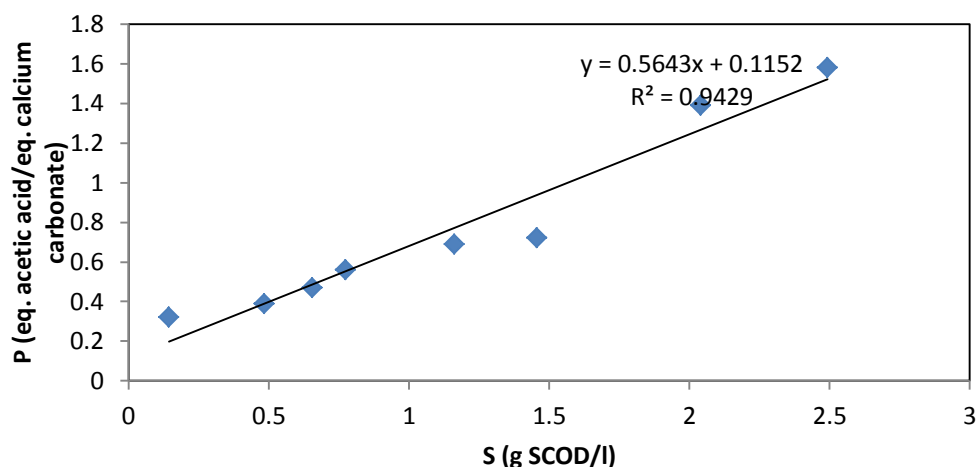


Figure 4.27: Influence of residual SCOD on TVFA/Alkalinity (P) ratio.

According to Table 4.8, the alkalinity values obtained in this process suggested favourable buffering capacities between V_{OLR} ranges of 0.45 – 3.62 g TCOD/L d. The buffering system was regulated by alkalinity generated from dissolution of residual carbon dioxide gas trapped in the aqueous matrix, an observation also made by Wheatly (1990).

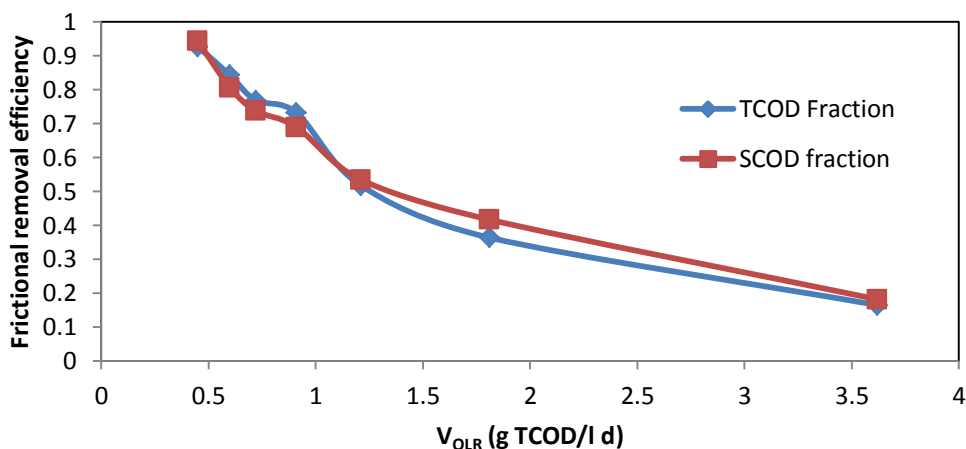


Figure 4.28: Proportional percentage reduction against volumetric OLR (V_{OLR}).

An increase in V_{OLR} resulted to a gradual decrease in percentage reduction as shown in Figure 4.28. Significant percentage reductions were achieved at V_{OLR} values ranging between 0.45 and 0.91 g TCOD/l d. The percentage reductions dropped abruptly between V_{OLR} of 1.81 to 3.62 g TCOD/l d which was directly associated with the TVFA/Alkalinity values greater than 0.7. If an exponential expression between V_{OLR} and the substrate percentage reductions adopted from

Sanchez et al., (2005), (equation 4.2), is evaluated, k values of 0.50 and 0.55 are obtained for SCOD and TCOD respectively.

$$E = e^{-kV_{OLR}} \quad (4.2)$$

where E , is the proportional percentage reduction and k is a rate constant given in $d/l/g$ and primarily dependent on selected parameters.

