

**Performance Evaluation of a New Multi-Environment Wastewater Treatment
System for the Removal of Carbon, Nitrogen and Phosphorus from Synthetic
and Real Agricultural Wastewaters**

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ABSTRACT

Performance Evaluation of a New Multi-Environment Wastewater Treatment System for the Removal of Carbon, Nitrogen and Phosphorus from Synthetic and Real Agricultural Wastewaters

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A new integrated multi-environment wastewater treatment technology was evaluated for simultaneous removal of organic carbonaceous compounds as well as inorganic contaminants, notably nitrogen and phosphorus from synthetic and hog wastewater. The influent concentrations of carbon, nitrogen and phosphorus during the reported experiments on synthetic wastewater were in the range of 500 to 4000 mg/L, 42 to 200 mg/L, and 16 to 40 mg/L, respectively. The treatment system operated with food-to microorganisms (F/M) ratio of 0.95 to 3.4 (d^{-1}) and SRT of 10 -200 days, producing removal efficiencies of 83.3% -99% for COD, 65.9%-85% for total nitrogen and 10%-100% for total phosphorus. The very high removal efficiencies obtained in this study show the proper performance of the integrated treatment system. The influent concentrations of hog waste were in the range of 1000 to 2400 mg/L, 200-230 mg/L, and 40-48 mg/L for COD, total nitrogen and total phosphorus, respectively. The system operated with organic loading rates of 0.51 to 1.43 kg COD/ $m^3.d$, nitrogen loading rates of 0.07 to 0.16 kg TN/ $m^3.d$, and phosphorus loading rates of 0.015 to 0.035 kg TP/ $m^3.d$. The solid retention time and hydraulic retention time were in the range of 12 to 33 days and 1.43 to 1.74 days, respectively. The overall COD/N/P and BOD/N/P ratio were maintained at the range of 27:4.5:1 to 70:3.64:1 and 26:4.5:1 to 69:3.64:1, respectively, for the maximum removal of contaminants

along with food-to-microorganism ratio (F/M) of 1.04 to 2.57 d⁻¹ in the mixed liquor. The removal efficiencies of COD, BOD, N and P for hog waste were in the range of as 60%-89%, 40%-89%, 10%-69% and 14%-40%, respectively. The increasing trend of contaminant removal efficiency with time during the treatment of hog waste suggests that higher removal efficiencies would be obtained if the treatment system had operated for a longer period.

Dedicated to

*My beloved parents and sisters for their love, affection, encouragement
and inspiration in every step of my life.*

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TABLE OF CONTENTS

LIST OF FIGURES	x
LIST OF TABLES	xii
LIST OF SYMBOLS AND ABBREVIATIONS	xiii
CHAPTER 1: INTRODUCTION AND OBJECTIVES	1
1.1 Introduction:.....	1
1.2 General Goal:.....	6
1.3 Specific Objectives:	6
1.4 Organization of the thesis:	7
CHAPTER 2: LITERATURE REVIEW	8
CHAPTER 3: MATERIALS AND METHODS	15
3.1 Experimental set up:	15
3.1.1 Integrated Multi-Zone Wastewater Treatment System:	15
3.2 Inoculum:	17
3.3 Synthetic Wastewater:	18
3.4 Real Agricultural Wastewater:.....	19
3.5 Operating Parameters:.....	20
3.6 Analytical Methods:.....	21
3.6.1 Total Solids (TS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS):.....	22
3.6.2 Total Solids, TS:	22
3.6.3 Total Suspended Solids, TSS:.....	23

3.6.4 Volatile Suspended Solids, VSS:	23
3.6.5 Chemical Oxygen Demand (COD):	24
3.6.6 Biochemical Oxygen Demand (BOD):	24
3.6.7 Total Nitrogen (TN):	26
3.6.8 Ammonia-Nitrogen (NH ₃ -N):	26
3.6.9 Nitrate-Nitrogen (NO ₃ -N):	26
3.6.10 Nitrite-Nitrogen (NO ₂ -N):	27
3.6.11 Total Phosphorus (TP):	27
3.6.12 Volatile Fatty Acids (VFA):	28
CHAPTER 4: RESULTS AND DISCUSSION-HOG MANURE	29
4.1 Operating Parameters:	29
4.1.1 Loading Rates:	29
4.1.2 Feast and Famine Period:	30
4.1.3 Dissolved Oxygen:	30
4.1.4 pH:	32
4.1.5 Oxidation Reduction Potential (ORP):	34
4.1.6 Temperature:	35
4.1.7 Solid Retention Time (SRT):	35
4.1.8 Hydraulic Retention Time (HRT):	35
4.2 Operating Conditions and Removal Efficiencies:	36
4.2.1 Chemical Oxygen Demand (COD):	36

4.2.2 Nitrogen Removal:.....	44
4.2.3 Phosphorus Removal:	50
4.3 Mixed Liquor Characteristics and Sludge Yield:.....	53
4.4 Composition of Sludge in Anoxic and Anaerobic Zones.....	54
4.5 Comparing the results with the previous work:	56
CHAPTER 5 : RESULTS AND DISCUSSION-SYNTHETIC WASTEWATER	63
5.1 Operating Conditions:.....	63
5.2 Removal Efficiencies:.....	64
5.2.1 Chemical Oxygen Demand:	65
5.2.2 Total Nitrogen, TN:.....	66
5.2.3 Total Phosphorus, TP:.....	68
5.2.4 Influence of N/P ratio on TN and TP removal:.....	70
5.2.5 Influence of C/N ratio on COD and TN removal:.....	71
5.3 Total Chemical Oxygen Demand:.....	72
5.4 Process Parameters:	72
5.5 Characterization of sludge:	74
5.6 Comparison with the previous work:	75
CHAPTER 6: CONCLUSIONS	79
CHAPTER 7: RECOMMENDATIONS AND FUTURE WORKS	80
REFERENCES	81

LIST OF FIGURES

Figure 3.1: Schematic diagram of integrated multi-zone wastewater treatment system. The air diffusers introduce air through the microbial support to the aerobic zone. The second reactor is connected to the first reactor.	17
Figure 4.1: Loading rates of COD, total nitrogen and total phosphorus in the system during the treatment of hog wastewater	29
Figure 4.2: Dissolved oxygen concentration during the feast and famine period of the system during the month of February.....	31
Figure 4.3: pH maintained in aerobic, anoxic and anaerobic zones of the reactor during the operation	32
Figure 4.4: Oxidation reduction potential in aerobic, microaerophilic and anoxic zones of the treatment system	34
Figure 4.5: Variations of the COD removal efficiency during the treatment of hog waste	37
Figure 4.6: Variations of the BOD removal efficiency during the treatment of hog waste	38
Figure 4.7: Dependence of COD removal efficiency on the organic loading rate.....	38
Figure 4.8: Removal efficiency of COD with food per microorganism ration	39
Figure 4.9: Removal efficiency of COD with the increase of COD/N ratio	39
Figure 4.10: Relationship between COD removal efficiency and COD/P ratio during the operation	40
Figure 4.11: Dependence of COD removal efficiency on the N/P ratio	41
Figure 4.12: COD removal efficiency with the variation of BOD/P ratio	42
Figure 4.13: COD removal efficiency with the variation of BOD/N ratio	42
Figure 4.14: Correlation between COD and BOD for hog wastewater	43
Figure 4.15: Concentrations of nitrogenous compounds in influent of hog wastewater during the operation of treatment system	45

Figure 4.16: Removal of nitrogenous compounds by the treatment system with the increased organic loading rate.....	46
Figure 4.17: Dependence of percentage nitrogen removal on the COD/N ratio.....	47
Figure 4.18: Relationship between TN removal efficiency and COD/P ratio	48
Figure 4.19: Relationship between TKN removal efficiency and COD/P ratio.....	48
Figure 4.20: Percentage removal of phosphorus with time.....	51
Figure 4.21: Relationship between phosphorus removal and COD/N ratio in the system.....	51
Figure 4.22: Dependence of phosphorus removal efficiency on organic loading rate.....	52
Figure 4.23: Biomass yield in the system	53
Figure 5.1: Loading rates of carbon, nitrogen and phosphorus in the system during the treatment of synthetic wastewater	63
Figure 5.2: Overall COD concentration in the influent and effluent samples.....	65
Figure 5.3: Variations of the COD removal efficiency with time.....	66
Figure 5.4: Total nitrogen and ammonia removal efficiencies with time	67
Figure 5.5: Variations of phosphorus removal efficiency with time	69
Figure 5.6: Removal efficiencies of total nitrogen and total phosphorus versus N/P ratio.....	70
Figure 5.7: Dependence of percentage removal of COD and total phosphorus on the C/N ratio.....	71

LIST OF TABLES

Table 3.1: Synthetic wastewater composition.....	18
Table 3.2: Composition of trace elements in the synthetic wastewater	19
Table 3.3: Average composition of agricultural wastewater	19
Table 3.4: Environmental conditions in the various treatment zones	21
Table 4.1: Biochemical oxygen demand for organic carbon and organic nitrogen compounds	44
Table 4.2: Concentrations of nitrate and nitrite in the influent	49
Table 4.3: Average concentrations of nitrite and nitrate in the effluent of the treatment system	50
Table 4.4: Characteristics of mixed liquor	53
Table 4.5: Specific utilization rate of contaminants.....	54
Table 4.6: Characteristics of sludge.....	55
Table 4.7: Comparison between Integrated Multi-Zone Wastewater Treatment System and reported work in literature	62
Table 5.1: Operating conditions and optimum removal efficiencies for the treatment of synthetic	64
Table 5.2: Nitrite and nitrate concentrations in effluent of the system	68
Table 5.3: TCOD concentrations in the system	72
Table 5.4: Parameters for biomass yield in mixed liquor	73
Table 5.5: Components of mixed liquor	74
Table 5.6: Characteristics of sludge in the anoxic zone.....	74
Table 5.7: Characteristics of sludge in the anaerobic zone.....	75
Table 5.8: Comparison between Integrated Multi-Zone Wastewater Treatment System and reported work in literature	78

LIST OF SYMBOLS AND ABBREVIATIONS

N	Nitrogen
P	Phosphorus
BOD	Biochemical oxygen demand
C/N	Carbon to nitrogen ratio
C/P	Carbon to phosphorus ratio
CBOD	Carbonaceous biochemical oxygen demand
COD	Chemical oxygen demand
DO	Dissolved oxygen
DNPAOs	Denitrifying phosphorus accumulating organisms
F/M	Food-to-microorganism
HRT	Hydraulic retention time
N/P	Nitrogen to phosphorous ratio
NBOD	Nitrogenous biochemical oxygen demand
NH ₃ -N	Ammonia-nitrogen
NLR	Nitrogen loading rate
NO ₂ -N	Nitrite-nitrogen
NO ₃ -N	Nitrate-nitrogen
OLR	Organic loading rate
ORP	Oxidation reduction potential
PAOs	Phosphorus accumulating organisms
PLR	Phosphorus loading rate
SRT	Solid retention time

TCOD	Total chemical oxygen demand
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TP	Total phosphorus
TS	Total solids
TSS	Total suspended solids
VFA	Volatile fatty acids
VSS	Volatile suspended solids

CHAPTER 1: INTRODUCTION AND OBJECTIVES

1.1 Introduction:

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. Therefore, wastewater requires treatment before discharge to the environment as it contains contaminants of organic and inorganic nature which have adverse effects on human health and the environment. The high concentration of organic compounds in the wastewaters can cause the death of aquatic animals and may exert other undesirable effects on aquatic species by decomposing organic compounds in the water and by consuming oxygen for BOD biodegradation which will reduce the oxygen concentration in the water. On the other hand, nutrients cause algal bloom in the water bodies which further cause eutrication of the lake and water streams, and produce large quantities of malodorous gases. Accordingly, wastewater has stringent environmental disposal limits that need to be maintained before discharge to the environment in order to overcome these adverse effects on the environment. This is commonly done by employing wastewater treatment technologies.