The k values obtained demonstrated that the removal efficiencies attenuation rates decreased with V_{OLR} in the following order: SCOD > TCOD. Additionally, the results showed that the uptake of insoluble organic carbonaceous compounds was always lower than that observed for soluble organic carbonaceous compounds. Similarly, it can be inferred that particulate COD was first broken down into aqueous COD and then converted into biogas.

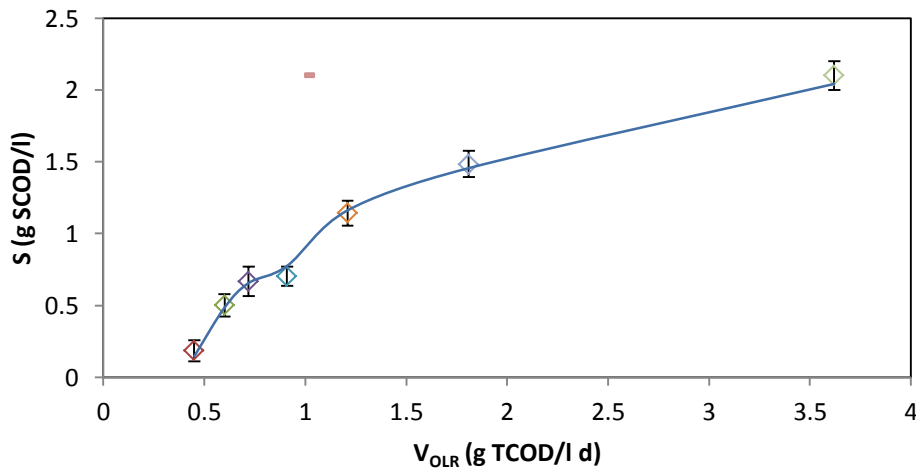


Figure 4.29: Effect of varying volumetric OLR (V_{OLR}) on the residual and theoretical SCOD (Eq. 4.3) concentration.

An expression described as hyperbolic in literature (Sanchez at al., 2005) relating the residual COD and V_{OLR} concentration is described as follows:

$$S = K_1 [V_{OLR} / (K_2 + V_{OLR})] \quad (4.3)$$

where K_1 indicates the maximum theoretical SCOD concentration (g SCOD/l) when V_{OLR} is high compared to K_2 .

The constant term K_2 , given in g TCOD/L d, describes the value of V_{OLR} for which the effluent SCOD concentration is tantamount to $K_1/2$. A plot of the inverse of S versus the inverse of V_{OLR}

gave a straight line with an intercept equal to $1/K_1$ and slope equal to K_2/K_1 with a correlation factor (r^2) equal to 0.98 (Appendix C). Consequently, the values of K_1 and K_2 were found to be 3.97 ± 0.24 g SCOD/l and 2.71 ± 0.16 g TCOD/l d, respectively. The theoretical S value, obtained by Eq. (4.3), and its variation with the V_{OLR} values are shown in Fig. 4.29. Deviations lower than 5.4% between the experimental and theoretical values of S were obtained. The second term of the denominator of this expression can be neglected for lower V_{OLR} values, hence, Eq. (4.3) can be transformed into a linear equation, as follows: $S = 1.46 V_{OLR}$, where 1.46 is the value of K_2/K_1 .

The SCOD percentage increased with an increase in V_{OLR} with respect to hyperbolic expression (4.4) (Sanchez et al., 2005):

$$R = R_M [V_{OLR} / (K + V_{OLR})] \quad (4.4)$$

where: R_M , is the maximum SCOD percentage reduction (g SCOD/L d), and K is a kinetic constant representing the value of V_{OLR} for which the value of R is equal to $0.5R_M$.