Conventional biological treatment systems use indigenous microorganisms (mostly autotrophic and heterotrophic bacteria) to decontaminate the wastewater to a certain limit for discharge into the environment. These microorganisms require food and nutrients to live. Carbon is essential food for all the microorganisms as they assimilate carbon in their body for their metabolism. Nutrients i.e. nitrogen and phosphorus can also be assimilated by the microorganisms for their growth and proliferation. The microorganisms take part in the removal of contaminants which mainly depend on the environmental dissolved oxygen concentration (DO), pH and oxidation

reduction potential (ORP). For example, aerobic bacteria need enough dissolved oxygen concentration and certain pH range for nitrification and for luxury phosphorus uptake, while facultative microorganisms require dearth of oxygen and adequate amount of nitrate for denitrification process during the treatment of wastewater. Anaerobic bacteria live and reproduce in the absence of both free oxygen and nitrate and in a limited pH range.

Conventional biological treatment processes use indigenous bacteria which are the common microorganisms in wastewater treatment, mainly for the removal of carbonaceous matter and solid separation from liquid. But they have some drawbacks which are challenges in wastewater treatment. For example in activated sludge process, a large amount of sludge is produced and creates sludge bulking which mostly consist of dead or settled bacteria/microorganisms and must be treated prior to disposal by various processes. In addition, the generated sludge consists of materials of organic nature, as well as a significant amount of inorganic matter (Elliot ,1986). However, sludge exhibits wide variations in the physical, chemical and biological properties (Colin et al. 1988; Bruce, 1990). Sludge handling during wastewater treatment operations has become a serious environmental concern. These concerns are particularly urgent when organic load in the wastewater is considerably high such as those originating from animal farms and agricultural activities that result in the generation of substantial amounts of biological solids when using traditional treatment technologies (Ahn et al., 2002; Liu, 2003; Wei et al., 2003). Since agricultural wastewater consists of high loading of organic material and nutrients in the feed or high flow rates of the influent to the treatment plant, the quantity of generated sludge is significant and it is very important to be treated prior to disposal.

The demand for efficient and cost-effective phosphorus (Clark et al., 1998) and nitrogen removal processes has now become apparent along with carbon removal. The discharge limits for nitrogen and phosphorus are becoming increasingly severe throughout the world due to the health hazards of these nutrients, the occurrences of algal blooms, death of animals and depletion of oxygen in lakes and streams which threatens aquatic life (de-Bashan and Bashan, 2004).

Wastewater treatment can be done with a variety of processes depending on the contaminants concentration and disposal limits, classified as primary, secondary, and tertiary wastewater treatment. Treatment of wastewater includes the removal of specific contaminants as well as the removal and control of nutrients (Metcalf and Eddy, 1991). Most existing wastewater treatment technologies were originally designed for secondary treatment, i.e. removal of organic carbonaceous compounds and solid-liquid separation, and not the removal of nutrients (Behzadian, 2010).

Treatment systems are generally divided into two systems: suspended-growth and attached-growth systems. The activated sludge process (suspended-growth system) mainly removes organic matter by introducing air in a basin and making microbial flocs. Sequencing batch reactors which are modified versions of activated sludge processes use a single tank for all treatment process without using external clarifiers. A complete settlement and removal of total suspended solids, operational flexibility, and effluent quality meet the stringent disposal limits with the drawback of producing a large amount of sludge and high sludge volume index (Sirianuntapiboon et al., 2007) which also creates problems in sludge handling. Fixed-film or attached growth systems include trickling filters and rotating biological contactors where the biomass grows on media and the wastewater passes over the surface of the generated biofilm.

This type of reactor can handle heavy loads and variable conditions, minimize the production of sludge, and offer process stability and resistance to shock loading. Effective hydraulic retention times can also be achieved for biochemical oxygen demand (BOD) removal, nitrification, and denitrification. However, the clogging of filter, requirements of a larger footprint, odor problems, high loading of wastewater feed and sensitivity to overloading are among the problems encountered in this type of technology.

Prominent international wastewater companies such as Brentwood Industries, Hyland Precast Inc, and Sunrise solutions use a technology named fixed activated sludge treatment process (FAST®) which can work as an adequate treatment process even in cold weather, and can compete with attached growth treatment systems. However, this technology only removes nitrogen and organic matter not phosphorus. Some well-known international companies are using combination of BIOPAQ® IC, UASB, high-rate activated sludge and sequencing batch reactors, and CIRCOX® (Frijters et al. 2007). Most of these treatment systems, similar to the conventional processes, only remove organic biodegradable contaminants. The CIRCOX® process removes organic matter and nitrogen at full scale. Phosphorus removal cannot be achieved by this process; it does not stabilize sludge and has a limited capacity for solid-liquid separation.

From the above discussion, it is clear that conventional wastewater treatment systems have limitations in respect to the treatment process, full scale contaminant removal, cost and operational aspects. For the required and anticipated wastewater treatment and for the acceptable removal of contaminants from the wastewater, scientists and engineers have been trying to develop a full scale and appropriate treatment technology which can remove organic and

inorganic contaminants while separating solids from liquid in an efficient and economic way. Among the technologies, airlift reactors have attracted attention because of their unique hydrodynamic characteristics, mixing, contaminant removal, and sludge production.

The wastewater treatment technology examined in this project addresses the limitations and weaknesses of existing technologies. This technology was designed to efficiently remove organic contaminants as well as suspended solids and inorganic contaminants, notably nitrogen and phosphorus from wastewater. The examined treatment system contains two interlinked bioreactors. The first bioreactor has a wastewater inlet, an aerobic zone, a microaerophilic zone, an anoxic zone, and a clarification zone. The aerobic zone comprises aeration means for supplying air or oxygen to the aeration zone for the aerobic biological processes while causing recirculation of wastewater between the aeration and microaerophilic zones. The second reactor comprises an anaerobic zone in a lower part, a clarification zone, a filtration unit and an outlet for the effluent. The biological treatment takes place in the four interactive zones of aerobic, microaerophilic, anoxic and anaerobic. The four zones are defined by their respective average concentrations of dissolved oxygen (DO) and oxidation-reduction potential (ORP). The zones have their defined values for pH, DO and ORP for the growth and proliferation of microorganisms. A diversified group of microorganisms in suspended or fixed film grow in the bioreactors for the removal of not only organic carbon but also nitrogen and phosphorus. The integrated treatment system had been operated for 310 days for synthetic and 150 days for hog wastewater. The results of the first six months of experiments with synthetic wastewater were obtained before the initiation of the current project. The entire results are reported in this thesis in order to present the complete picture of treatment operation, and to facilitate the analysis of results.

1.2 General Goal:

The main objective of this study was to evaluate the efficiency of the new integrated treatment system for the removal of carbon, nitrogen and phosphorus from synthetic and real agricultural wastewater at laboratory scale.

1.3 Specific Objectives:

1. Investigation of the removal efficiencies of carbon, nitrogen and phosphorus by the integrated treatment system in response to changes of organic loading rate (OLR), nitrogen loading rate (NLR) and phosphorus loading rate (PLR) during the treatment of synthetic wastewater and real agricultural wastewater.
2. Determination of the impact of various ratios between carbon, nitrogen and phosphorus concentrations, i.e. C/N, C/P, C/N/P, in the influent wastewater on the removal of carbon, nitrogen and phosphorus.
3. Determination of the impact of food-to-microorganism ratio and solid retention time (SRT) on the removal of carbon, nitrogen and phosphorus.
4. Determination of the utilization rates, specific utilization rates and biomass yield in the system during the operation under various operating conditions.
5. Characterization of mix liquor and sludge from the anaerobic and anoxic zone during the operation.
6. Comparison of the system efficiency with existing wastewater removal technologies.

1.4 Organization of the thesis:

- Chapter 1; A brief introduction on conventional wastewater treatment technologies and the advantages of the studied technology.
- Chapter 2; Literature search of the previous work of synthetic and real wastewater treatment (hog manure) based on operating conditions, removal of contaminants and all other aspects related to this study.
- Chapter 3; Detailed description of materials and methods used in this study is described in this chapter.
- Chapter 4; Results and discussion of the operation of the system with hog wastewater, the removal efficiencies, their dependence on the operating parameters, characterization of the mixed liquor and sludge from anoxic and anaerobic zone, comparison with the reported works in literature.
- Chapter 5; Results and discussion of the operation of the system with synthetic wastewater, the removal efficiencies, their dependence on the operating parameters, characterization of the mixed liquor and sludge from anoxic and anaerobic zone, comparison with the reported works in literature.
- Chapter 6; Conclusion from the study from the operation for synthetic wastewater and hog manure.
- Chapter 7; Recommendations on the system performance and future work has been proposed in this chapter.

CHAPTER 2: LITERATURE REVIEW

Water can be contaminated by human activities which creates a great impact on the environment. Liquid wastes produced by domestic, commercial, industrial, and/or agriculture activities contain a wide range of potential contaminants i.e. organic compounds as well as nitrogen and phosphorus. Nitrogen (N) and phosphorus (P) at high concentrations may lead to serious environmental problems when discharged into receiving waters as they cause eutrophication in water environment.

Contaminants can be composed of organic and inorganic materials such as hydrocarbons, lipid, polysaccharides etc. which seriously affect environmental quality and human health (Hung, 2006). Contaminated wastewater also contains inorganic nutrients, i.e. nitrogen and phosphorus, which have a great effect on the environment mainly in the water environment. These nutrients, after disposing to water bodies, create algal bloom and reduce oxygen concentration in the water which can cause the death of water animals or mutation of their reproduction system (P.L. Sewell, 2004). Since contaminants can make adverse impacts on the environment, ecosystem and human being, environmental discharge limits are required as well as treatment of wastewater prior to discharge to the environment, if the concentrations of contaminants exceed the established limits. For example, in California, the maximum discharge limits for phosphorus and nitrogen are set at 2 mg/L and 9 mg/L, respectively (Horan et al., 1994).

Most previous biological treatment technologies used suspended-growth or attached growth microorganisms for biological treatment processes. They were mainly concerned with the removal of carbonaceous compounds and solid –liquid separation. For example, the activated

sludge process which is a suspended growth system, encounters problems including formation of poor settling sludge, while requiring high biomass retention time, and only removes carbonaceous compounds and solids from the wastewater and not the nutrients. Considering their adverse impacts on the environment, treatment systems should remove nutrients i.e. nitrogen and phosphorus, as well as carbon. Conventional treatment systems are simple and face complications during the treatment of nutrients.

Nutrients can be biologically removed in biological nutrient removal (BNR) processes. Nitrogen removal requires simultaneous nitrification under aerobic condition, and denitrification in anoxic condition. Phosphorus removal requires a combination of aerobic and anaerobic conditions. For these processes, creation of the appropriate zones in the treatment system is necessary which can be represented by dissolved oxygen (DO), pH and oxidation reduction potential in the system.

During phosphorus removal processes, COD is taken up by phosphorus accumulating microorganism (PAOs) in the anaerobic zone and is stored as polyhydroxyalkanoates (PHAs) in the absence of both nitrate and oxygen. This process is accompanied by phosphorus release in the anaerobic zone. In the following aerobic stage, PHAs are oxidized producing energy for the microorganisms while phosphorus is taken up from the aerobic zone by this microorganisms using that energy. This process is called "Luxury Phosphorus Uptake". The glycogen accumulating microorganisms are also present in anaerobic zone to accumulate carbon source in their cells (Thomas et al., 2003). But the biochemistry pathway of them is different in terms of phosphorus release in the anaerobic zone and phosphorus uptake in the aerobic zone. So the contribution of GAOs is negligible in term of phosphorus uptake (Saunders et al., 2003). In the aerobic zone, ammonium is converted to nitrate nitrogen by autotrophic microorganisms.

Bacteria known as *Nitrosomonas* convert ammonia and ammonium to nitrite and *Nitrobacter* bacteria complete the conversion of nitrite to nitrate.

The subsequent process of nitrogen removal is the denitrification process. The biological reduction of nitrate (NO_3) to nitrogen gas (N_2) is carried out by facultative heterotrophic bacteria (aerobic or anaerobic depending on the availability of O_2 in the environment). “Heterotrophic” bacteria need carbon sources as food to live in the anoxic condition where oxygen levels are depleted and nitrate becomes the primary electron acceptor for microorganisms for their respiratory system. When they use nitrates as an electron acceptors, nitrate is converted to nitrous oxide by reduction, and further to nitrogen gas. Since nitrogen gas has low water solubility, it escapes into the atmosphere as gas bubbles. So carbon sources are required for both phosphorus and nitrogen removal in a biological treatment system.

A number of effective biological treatment technologies have been developed for simultaneous removal of nitrogen and phosphorus. Examples include the five-stage Bardenpho process, the anaerobic-anoxic-aerobic process and the University of Cape Town (UCT) process (Metcalf and Eddy, 1991). In these systems, the zones are created by using several vessels in series to create different environmental conditions which makes the treatment plant costly to operate, requires high infrastructural arrangements and equipment, and excessive manpower which complicates the operation of system. These treatment systems also produce a high amount of sludge which requires tertiary treatment. Due to the encountered problems in conventional wastewater treatment technologies, the treatment market has been looking for new ideas and better technologies which can serve for simultaneous removal of carbon and nutrients and separation of solids from liquid. Among the technologies, airlift reactors have attracted attention because of

their unique hydrodynamics and mixing characteristics, as well as heat and gas transfer properties (Chisti & Young, 2007), and diverse environmental conditions for carbon, nitrogen and phosphorus removal and solid separation.

For nitrification process, bacteria require free dissolved oxygen at concentrations above 2 mg/L for optimum performance. In most industrial operations, a minimum DO concentration of 5 mg/L is maintained in the aerobic reactor. Maximum nitrification and luxury phosphorus uptake occurs in the aerobic zone at DO concentrations greater than 2 mg/L (Rao et al., 1997). The growth rate of microorganisms is minimal at dissolved oxygen (DO) concentrations less than 0.5 mg/L. Nitrification requires a low food-to- microorganism ratio (F/M), adequate alkalinity, and a high mean cell residence time. As the bulk liquid DO concentrations below 2 mg/L inhibit nitrification process in the aerobic zone, nitrification systems need to be operated at high DO concentrations (US EPA, 1993).

The variation of pH value of a biological system indicates the microbial reactions and provides an indication of the ongoing biological process. The optimum pH in the mixed liquor for *Nitrosomonas* is 8.1 and for *Nitrobacter* is 7.9 (Grunditz and Dalhammar, 2000) which is supported by Hofman and Lees (1953) reported the pH for *Nitrobacter* around 7.7. The nitrification efficiency increases 13% with the increase of one unit of pH, if the pH range is kept between 5.0–9.0 (Villaverde, 1997). The effect of temperature is worth mentioning as the nitrification reaches a maximum rate at temperatures between 30 °C and 35 °C, and approaches zero at temperatures higher than 40 °C. Nitrification proceeds at a very slower rate if the temperature falls below 20 °C. The maximum specific growth rate of microorganism was found to be a function of temperature in the range of 15–25°C with an optimum pH of approximately

7.8 (Antoniou, 1990). The treatment process should operate at temperatures higher than 16 °C to obtain removal efficiencies greater than 95% (Obaja, 2002).

Nitrifying microorganisms are present in almost all aerobic biological treatment processes but their number and presence depend on the mean cell residence time and on the BOD/N or COD/N ratio. The fraction of nitrifying microorganisms is estimated to be less than 0.083 with a BOD/N ratio of 3 in activated sludge process. For the BOD/N ratio of 5 to 9, the estimated percentage is between 0.054 and 0.029 (Metcalf and Eddy, 1991). The benchmark for BOD/N/P ratio is often used is 100:5:1 (Slade et al., 2011). Microorganisms require nitrogen for growth. Heterotrophic organisms which grow on domestic wastewater require carbon, nitrogen and phosphorus (expressed as BOD₅/N/P) in a ratio of 100:5:1 (Orhon and Artan, 1994). The C/N ratio has a great effect on simultaneous removal of nitrogen and phosphorus.

Nitrogen removal efficiency is increased from 44% to 84% with the increase of C/N ratio from 2.8 to 5.7. But if the C/N ratio is further increased, the removal rate proceeds very slowly. Phosphorus removal can be achieved from 27% to 88% in the above-mentioned C/N range with C/P ratio increasing up to 33, keeping minimal impact of C/P on TN removal at the same time (Zhao et al., 2008). According to Zhao, (2011), TN removal efficiency increases considerably if the C/N ratio is 10:1. The COD/N ratio should be maintained between 5 and 9 for maximum nitrogen removal (Grady et al., 1999). The COD/P ratio should be at least 35 and the BOD/P should be at least 20 (SCOPE, 1998). For optimum removal efficiencies, the C/N/P-ratio of 100:5:1 is recommended (Steffen, 1998). For dairy wastewaters, the optimum COD/P ratio should be 13:1 for proper phosphorus (Broughton, 2007) removal.

For COD removal from wastewater, the solid retention time is a very important factor (Hajiabadi et al., 2009). The removal of COD as well as the concentration of biomass (MLSS) in the mixed liquor is directly proportional to the sludge retention time in the mixed liquor. Proper function of the nitrification process also depends on the fraction of nitrifiers in the mixed liquor. This can be achieved by increasing the aeration rate which increases the concentration of nitrifiers in the mixed liquor (Process Design Manual for Nitrogen Control, 1993). Phosphorus removal also depends on solid retention time (SRT) and it has been showed that acceptable phosphorus removal requires 3-68 days of SRT (Reddy, 1998).

In the denitrification process, facultative microorganisms reduce oxygen from nitrate in the absence of oxygen in the anoxic zone where DO concentration is less than 0.5 mg/L, and ideally less than 0.2 mg/L. The dissolved oxygen concentration should be considerably low in the anoxic zone as DO concentrations greater than 1 mg/L can inhibit denitrification (Rao et al., 1997). Another important aspect of denitrification is the presence of sufficient carbon source for the denitrifying PAOs (DNPAOs) to survive for the denitrification process. This carbon source can be in the form of raw wastewater or an external carbon source. Temperature should be maintained between 5 and 30 °C. The type of available carbon source is also an important factor as it affects the denitrification process. The short chain fatty acids, especially acetates are easily taken by the microorganisms as feed stock as they can be broken down easily during microbial metabolism. pH has a great effect on denitrification process and the optimum pH range for denitrification is between 6.5 to 8. Denitrification decreases below pH 6 and above pH 9.

Airlift reactors are among the best type of reactors for simultaneous nitrogen and phosphorus removal (Guo et al., 2004). Simultaneous nitrogen and phosphorus removal can be done with the

same carbon source and the same microorganisms in anoxic-anaerobic systems (Kern-Jespersen et al., 1994; Kuba et al., 1993). The anaerobic zone provides a positive environment for the phosphorus accumulating microorganisms to uptake the carbon sources inside their cells (Matsuo et al., 1992). In the anaerobic zone, polyphosphate accumulating bacteria (PAOs) accumulate carbon sources, thus gaining energy from the breakdown of glycogen and hydrolysis of polyphosphate. Accordingly, the concentration of orthophosphorus increases in the anaerobic zone as polyphosphate transforms to orthophosphate for energy supply. In the succeeding aerobic stage, phosphorus is taken by the microorganisms and phosphorus concentration decreases in the mixed liquor (Yeoman, 1988). In biological treatment processes, phosphorus can be removed by 10% - 25% during this stage (Metcalf and Eddy, 1991). The accumulated phosphorus is subsequently removed by the wasted sludge which could contain up to 10% phosphorus (Wenzel and Ekama, 1997). The anoxic zone also contributes to phosphorus removal by the action of DNPAOs, but anoxic phosphorus removal is lower than aerobic uptake. The most recent CIRCOX technology has proven to be a suitable technology for COD and nutrient removal (Frijters et al., 2007). This technology uses a biofilm airlift reactor for full scale removal of carbon and nitrogen and not for the removal of phosphorus.

The new removal technology described in this thesis has been developed to achieve the desired removal efficiencies of organic contaminants and inorganic nutrients. This technology uses an airlift reactor as the aerobic zone and contains additional zones with different environmental conditions for the removal of nitrogen and phosphorus. In this study, removal efficiencies of contaminants i.e. COD, BOD, nitrogen and phosphorus from the wastewater were evaluated under varying operating conditions, and the results were compared with those obtained by the previous treatment technologies.

CHAPTER 3: MATERIALS AND METHODS

3.1 Experimental set up:

The laboratory-scale wastewater treatment system has been installed in the Environmental Engineering Laboratory at Concordia University. In this system, two separate but interlinked bioreactors containing four biological and three solid-liquid separation zones were operated under various operating conditions (ORP, pH, alkalinity) for the simultaneous removal of carbon (C), nitrogen (N) and phosphorus (P) from synthetic and hog wastewaters.

3.1.1 Integrated Multi-Zone Wastewater Treatment System:

The treatment system contains four biological zones, namely aerobic, microaerophilic, anoxic and anaerobic for the treatment of wastewater. Two clarification zones and a filtration unit for the separation of solids from liquid are also integrated in this system. The volume of various reactor zones were 27, 62 and 17 liters for the aerobic, microaerophilic, anoxic zones, respectively (Behzadian, 2010). The operating parameters including temperature, aeration and dissolved oxygen concentration in the aerobic and microaerophilic zones were continuously controlled or monitored by a real-time control system developed by Behzadian et al. (2010).

The first reactor of the treatment system contains aerobic, microaerophilic and anoxic zones as well as a clarification zone. The aerobic zone contains an air diffuser at the bottom and above the anoxic zone. The air bubbles mix the liquid and its content of microorganisms, and provide oxygen for the aerobic biological processes that take place in this zone. Aeration also produces circulation of liquid between the aerobic zone and its adjacent microaerophilic and anoxic zones that are located at the sides and under the aerobic zone, respectively. The aerobic zone contains

suspended microorganisms of heterotrophic and autotrophic groups that grow inside the circulating liquid, known as mixed liquor. The aerobic and microaerophilic zones operate on the principles of concentric draught-tube airlift reactors. Airlift reactors in general consist of two sections of riser and down comer with diffusers at the bottom of riser to lift the liquid upward in the riser and downward in the down comer, thus facilitating the circulation of liquid between these two sections. In the examined treatment system, aerobic and microaerophilic zones are the riser and down comer of the airlift reactor, respectively. The placement of a half cone at the bottom of down comer (microaerophilic zone) facilitates the movement of liquid flow from the down comer to riser while minimizing energy loss. A cylindrical steel object wrapped with geotextile was placed inside the aerobic zone to support the attachment of microbial biomass and the formation of microbial biofilm, thus facilitating the growth and retention of slow growing nitrifying microorganisms.

The second reactor which is connected to the first reactor, contains an anaerobic zone at the bottom, a clarification zone in the middle and an filtration unit at the top. This reactor participates in the removal of phosphorus by the Luxury Phosphorus Uptake process that requires the presence of an anaerobic environment in addition to aerobic environment. Figure 3.1 presents the schematic diagram of the integrated multi-zone wastewater treatment system.