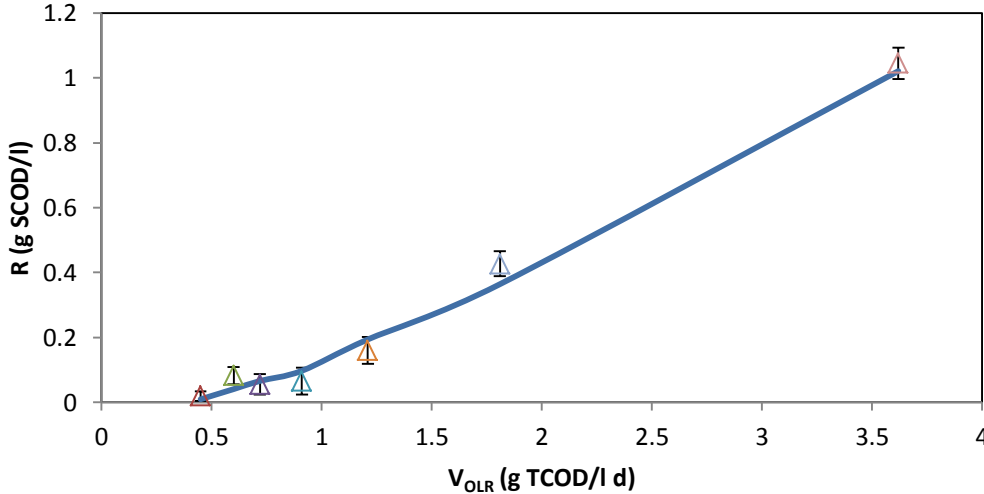


Figure 4.30: SCOD removal rate (R) against the volumetric OLR (V_{OLR}).

The kinetic constant values were determined by plotting the inverse of V_{OLR} against the inverse of R . A linear trend whose coefficient of correlation was 0.96 necessitated the evaluation of R_M from the gradient of the linearized equation. The evaluated K and R_M values were 1.13 and 0.98, respectively. When K and R_M values were substituted in equation (4.4), the disparity between

calculated and experimental results were less than 12%. A decrease in V_{OLR} decreased the biogas yield (Figure 4.31) per reactor volume (Q_M) due to the reduced organic substrate provision.

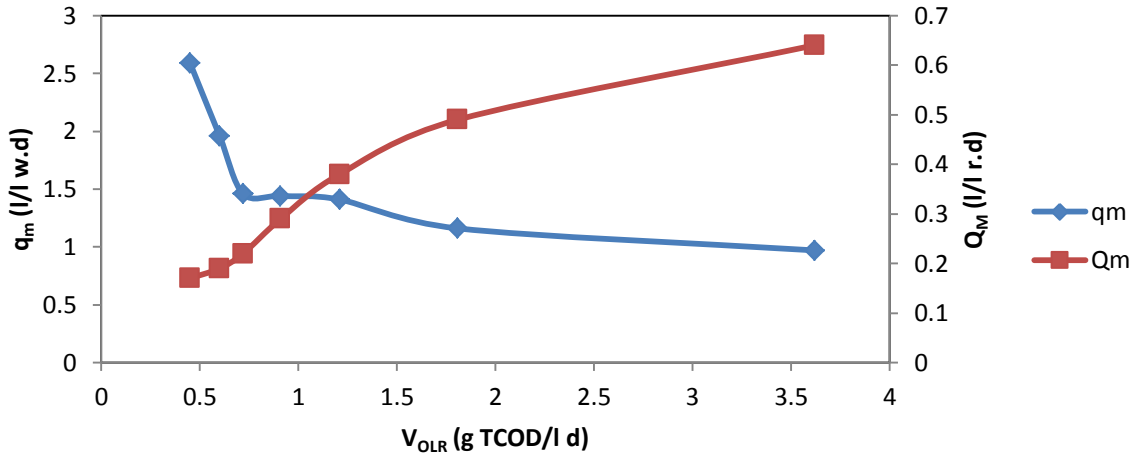


Figure 4.31: Effect of the volumetric OLR (V_{OLR}) on biogas yield per volume of influent (q_m) and per volume of reactor (Q_M).