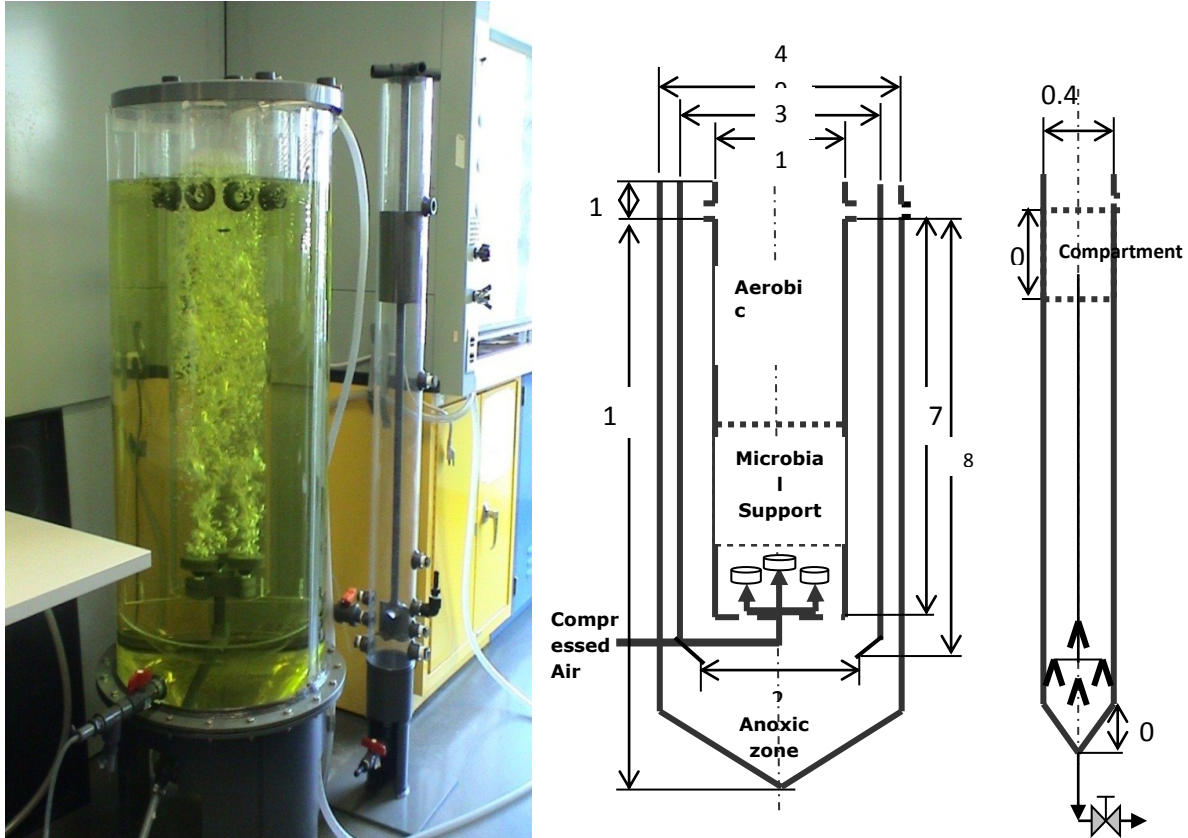


Figure 3.1: Schematic diagram of integrated multi-zone wastewater treatment system. The air diffusers introduce air through the microbial support to the aerobic zone. The second reactor is connected to the first reactor.

3.2 Inoculum:

The new integrated wastewater treatment system was inoculated by equal volumes of a sample of aerobic biomass from a food processing plant in Candiac, Quebec, Canada and a sample of anaerobic biomass from ADI Systems Inc., in New Brunswick, Canada, producing an overall biomass concentration of 420 mg/L in the mixed liquor.

3.3 Synthetic Wastewater:

The synthetic wastewater was composed of glucose ($C_6H_{12}O_6$), sodium bicarbonate ($NaHCO_3$) and inorganic compounds. The inorganic compounds included ammonium sulfate ($(NH_4)_2SO_4$), anhydrous potassium di-hydrogen phosphate (KH_2PO_4), anhydrous di-potassium hydrogen phosphate (K_2HPO_4), magnesium sulfate ($MgSO_4 \cdot 7H_2O$), and calcium chloride ($CaCl_2 \cdot H_2O$). A trace mineral solution was also used in the synthetic wastewater to complete the nutritional requirements of microorganisms. Table 3.1 presents the composition of synthetic wastewater while Table 3.2 presents the composition of trace elements used.

Table 3.1: Synthetic wastewater composition

Compound	Formula	Nutrition supplied	Concentration (mg/L)
Glucose	$C_6H_{12}O_6$	Carbon	2000-4000
Sodium bicarbonate	$NaHCO_3$	Alkalinity	1000-2000
Ammonium sulphate	$(NH_4)_2SO_4$	Nitrogen	750-1300
Potassium dihydrogen phosphate	KH_2PO_4	Phosphorus	180-250
Dipotassium hydrogen phosphate	K_2HPO_4	Phosphorus	180-250
Magnesium sulfate	$MgSO_4$		62-75
Calcium chloride	$CaCl_2$		62-75
Trace mineral solution	$MnSO_4 \cdot H_2O$, $MnCl_2$, $FeCl_3 \cdot 6H_2O$, $ZnSO_4$, KCl , $CuSO_4 \cdot 5H_2O$, $EDTA$, $CoCl_2$, H_3BO_3	Nutrition of Microorganism	

Table 3.2: Composition of trace elements in the synthetic wastewater

Trace elements solution component	Concentration (mg/L)
MnSO ₄ . H ₂ O	100
CuSO ₄ .5H ₂ O	60
ZnSO ₄ .7H ₂ O	300
KCl	30
EDTA	4000
FeCl ₃ .6H ₂ O	1500
CoCl ₂	100
NiCl ₂ .6H ₂ O	15
H ₃ BO ₃	100

3.4 Real Agricultural Wastewater:

The real agricultural wastewater (hog waste) was supplied by the Institut de Recherche et de Developpement en Agroenvironnement in Deschambeault, Quebec. The wastewater was kept in the refrigerator at 3-5 °C in order to maintain its quality. The average composition of agricultural wastewater used in this study is presented in Table 3.3.

Table 3.3: Average composition of agricultural wastewater

Type \ Parameters	COD	TN	TP	NH ₃	NO ₃	NO ₂
Unfiltered (mg/L)	85000	9989	1321	6007	357	33
Filtered (mg/L)	35250	5580	944	3937	147	23

The agricultural wastewater was diluted 30 times in order to reduce the concentrations of COD, nitrogen and phosphorus, thus making the wastewater amenable to biological degradation. The influent to the treatment system went through pre-fermentation process during its stay in the influent tank for several days at room temperature. During the pre-fermentation process, volatile fatty acids (VFAs) were produced which are easily biodegradable carbon source for microorganisms and promote nitrogen and phosphorus removal since the success of enhanced biological phosphorus removal (EBPR) depends on constant availability of short chain volatile fatty acids (VFAs). The optimum pH for adequate VFA generation is 5-6 was maintained by adding acetic acid to the influent tank. Acetic acid addition also served to maintain the influent COD at the desired concentration since COD/N and COD/P ratios in the agricultural wastewater were not at the optimum levels. This acetic acid addition and adjustment of COD/N and COD/P were done after a couple of weeks of starting of the operation of reactor for the treatment of hog manure. However, among all other fatty acids, acetic acid is tested as the best carbon source for biological phosphorus removal followed by propionic acid (Ubay-Cokgor, 2005).

3.5 Operating Parameters:

The four zones of the wastewater treatment system are defined by their respective dissolved oxygen (DO) concentrations and oxidation-reduction (redox) potential (ORP). The environmental conditions in various treatment zones are presented in Table 3.4. The DO concentration (measured by a DO probe, model alpha-DO2000W) was highest in the aerobic zone. The dissolved oxygen concentration in the aerobic zone was kept around 3-6 mg/L for real hog wastewater during the feast period and 1.5- 3 mg/L during the famine period which was introduced to the system after two and half months (March, 2011) after the starting of the operation (January, 2011). The ORP measured in the aerobic zone was slightly greater than +100

mV. In the microaerophilic zone, the DO concentration is in the range of 0-2 mg/L and the ORP is around same as aerobic zone. The DO concentration in the anoxic zone was negligible while the oxidation reduction potential (ORP) < -100 mV. However, the anoxic zone may contain traces of oxygen. The anaerobic zone practically does not contain any oxygen with a steady DO concentration of zero and an ORP of -300 to -350 mV (measured by Cole-Parmer ORP electrode, submersible). The pH of the aerobic, microaerophilic, anoxic and anaerobic is around 7.5- 8.5, 7.5-8.5, 6.5-7.5 and 7-7.5, respectively which have been measured by a submersible pH electrode (model Cole-Parmer 27001-80). The temperature in the liquid phase which was not controlled was also measured by a temperature probe (model Alpha-DO200w).

Table 3.4: Environmental conditions in the various treatment zones

Parameter Zone	DO (mg/L)	pH	ORP (mV)
Aerobic	3-6	7.5-8.5	> +100
Microaerophilic	0-2	7.5-8.5	> +100
Anoxic	0	6.5-7.5	<-100
Anaerobic	0	7-7.5	< -100

3.6 Analytical Methods:

All materials used for sample analysis were purchased from Fisher Scientific, Montreal, Canada. The analytical methods used during the experiments for the measurement of pertinent parameters are described in the following paragraphs. The parameters include: Total solids, (TS),

total suspended solids (TSS), volatile suspended solids (VSS), total chemical oxygen demand (TCOD), soluble chemical oxygen demand (COD), total biological oxygen demand (TBOD), carbonaceous biological oxygen demand (CBOD), nitrogenous biological oxygen demand (NBOD), total nitrogen (TN), ammonia-nitrogen (NH₃-N), nitrate-nitrogen (NO₃-N), nitrite-nitrogen (NO₂-N), total phosphorus (TP), volatile acids (VFA) and total Kjeldahl nitrogen (TKN).

3.6.1 Total Solids (TS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS):

Total solids, total suspended solids and volatile suspended solids were measured by the standard gravimetric method (EPA Approved Standard Method-2540 Solids) using two ovens at 105 °C and 550 °C.

3.6.2 Total Solids, TS:

Total solid is the combination of total suspended solids and volatile suspended solids. Samples were heated at 150 °C for around 12 hours. During this time, all water was evaporated and only the total solids remained in the crucibles. The crucibles were then weighed to measure the weight

of the total solids. Total Solids = $\frac{B - A}{X}$

A = Empty weight of the crucibles (mg)

B = Weight of the crucibles with the samples after evaporation at 105⁰C (mg)

X = Volume of samples during the test (L)

3.6.3 Total Suspended Solids, TSS:

Samples from influent, aerobic, anoxic, anaerobic, effluent from first reactor, and effluent from second reactor were taken and distilled water was added at the same volume to the plastic vials. The samples were then centrifuged for 30 minutes to separate the liquid from solids. The supernatant of the samples was discarded and the solid portion was transferred to the porcelain crucibles and was heated to 105 °C for around 12 hours. The crucibles with the remaining samples were weighted after cooling.

$$\text{Total Suspended Solids} = \frac{D - C}{Y}$$

C = Empty weight of the crucibles (mg)

D = Weight of the crucibles with the samples after evaporation at 105 °C (mg); Y = Volume of samples taken during the test (L)

3.6.4 Volatile Suspended Solids, VSS:

After heating at 105 °C in the oven, the crucibles of the total suspended solids were put in the oven at 550 °C for one hour to evaporate all the volatile matters from the sample. The crucibles were then cooled down to the room temperature and weighted by a digital balance.

$$\text{Volatile Suspended Solid} = \frac{D - E}{Y}$$

D = Weight of the crucibles with the samples after evaporation at 105 °C (mg)

E = Weight of the crucibles (105 °C) with the samples after evaporation at 550 °C (mg)

3.6.5 Chemical Oxygen Demand (COD):

Total and soluble chemical oxygen demands were analyzed by the Standard Method 5220 D (USEPA reactor digestion method) using a spectrophotometer (Cole Parmer, model DR 2800). In this method, the sample was heated at 150 ° C for two hours with sulfuric acid and a strong oxidizing agent, potassium dichromate (Test Vial concentration range 20-1500 mg/L). Oxidizable organic compounds reacted and the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) was reduced to green chromic ion (Cr^{3+}). The COD reagent also contained silver and mercury ions. Silver is a catalyst and mercury is used to complex chloride interferences.

3.6.6 Biochemical Oxygen Demand (BOD):

The measurement of biochemical oxygen demand in a 5 day test period was done by the Standard Method -5210B. In this test, the total biochemical oxygen demand (TBOD), carbonaceous biochemical oxygen demand (CBOD) and nitrogenous biochemical oxygen demand (NBOD) were measured. For every sample, four standard BOD bottles with the volume of 300 ml were used; two for total BOD and two for CBOD measurement. In order to inhibit the NBOD, the inhibitor (2-chloro-6-(trichloromethyl) pyridine) was added to the relevant bottles of CBOD measurement.

During the tests, the 300 ml bottles were half-filled with tap water and the samples from the influent and effluent were added to the water at a desired volume so that the final dissolved oxygen of the test bottles would not be less than 2 mg/L from the initial dissolved oxygen. A 0.6 ml of diluted sample from the anoxic zone was taken in each bottle as the inoculum for the BOD tests. Tap water was then added to fill the bottles to 300 ml. The initial BOD of each bottle was measured by a DO probe before incubating the bottles at room temperature in the dark to prevent

photosynthetic reactions. After 5 days, the BOD bottles were removed from the incubator and the final dissolved oxygen concentration was measured. The BOD values were estimated using the following equations:

$$TBOD = \frac{(A - B) * (X - Y) * DF * V1}{v}$$

$$CBOD = \frac{(C - D) * (X - Y) * DF * V1}{v}$$

$$NBOD = TBOD - CBOD$$

Where A = Average initial dissolved oxygen in the BOD bottles without inhibitor

B = Average final dissolved oxygen in the BOD bottles without inhibitor

X = Average initial dissolved oxygen in the BOD bottles of control without inhibitor

Y = Average final dissolved oxygen in the BOD bottles of control with inhibitor

C = Average initial dissolved oxygen in the BOD bottles with inhibitor

D = Average final dissolved oxygen in the BOD bottles with inhibitor

V1 = Volume of the BOD bottles

DF = Dilution Factor of the substrate

v = Volume of the substrate

3.6.7 Total Nitrogen (TN):

Total nitrogen is the sum of all nitrogen species in the wastewater, including ammonia, nitrite, nitrate (inorganic nitrogen) and organic nitrogen. The combination of ammonia and organic nitrogen is called total Kjeldahl nitrogen (TKN). The total nitrogen (TN) was analyzed by persulfate digestion method. The procedure and analysis is given below:

When the samples were added to the test vials, inorganically and organically bonded nitrogen was oxidized to nitrate by digestion with peroxy disulphate. The nitrate ions reacted with 2, 6-dimethylphenol in a solution of sulphuric and phosphoric acid to form a nitro phenol.

3.6.8 Ammonia-Nitrogen (NH₃-N):

Ammonia nitrogen was analyzed by using the salicylate method (Method 10205). In this method 0.2 ml of sample was added to the test vials. Ammonium ions reacted with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside. Sodium nitroprusside acted as a catalyst. After 10 minutes a new green compound was formed. The color formed during this test is directly proportional to the concentration of ammonia nitrogen present in the sample.

3.6.9 Nitrate-Nitrogen (NO₃-N):

Nitrate-nitrogen is analyzed by di-methyl phenol method (Method 10206). In this method, nitrate ions in solutions containing sulfuric and phosphoric acids reacted with 2, 6-dimethylphenol to form 4-nitro-2, 6-dimethylphenol. Test results were measured at the wavelength of 345 nm (for DR 2800).

3.6.10 Nitrite-Nitrogen (NO₂-N):

This was analyzed by the diazotization method (USEPA, Method 10205). In acidic solution; nitrite in the sample reacted with a primary aromatic amine and formed a diazonium salt. This coupled with an aromatic compound to produce color directly proportional to the amount of nitrite present.

3.6.11 Total Phosphorus (TP):

Phosphorus is found in natural waters and in wastewaters mainly as phosphates. Phosphates can be divided into organic, poly (particulate phosphate and orthophosphate) and inorganic phosphate. The ascorbic acid method (Method 10210 Total Phosphorus) was adapted for the analysis of total phosphorus.

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) were first converted to reactive orthophosphate. After heating at 100°C for one hour, the vials cooled down at room temperature, before adding reagent. Then they were kept for 15 minutes. Organic phosphates were also converted to orthophosphates in this total phosphorus measurement method.

To determine the phosphorus content in the ash (from anoxic and anaerobic zones), the remaining ash in the crucibles from both anoxic and anaerobic zones after heating at 550 °C and cooling down, were diluted by adding 25 ml of 5N hydrochloric acid (HCL) . After dilution, the samples were kept in the plastic vials and were placed on the shaker for 17 hours in 150 rpm. These samples were taken for measurement of the phosphorus content in the ash.

3.6.12 Volatile Fatty Acids (VFA):

The esterification method (Method 10240) was used for the VFA (Volatile Fatty Acids) analysis of samples from the influent, anoxic and anaerobic zones. In this method, volatile acids present in the samples reacted with diols in an acidic environment, forming fatty acid esters. These esters were reduced by iron (III) salts to form red colored complexes which became visible during the formation and were measured photometrically at 497 nm.

CHAPTER 4: RESULTS AND DISCUSSION-HOG MANURE

4.1 Operating Parameters:

4.1.1 Loading Rates:

The loading rates of carbon, nitrogen and phosphorus for the treatment of hog waste by the integrated multi-zone treatment system are shown in Figure 4.1. The organic loading rate (OLR) was maintained in the range of 0.51 to 1.43 kg COD/m³.d, nitrogen loading rates (NLR) was in the range of 0.07 to 0.16 kg TN/m³.d, and phosphorus loading rates (PLR) changed from 0.015 to 0.035 kg TP/m³.d. The loading rates were maintained in a range that simultaneous and desirable removal of carbon, nitrogen and phosphorus could be achieved by this wastewater treatment system.

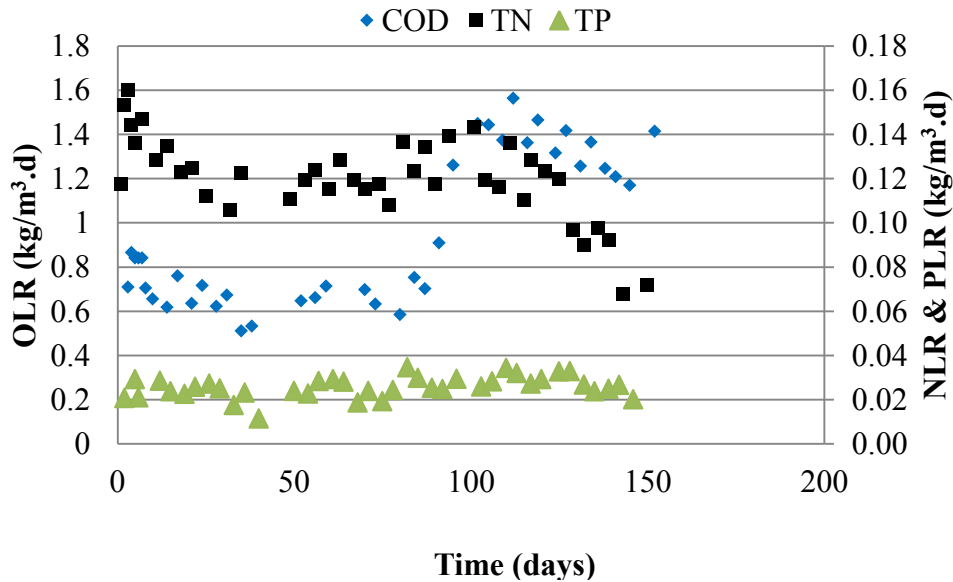


Figure 4.1: Loading rates of COD, total nitrogen and total phosphorus in the system during the treatment of hog wastewater

4.1.2 Feast and Famine Period:

The feast and famine regime was introduced to the system during the operation in order to improve the activity of microorganisms on hog waste and to enhance the removal of contaminants (Tay et al., 2006). The shorter feast period (20 min) and longer famine period (40 min) was implemented in one hour feeding time keeping the substrate loading rate of 60 L/d. With the short feast period, the microorganisms can store carbon source in the form of poly- β -hydroxybutyrate to be used in the famine period when the external carbon source was not available for their survival (Beun et al., 1999). In this starvation cycle, the microorganisms become extensively hydrophobic which facilitates the microbial aggregation in the mixed liquor (Tay et al., 2001). Consequently, the requirement for the dissolved oxygen concentration was being changed depending on the requirement of microorganisms in the feast and famine period, which was continuously monitored by the real time technology installed with the operating systems.

4.1.3 Dissolved Oxygen:

An adequate dissolved oxygen concentration was required in the aerobic zone for the proper operation of nitrification process and phosphorus uptake by the microorganisms. In this system, the dissolved oxygen concentration changed periodically during the feast and famine period, exhibiting a maximum and a minimum value in the dissolved oxygen trend. Figure 4.2 shows the DO concentration in the mixed liquor during the operation in a specific day.

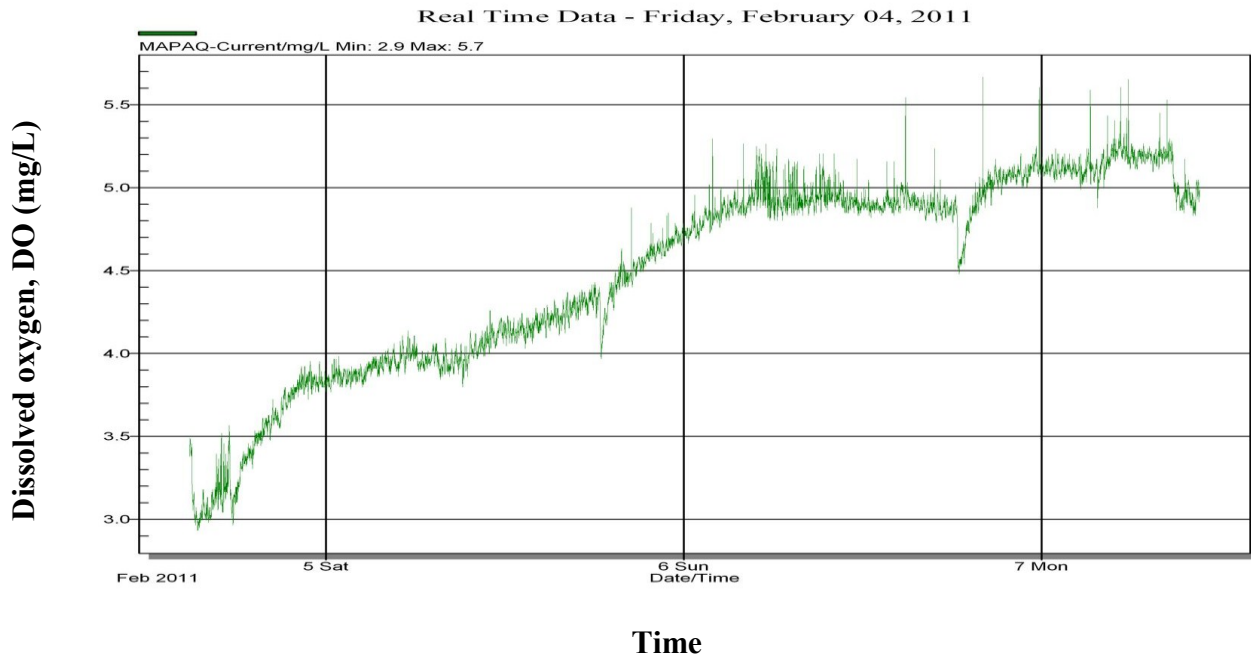


Figure 4.2: Dissolved oxygen concentration during the feast and famine period of the system during the month of February

Figure 4.2 shows that dissolved oxygen concentration changed between 3-6 mg/L, responding to the substrate flow rate, organic loading rate, and air flow rate maintained in the system during the operation. The high peak of the DO concentration represents the feast period and the low peak represents the famine period. During the feast period, the microorganisms were exposed to organic substances and assimilated the carbon source, thus requiring high dissolved oxygen concentrations in the mixed liquor for the breakdown of organic substances. The lowest peak of the trend shows the famine period when the microorganisms use the stored carbon source as there is low organic loading rate at this time.

4.1.4 pH:

pH is an important real time control parameter (Ghusain et al., 1994). Different microorganisms require different ranges of pH for their activity and removal of contaminants. As the biological processes in this study were facilitated by proper zoning for contaminant removal, pH was the most important operating parameter which was further maintained by maintaining the pH of influent wastewater. The variations of liquid pH in different zones of the treatment system are depicted in Figure 4.3.