The organic volumetric loading rate influences the anaerobic degradation performance immensely and is a critical parameter as far as the process scale-up is concerned. V_{OLR} is a function of HRT and initial organic substrate as described in equation (4.5);

$$V_{OLR} = S_0 Q/V = S_0/HRT \quad (4.5)$$

where S_0 , is the initial organic substrate (g TCOD/l); Q , is the feedstock flow rate (l/d); V , is the reactor capacity (L).

There was a decrease in the feedstock flow rate (Q) with every decrease in V_{OLR} at fixed initial substrate concentration, thereby increasing the HRT.

4.6.2 Grau second-order multicomponent substrate removal model

The general equation of a second-order kinetic model is illustrated in Eq. (4.6) (Grau et al., 1975; Ozturk et al., 1998).

$$-\frac{dS}{dt} = k_s \cdot X \cdot \left(\frac{S}{S_0}\right)^2 \quad (4.6)$$

Integration and linearization of equation (4.6) yields equation (4.7);

$$(S_0 - \theta_H)/(S_0 - S) = \theta_H - S_0/(k_s \cdot X) \quad (4.7)$$

Assuming that ' $S_o/(k_s \cdot X)$ ' in equation (4.7) is a constant term, then the equation can also be written as equation (4.8);

$$(S_o - \theta_H)/(S_o - S) = b \cdot \theta_H + a \quad (4.8)$$

$(S_o - S)/S_o$ represents the substrate percentage removal denoted by 'E'.

Finally, equation (4.8) is transformed to equation (4.9);

$$\theta_H/E = a + b \cdot \theta_H \quad (4.9)$$

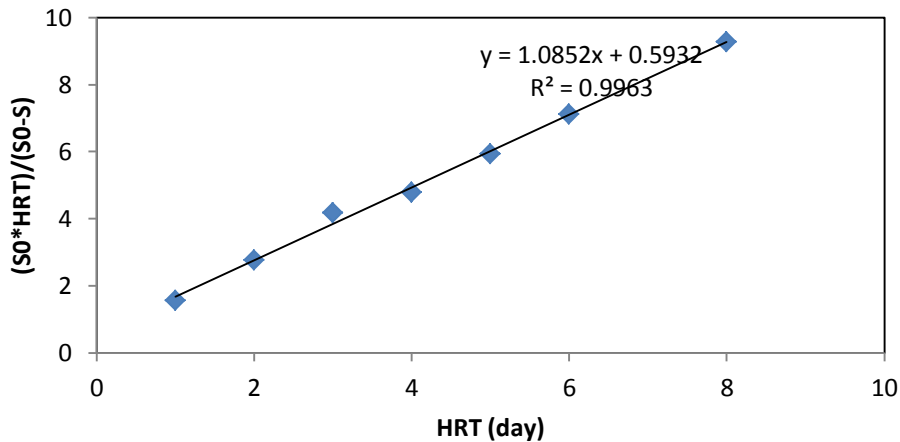


Figure 4.32: Evaluation of kinetic constants (a , b and k_s) for Grau's second-order multicomponent substrate removal model.

Plotting equation (4.9), as demonstrated in Figure 4.32 yields a linear trend from whose slope and ordinate intercept the kinetic constant values (a , b and k_s) were evaluated. The value of 'a' was 0.593 and the value of 'b' was 1.085 with a 0.996 coefficient of correlation (r^2). The kinetic rate constant (k_s) for multicomponent substrate removal was found to be 0.389 per day as worked out from the expression; $a = S_o/k_s \cdot X$.

4.6.3 Evaluation of the kinetic model

Kinetic data evaluated through Grau's second-order multicomponent substrate removal model (Table 4.9), successfully described the kinetics of a stable anaerobic co-digestion judging from the coefficient of correlation (0.996) and kinetic constant achieved ($k_s = 0.389$). The kinetic coefficient calculated exhibited similar results to the kinetic data discussed by Isik et al. (2005) where several kinetic models were investigated (Grau's second-order multicomponent, Stover-Kincannon and Contois substrate removal kinetic models) treating simulated textile wastewater

containing sizing agents azo dyes, salts and other additives. This study proved that Grau's second-order multicomponent, Stover-Kincannon and Contois substrate removal kinetic models were more suitable for evaluating anaerobic co-digestion kinetics than any other model with respect to regression coefficients. A comparison made between kinetic constants evaluated in literature is shown in Table 4.10. The k_s value in this study was higher than that in most studies because the microorganism concentration (X), which is inversely proportional to the k_s value, was lower in the co-digestion mixture compared to other studies since the toxicity of aromatic amines tended to hamper microbial performance. According to the model, k_s values increased with increasing rate of substrate removal subject to the influent COD and reactor biomass concentration (X). Furthermore, literature postulates that the OLR affects the substrate removal rate which can best be elaborated by the Modified Stover-Kincannon model (Isik et al., 2005).