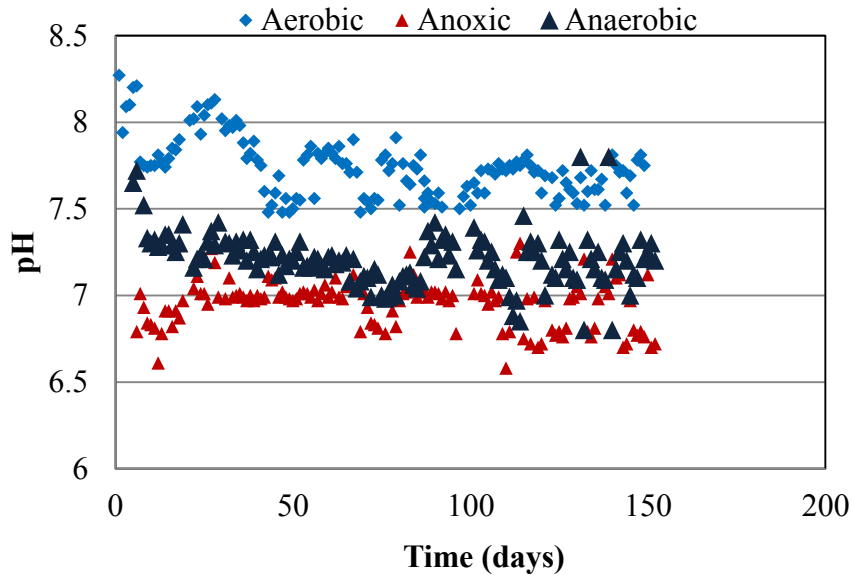


Figure 4.3: pH maintained in aerobic, anoxic and anaerobic zones of the reactor during the operation

For the proper operation in the system, the pH in this integrated system was kept in the range of 7.5 to 8.5 in the aerobic and microaerophilic zones, 6.5 to 7.5 mg/L in the anoxic zone and 7 to 7.5 in the anaerobic zone.

Nitrification and Denitrification occur in a wide range of pH in the aerobic, microaerophilic and anoxic zones. Denitrification is normally insensitive to acidity but may show increased sensitivity at low pH. The range of pH values acceptable for proper floc formation for facultative anaerobes is 6.5 to 8.5 which is also acceptable for denitrification. The optimum range of pH for denitrification is 7 to 7.5. Also, nitrification proceeds properly at the pH range 7.5 to 8.5. Since nitrification occurs in the aerobic zone, in the system the pH was kept in this range. For denitrification, pH should be in the range of 6.5 to 7.5 .

The anaerobic metabolism of PAOs (phosphorus accumulating organisms) is clearly affected by pH. Several studies have shown that the amount of phosphorus released is highly dependent on pH (Kuba et al., 1997; Liu et al., 1996; Smolders et al., 1994). The effect of pH on the behavior of PAOs under aerobic conditions was studied by Filipe et al. (2001) who performed batch tests with an enriched culture at three pH values (6.5, 7.0, and 7.5). Phosphorus uptake rates were essentially the same at pH 7.0 and 7.5 but decreased greatly at pH 6.5.

4.1.5 Oxidation Reduction Potential (ORP):

Oxidation-reduction potential (ORP) is a measure of oxidative state in an aqueous system and can be a useful tool for indicating the biological state of the system. The presence of an oxidizing agent such as oxygen increases the ORP value, while the presence of a reducing agent such as substrate or CBOD decreases the ORP value (Lowry and Dickman, 2011).

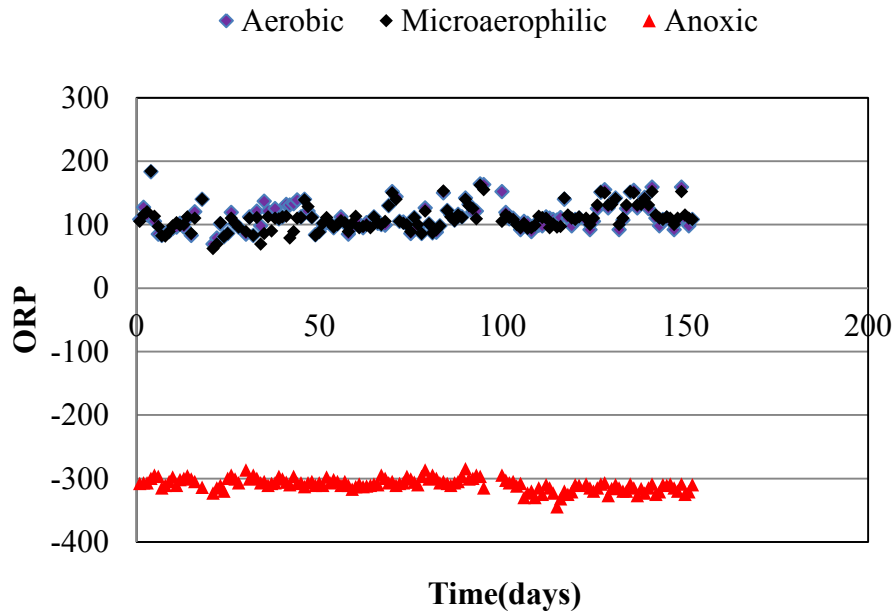


Figure 4.4: Oxidation reduction potential in aerobic, microaerophilic and anoxic zones of the treatment system

The change of oxidation reduction potential in our system is shown in Figure 4.4. Generally, OPR values below -200 mV are indicative of anaerobic or reducing conditions. ORP values between -200 mV and +200 mV indicate anoxic conditions. Aerobic or oxidative conditions are present above + 200 mV. Oxidation-reduction potential cannot be maintained in biological

treatment systems; it is normally established due to the reactions occurring in the system (Inniss, 2005).

4.1.6 Temperature:

Real-time technology (Kim et al., 2004) was used to measure the operating temperature along with the dissolved oxygen concentration which was close to the room temperature (19-23 °C).

4.1.7 Solid Retention Time (SRT):

The solid retention time (SRT) is a very important parameter in biological treatment processes. In our treatment system the solid retention time ranged between 12 to 33 days. This parameter has a great influence on nitrification and luxury phosphorus uptake processes. The nitrification process also depends on the fraction of nitrifiers in the mixed liquor. This is done by increasing the aeration rate which increases the concentration of nitrifiers, hence the solid retention time (SRT) in the system (Tech et al., 2006). Phosphorus removal also depends on SRT. An acceptable removal of phosphorus requires 3-68 days of SRT (Reddy, 1998). According to Collins et al. (2003), the overall SRT should be maintained between 8 to 14 days to achieve the desirable treatment by the system.

4.1.8 Hydraulic Retention Time (HRT):

Hydraulic retention time is the measure of the length of time that a soluble compound remains in the reactor. In this study the hydraulic retention time ranged from 1.43 to 1.74 days.

4.2 Operating Conditions and Removal Efficiencies:

The influent concentrations of COD, TN and TP were maintained in the range of 1000-2400 mg/L, 200-230 mg/L and 40-48 mg/L respectively. The solid retention ranged from 12 to 33 days and hydraulic retention time from 1.43 to 1.74 days. The overall COD/N/P and BOD/N/P ratio were 27:4.5:1 to 70:3.64:1 and 26:4.5:1 to 69:3.64:1, respectively, and the food per microorganism ratio (F/M) were in the range of 1.04 to 2.57 d⁻¹.

The average removal efficiencies of carbon, nitrogen and phosphorus were estimated to be 89%, 69% and 40%, respectively. The percentage removal of contaminants (carbon, nitrogen, and phosphorus) was calculated from the following equation:

$$\% \text{ Removal} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

Where C_{in} (mg/L) = Concentration of the contaminant in the influent

C_{out} (mg/L) = Concentration of contaminant in the effluent

4.2.1 Chemical Oxygen Demand (COD):

The integrated wastewater treatment system operated for 150 days during the treatment of hog waste to investigate its performance. The concentration of COD in the wastewater and the removal efficiencies of contaminants were calculated to evaluate the performance of the treatment system. The overall COD removal efficiency increased from 60% to 89% during 7 months of operation (figure 4.5). This happened because of the assimilation of carbon source by the heterotrophic microorganisms in the aerobic, microaerophilic and anoxic zones, oxidation of

inorganic compounds (NH_4^{+-}) in the mixed liquor, and carbon requirement in the anaerobic zone for phosphorus removal.

The trends for the removal rate of COD and BOD also represents the increasing activity of microorganisms in the system. As the reactor started performing with the microorganisms acclimated with synthetic wastewater, it took a couple of weeks to be functional on hog waste which had a different composition of contaminants, i.e., the types and concentrations of carbon sources, nitrogen and phosphorus etc.. The removal rate of COD increased with the increase of organic loading rate (OLR) and F/M ratio. Figures 4.7 and 4.8 show that the COD removal efficiency is highly dependent on the organic loading rate, and moderately dependent on the F/M ratio.

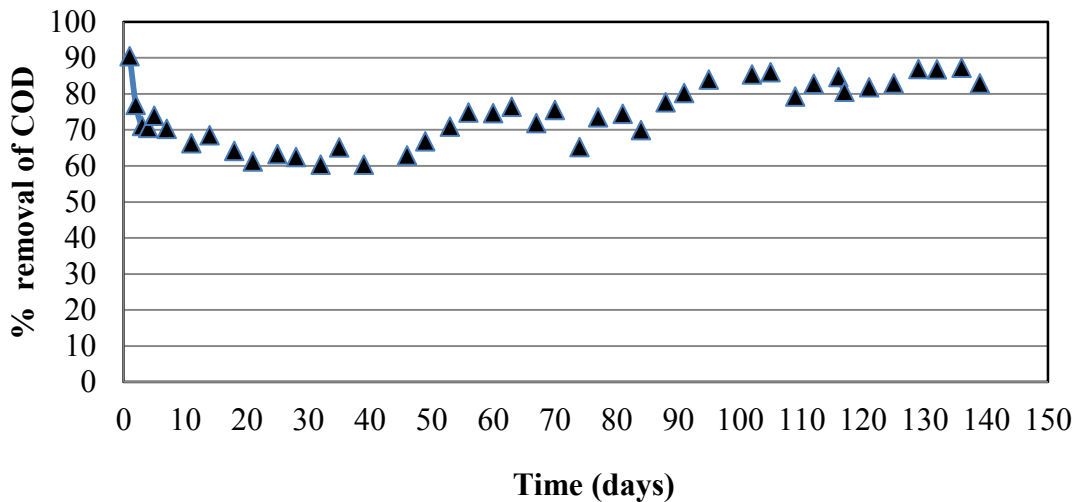


Figure 4.5: Variations of the COD removal efficiency during the treatment of hog waste

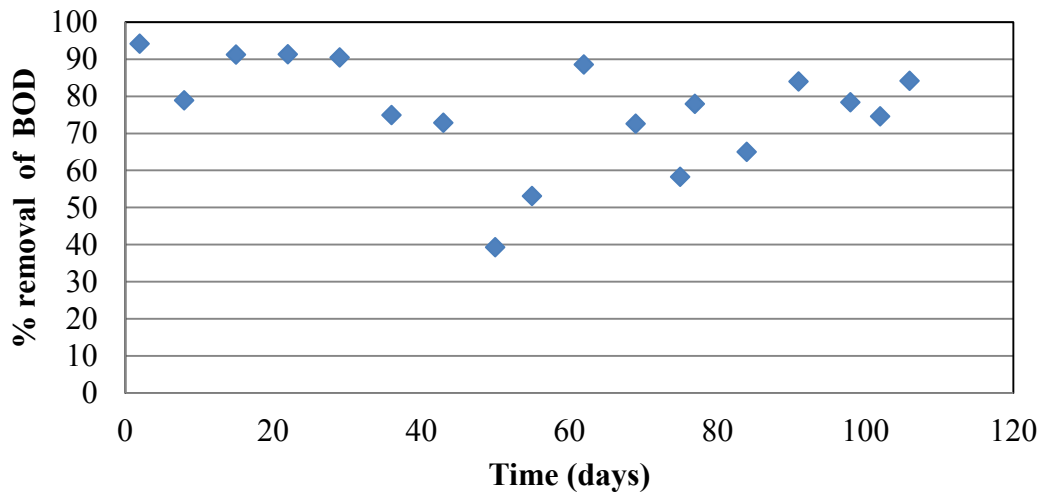


Figure 4.6: Variations of the BOD removal efficiency during the treatment of hog waste

It is seen from Figures 4.5 and 4.6 that low removal efficiencies of COD and BOD occurred during the initial 20-45 days which were 60-65% and 40-65%, respectively. This is due to the fact that the OLR and F/M ratios were 0.63-0.79 kg COD/m³.d and 1.04 to 1.15 d⁻¹, respectively, which were the lower ranges of these parameters during the operation. The curves for the removal of COD and BOD exhibited oscillatory trends with time due to the applied feast (positive weave) and famine (negative weave) regime.