Table 4.9: Kinetic parameter of UASB reactor treating abattoir and textile co-digestion mixture.

Kinetic models	Kinetic parameters	Values	Regression coefficients (R^2)
Grau second order	a (per day)	0.593	0.996
	b (dimensionless)	1.085	0.996
	k_s (per day)	0.389	0.996

Table 4.10: Comparison of kinetic constants for Contois, Grau's second-order and Monod kinetic models.

Models	Substrate	Reactor type	Influent COD (mg l ⁻¹)	HRT (day)	Kinetic Parameters					References
					k_s	a	b			
Grau second order	Municipal wastewater	UASB	230 - 445	0.25 - 1.0	0.217	0.002	1.346			Ubay (1994)
Grau second order	Simulated Wastewater	UASB	4214	0.25 - 4.16	0.337	0.562	1.095			Isik et al., 2005
Grau second order	Abattoir and Textile effluent (co-digestion)	UASB	3622	1 - 8	0.389	0.593	1.085			This study
					R_{max}	K_B				
					μ_{max}	β	Y	K_d		
Contois	Ice-cream wastewater	UASB	4214	0.25 - 4.16	0.105	0.125	0.006	0.006		Isik et al., 2005
							5	5		
					μ_{max}	K_{max}	Y	K_d	K_s	
Monod	Simulated Wastewater	UASB	4214	0.25 - 4.17	0.105	0.84	0.125	0.006	>400	Isik et al., 2006
							5	0		

5.1 Conclusion

Raw pre-treated abattoir wastewater was sampled and characterized and the results used to prepare the synthetic abattoir wastewater. Textile wastewater was also synthesized and co-digested together anaerobically. The optimum percentage mix ratio of abattoir to textile wastewater mixture was determined. The mixture was then co-digested anaerobically and compared with results of a mono-digestion of abattoir and textile effluent streams. Results of the mono-digestion of the abattoir and textile were evaluated to establish the feasibility of co-digesting abattoir and textile wastewater anaerobically (effluent mix ratio, organic loading rate, pH, temperature).

5.1.1 Wastewater characterization.

The synthetic wastewater streams were characterized and abattoir wastewater exhibited high biodegradability as opposed to textile wastewater. The biodegradability ratio (BOD:COD) of abattoir effluent was 0.58 whereas the BOD:COD of textile effluent was 0.29. The characteristics of both abattoir and textile wastewater concurred with those reported in literature.

5.1.2 Optimum abattoir to textile wastewater ratio

Abattoir and textile effluent were synthesized for efficient reproducibility. The two effluent streams were then mixed in particular proportions in order to establish the optimum mix ratio for efficient reactor performance. The optimum abattoir to textile wastewater ratio obtained was 60:40, which had TCOD of 3622 mg/L. The mixture was found to be more biodegradable compared to the synthetic textile effluent stream since the biodegradability ratio (BOD:COD) of the synthetic effluent mixture (abattoir and textile) was 0.53.

5.1.3 Evaluation of the substrate and dye removal efficiencies of the co-digestion mixture at mesophilic and ambient temperatures.

The results of this study demonstrate that the variations of COD, TVFA, alkalinity, pH and methane production with time during the batch anaerobic digestion of synthetic abattoir and textile mixed wastewater followed the same pattern both at mesophilic and ambient temperatures. Experimental data obtained adequately fit in the Grau first order kinetic model. The azo dyes were positively degraded yielding Total Aromatic Amines.

5.1.4 Evaluation of the operating parameters for steady state co-digestion process in the UASB

The results of this study showed that synthetic effluent mixture of abattoir and textile industries could be degraded effectively using UASB reactor at different HRTs varying between 1 and 8 days. The kinetics evaluated according to Grau's second order multicomponent substrate removal kinetic model yielded a correlation coefficient of 0.996 and a significant kinetic coefficient (k_s) of 0.389 (Figure 4.32), which were found suitable for predicting the performance of a lab-scale UASB reactor.

The feasibility of co-digesting abattoir and textile wastewater was successful because the synergy established between high nutrient content of abattoir wastewater and low nutrient content of the recalcitrant textile wastewater aided the reduction of HRT and an increase in COD reduction. The textile wastewater which is essentially complex and hard to degrade anaerobically was effectively broken down in the co-digestion process.

5.2 Recommendations

Due to low biodegradability ratios obtained for textile wastewater, anaerobic treatment methods are highly unsuitable for treating the effluent effectively. The degradation of textile effluents yields aromatic amines which are more detrimental to the environment than raw wastewater. Therefore, appropriate wastewater post-treatment techniques should be investigated to eliminate the aromatic compounds.

Co-digesting textile industry effluents with abattoir plant effluents at mesophilic temperature conditions improves the degradation of textile effluents. Temperature control is a crucial aspect in anaerobic co-digestion because temperature variations influence the reactor performance significantly. Proper inoculum sampling and acclimatization enhances UASB reactor start-up process thus improving the substrate removal rate of industrial effluents.

In as much as there was a distinct relationship between the TAA removal efficiencies with COD removal efficiencies, further studies should be conducted to establish the relationship between TAA and COD concentrations in the co-digestion of synthetic abattoir and textile industrial effluents. Kinetic studies carried out from the lab scale UASB reactor can be applied when

predicting the performance of full-scale UASB reactors if the mixture of abattoir and textile industry wastewater was co-digested at similar loading and temperature conditions.

The kinetics developed in this study is sufficient to scale-up the anaerobic co-digestion of industrial effluent from a lab scale UASB to an industrial scale UASB reactor.

Industrial effluents of complementing characteristics can be co-degraded anaerobically in order to hasten the substrate breakdown process of otherwise complex and recalcitrant wastewaters.