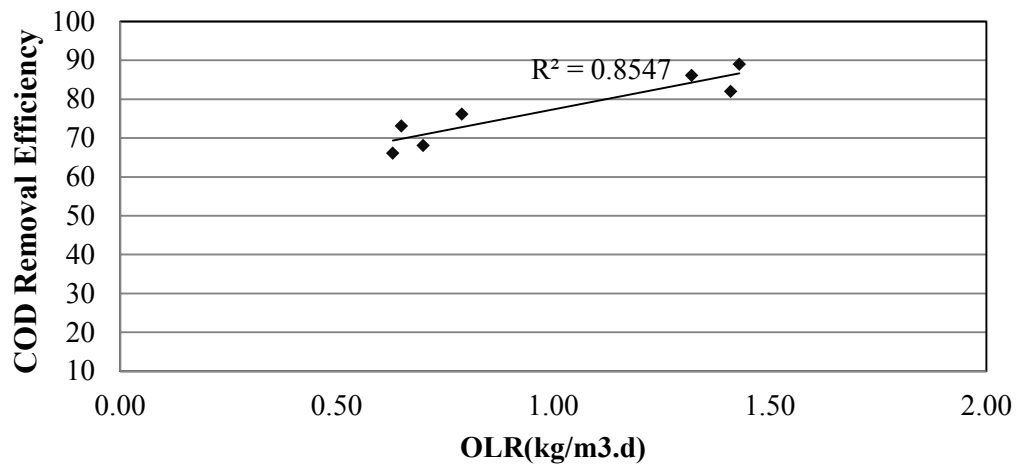


Figure 4.7: Dependence of COD removal efficiency on the organic loading rate

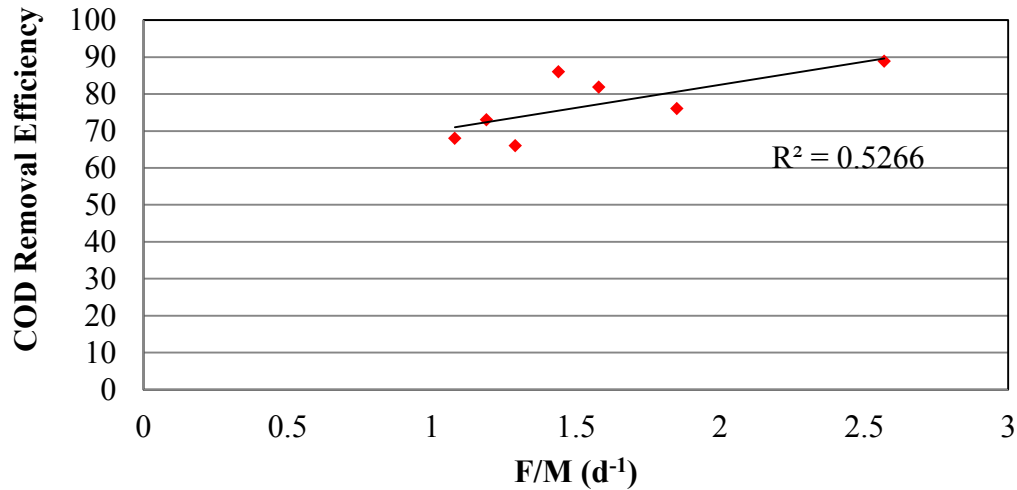


Figure 4.8: Dependence of the COD removal efficiency on food-to-microorganism ratio

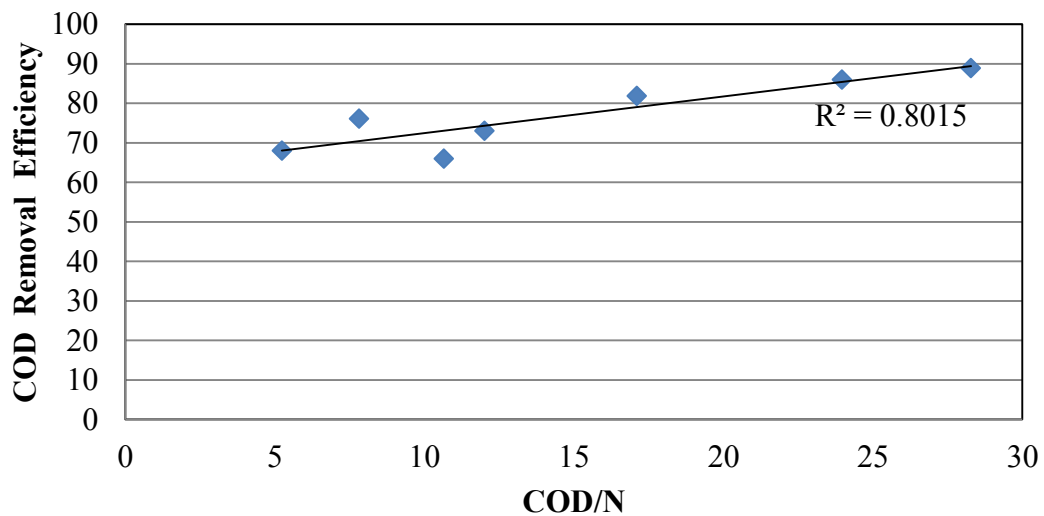


Figure 4.9: variations of the COD removal efficiency with the increase of COD/N ratio

The COD/N ratio has a positive impact on COD removal efficiency as shown in Figure 4.9.

The removal efficiency of COD increases with the increase of COD/N ratio. The initial COD/N ratio was 5.23:1 and the final COD/N ratio was 28.28:1. Carrera et al. (2003) and Zafarzadeh et al. (2011) found that COD removal rate increased when the COD/N increased, which is also

found in this study, as shown in Figure 4.9. This might be due to the fact that the heterotrophic microorganisms present in the anoxic, anaerobic and aerobic zones were exposed to large amount of easily degradable carbon source during the operation, as the VFA/COD ratio in the influent wastewater was in the range of 0.55 to 0.65. Also, it is possible that the concentration of easily degradable carbon source increased with the breakdown of organic particulate COD (TCOD) in the system.

The heterotrophic microorganisms require organic carbon source as their food for growth and proliferation. The autotrophic microorganisms gain energy from the oxidation of reducing substances (inorganic compounds) by chemosynthesis process which requires the presence of oxygen as electron acceptor. From Figure 4.10 it is clear that there is a positive correlation between COD removal efficiency and COD/P ratio. This is due to the near constant phosphorus loading rate applied during the operation which increased the activity of heterotrophs in taking up COD after adaptation to the operating conditions. Their activity improved at high COD concentrations.

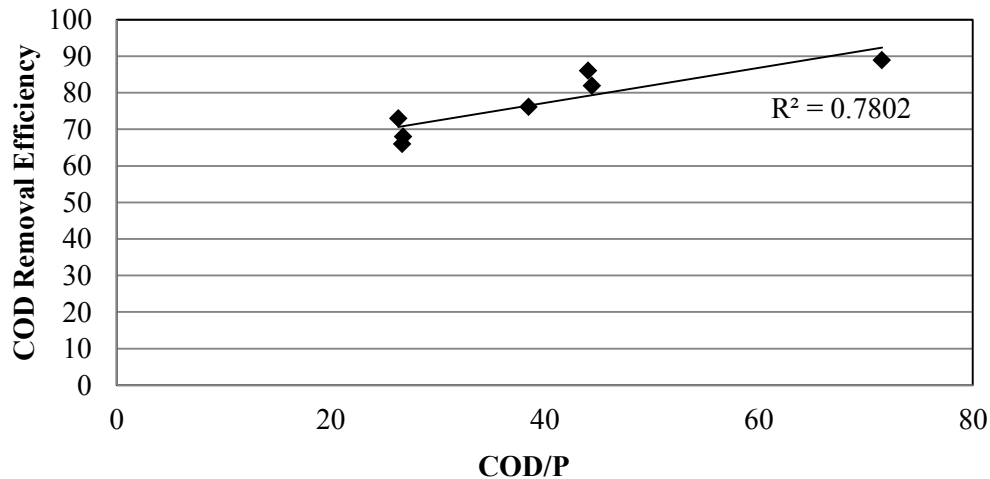


Figure 4.10: Relationship between COD removal efficiency and COD/P ratio during the operation

There is a decreasing relationship between COD removal efficiency and TN/TP ratio as shown in Figure 4.11.

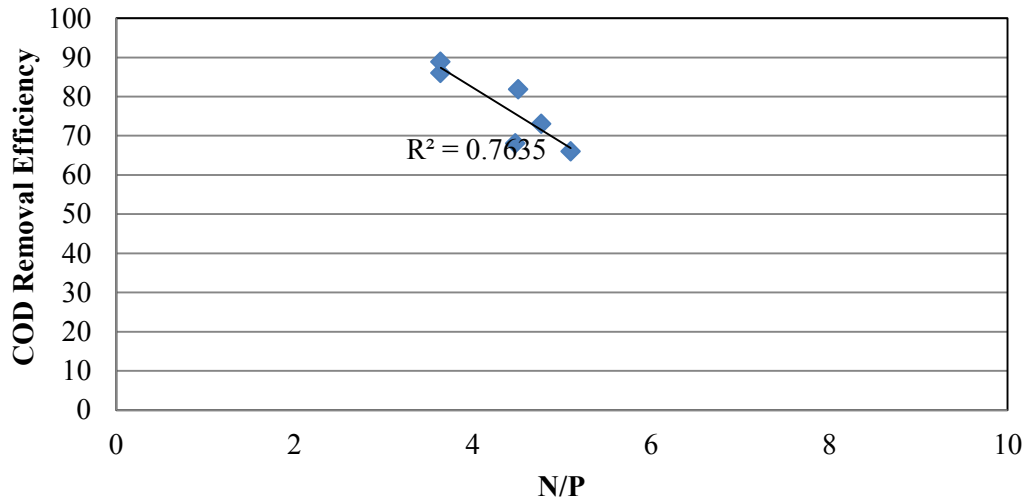


Figure 4.11: Dependence of COD removal efficiency on the N/P ratio

The examined integrated treatment system treated the hog waste at N/P ratio ranging from 3.64:1 to 4.5:1. At the N/P ratio of 3.64:1, the COD removal efficiency averaged around 89% and at N/P ratio of 4.5:1, the removal efficiency of COD was around 65%. This may be due to the fact that the nitrifiers in the mixed liquor were properly responding to the higher N/P ratio, out-competing the heterotrophic microorganisms that are responsible for COD removal.

The removal efficiency of COD is also increasing with the increasing BOD/P and BOD/N ratio which is shown by Figures 4.12 and 4.13. The BOD/N ratio was maintained between 5:1 to 18:1 and the BOD/P ratio between 26:1 to 69:1. It is clear that most of the COD removal is due to the biodegradable organic substance present in the wastewater, which corresponds to the relationship between COD and BOD operating in the system.