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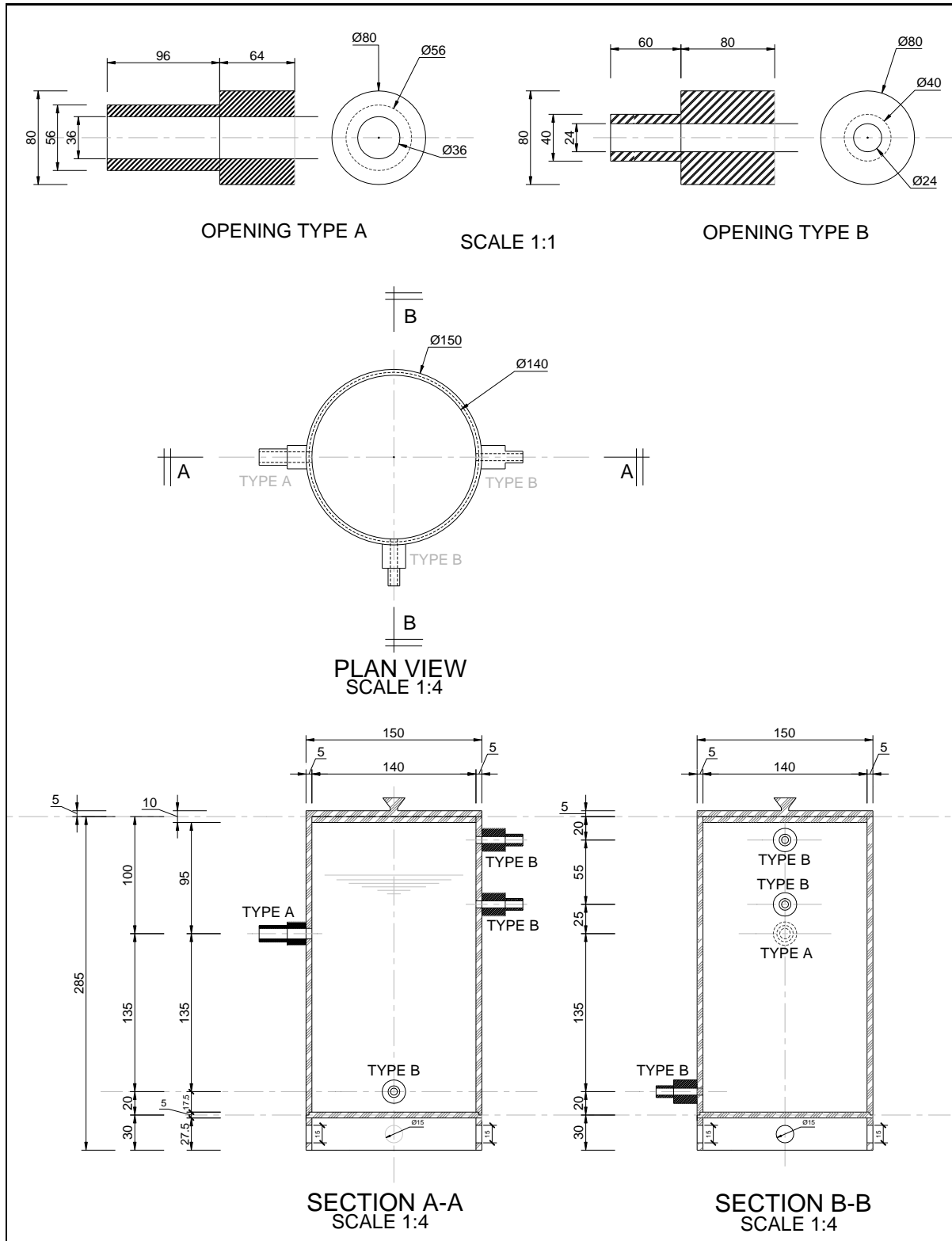
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APPENDIX

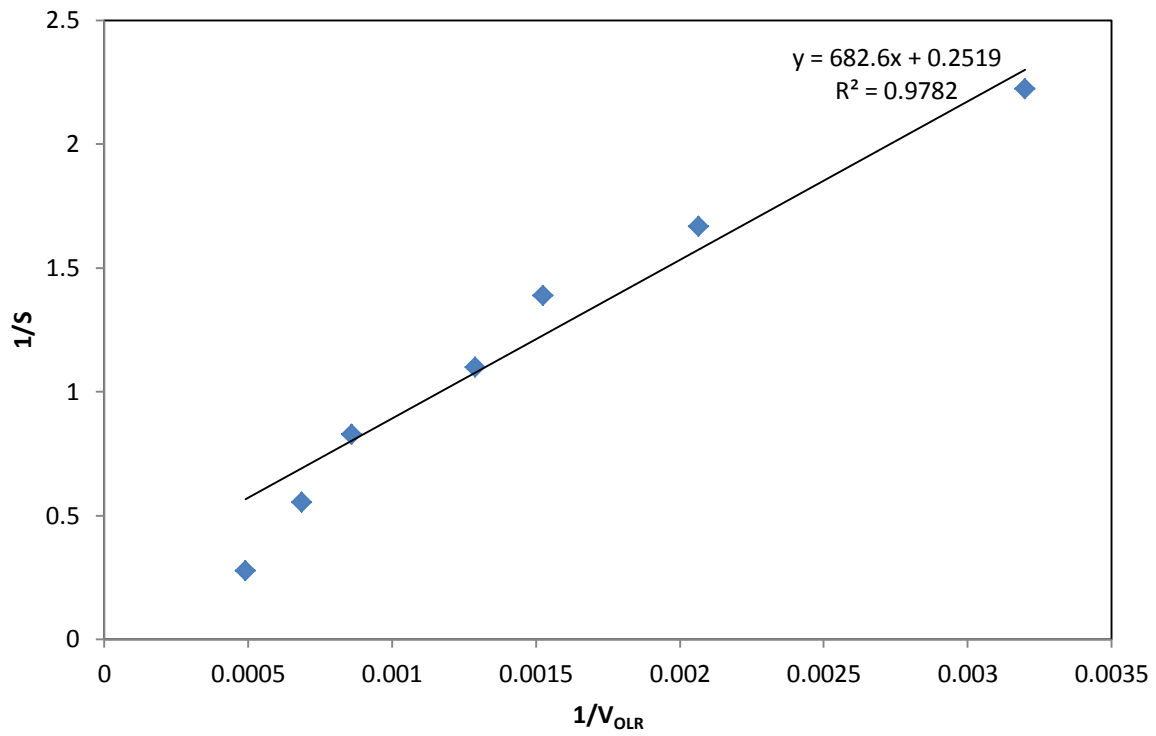
APPENDIX A: UASB REACTOR SPECIFICATIONS DRAWN TO SCALE.



APPENDIX B: TABLE SHOWING STEADY STATE PARAMETERS.

Days	TCOD	TCOD EFFICIENCY %	SCOD	SCOD EFFICIENCY %	TSS	TSS EFFICIENCY %	VSS	VSS EFFICIENCY %	TVFA	TVFA EFFICIENCY %
0	3622	0.00	2493	0	697	0.00	506	0.00	740	0.00
1	3598	0.66	2466	1.08	695	0.28	501	0.97	732	1.26
2	3521	2.79	2417	3.05	681	2.25	491	2.94	714	3.51
3	3495	3.51	2356	5.50	664	4.70	479	5.39	703	4.81
4	3362	7.18	2285	8.34	644	7.54	464	8.23	694	6.22
5	3220	11.10	2145	13.96	605	13.16	436	13.85	661	10.68
6	3156	12.87	1988	20.26	561	19.46	418	17.30	651	12.03
7	3089	14.72	1822	26.92	515	26.12	385	22.96	632	14.59
8	2865	20.90	1623	34.90	459	34.10	344	28.94	612	17.30
9	2678	26.06	1425	42.84	404	42.04	304	35.34	595	19.59
10	2486	31.36	1311	47.41	372	46.61	281	39.31	562	24.05
11	2365	34.70	1127	54.79	326	53.23	248	44.63	544	26.49
12	2164	40.25	988	60.37	287	58.81	219	49.41	520	29.73
13	1856	48.76	921	63.06	268	61.50	206	53.05	513	30.68
14	1525	57.90	801	67.87	235	66.31	181	58.71	505	31.76
15	1146	68.36	651	73.89	193	72.33	151	66.03	498	32.70
16	945	73.91	586	76.49	175	74.93	138	69.73	475	35.81
17	722	80.07	526	78.90	158	77.34	126	73.24	435	41.22
18	634	82.50	447	82.07	136	80.51	110	78.01	417	43.65
19	523	85.56	392	84.28	120	82.72	98	80.56	395	46.62
20	497	86.28	288	88.45	91	86.89	77	81.89	374	49.46
21	347	90.42	254	89.81	82	88.25	70	83.75	364	50.81
22	322	91.11	221	91.14	69	90.07	62	85.77	351	52.57
23	297	91.80	203	91.86	64	90.79	58	87.19	336	54.59
24	256	92.93	186	92.54	59	91.47	55	89.21	312	57.84
25	272	92.49	171	93.14	55	92.07	52	89.81	304	58.92
26	266	92.66	166	93.34	54	92.27	51	90.01	288	61.08
27	260	92.82	168	93.26	54	92.19	50	90.07	264	64.32
28	248	93.15	159	93.62	52	92.55	48	90.43	252	65.95
29	259	92.85	153	93.86	50	92.79	47	90.67	237	67.97
30	288	92.05	152	93.90	50	92.83	47	90.71	229	69.05
31	290	91.99	148	94.06	49	92.99	46	90.87	219	70.41
32	274	92.44	146	94.14	48	93.07	46	90.87	215	70.95

APPENDIX C: GRAPH SHOWING HOW TO OBTAIN THE VALUE OF K_1 AND K_2 .



APPENDIX D: APHA EXTRACTS FOR COD AND BOD₅.

Attached from the next page.