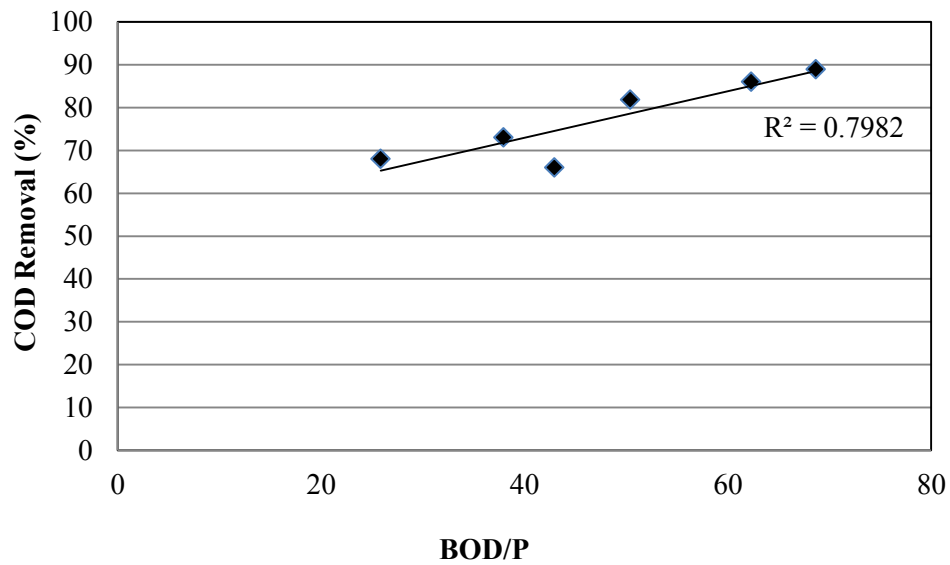


Figure 4.12: COD removal efficiency with the variation of BOD/P ratio

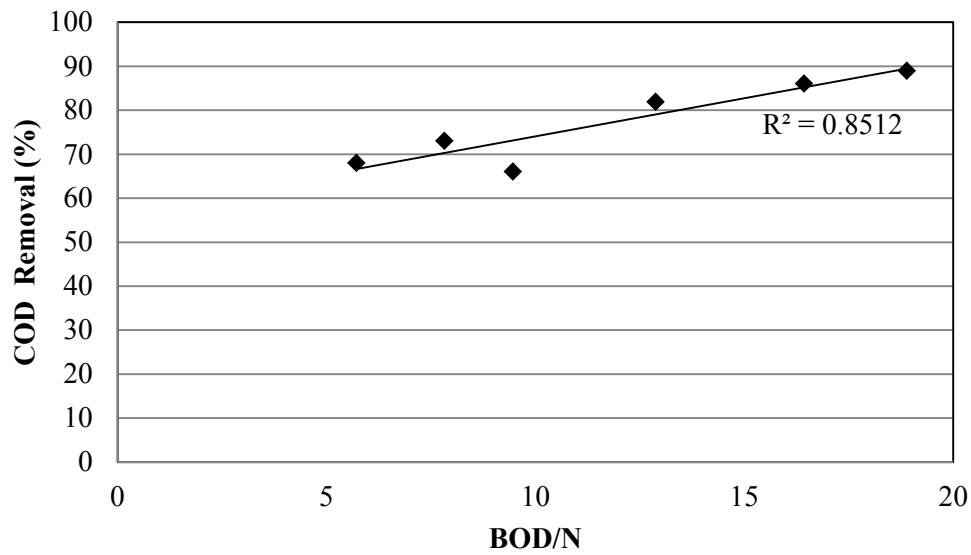


Figure 4.13: COD removal efficiency with the variation of BOD/N ratio

The overall COD and BOD relationship is calculated as $COD = 1.22 BOD$. This correlation shows the presence of a higher percentage of organic matter in the system than the oxidizable

inorganic substances. The common ratio of COD/BOD is 2:1 which does not usually apply to real agricultural wastewaters and can vary, especially for hog manure. The higher percentage of BOD in the system is an indication of the quality of the wastewater to be treated by the biological systems.

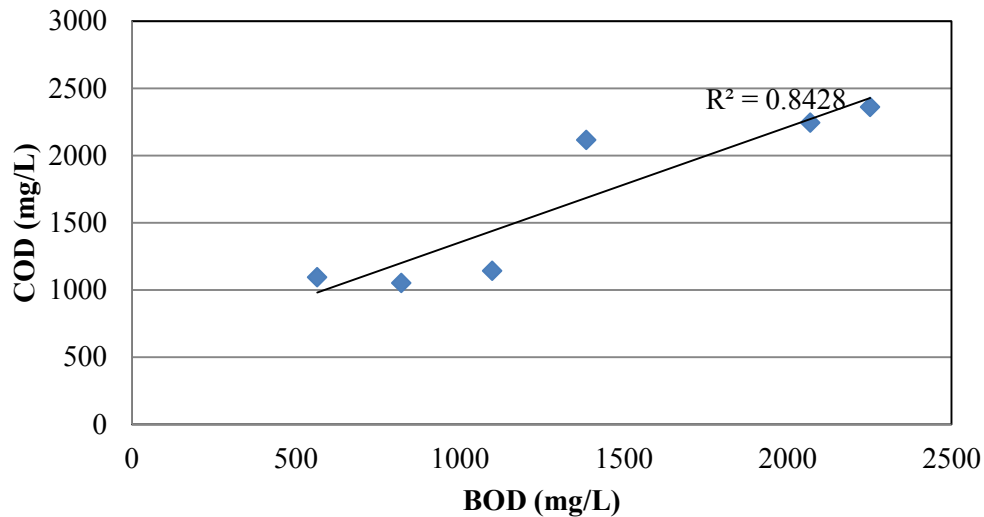


Figure 4.14: Correlation between COD and BOD for hog wastewater

Figure 4.14 demonstrates the correlation between chemical oxygen demand and biochemical oxygen demand. The correlation coefficient has been calculated as 0.918. The biochemical oxygen demand in the system is the result of the requirement of oxygen for the biodegradation of organic carbonaceous and organic nitrogenous substances (amino acids, urea etc.) present in the raw wastewater. The nitrogenous and carbonaceous BOD operating in the influent wastewater is given in the Table 4.1:

Table 4.1: Biochemical oxygen demand for organic carbon and organic nitrogen compounds

Time	Carbonaceous biochemical oxygen demand (CBOD) (mg/L)	Nitrogenous biochemical oxygen demand (NBOD) (mg/L)
Month 2	939	229
Month 3	981	953
Month 4	945	627
Month 5	1191	877
Month 6	1438	977
Month 7	1896	366

Table 4.1 shows that the overall requirement of BOD for the decomposition of organic nitrogen is less than the overall BOD requirement for the decomposition of carbonaceous organic substances in the influent. The relationship between BOD requirements for nitrogenous and carbonaceous substances is random which is realistic for real agricultural wastewater like hog waste.

4.2.2 Nitrogen Removal:

In order to determine the total nitrogen concentration, laboratory testing of TKN, nitrate and nitrite is required. Total Kjeldahl Nitrogen (TKN) includes ammonia and organic-nitrogen. Animal manure is a proper source of nitrogen but harmful for the environment if exceeds the environmental limit. The influent concentration of total nitrogen was 200-230 mg/L and the NH_3

concentration was 150-200 mg/L. The concentrations of nitrogenous compounds in the hog waste are presented in Figure 4.15:

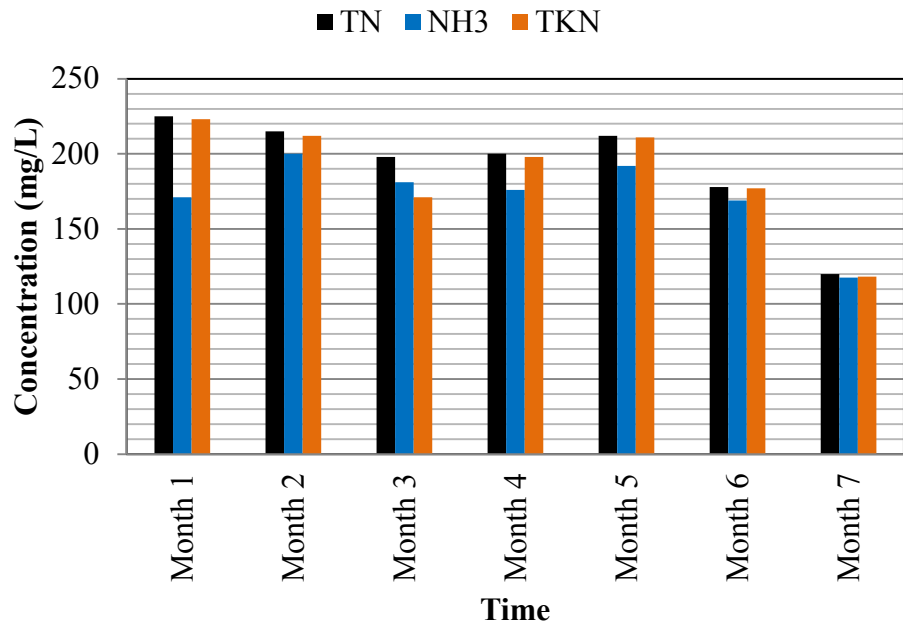


Figure 4.15: Concentrations of nitrogenous compounds in influent of hog wastewater during the operation of treatment system

The total nitrogen removal of 10%-69%, ammonia removal of 10%-76% and total Kjeldahl Nitrogen removal of 10-50% were obtained with the nitrogen loading rate of 0.07 to 0.16 ($\text{kg}/\text{m}^3 \cdot \text{d}$). After 150 days of operation, the overall nitrogen removal efficiency increased to 69%.

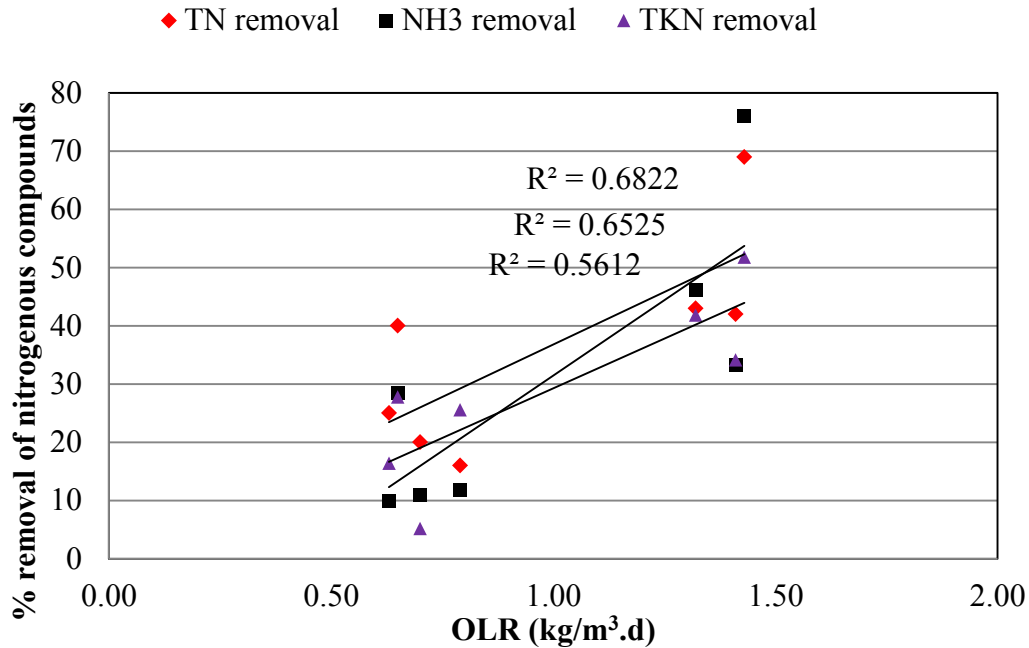


Figure 4.16: Removal of nitrogenous compounds by the treatment system with the increased organic loading rate

The removal of total nitrogen, NH_3 and TKN showed the same trend with an overall determination coefficient of 0.62, as presented in Figure 4.16. The increased removal of nitrogen with the increase of OLR is due to the increase of biomass concentration, i.e. biomass production in the mixed liquor, as reported before (Figuroa et al., 2011). Adequate OLRs are required for simultaneous nitrification and denitrification since a proper concentration of carbon source should be provided to the denitrifying bacteria for proper denitrification (Obaja et al., 2004). After a few months of operation, easily biodegradable acetic acid was added to the influent in order to increase the availability of carbon source. Lower values of pH around 4-6 were kept so that the VFAs (short chain fatty acids) could be produced in the influent which further enhanced simultaneous nitrification and denitrification processes (Weimer et al., 2011). The loading rate of

nitrogen was maintained between of 0.07 to 0.16 kg N/m³.d during the operation period. In general, the nitrogen in the influent wastewater should not exceed 0.15 kg N/m³.d as per water quality regulation (Park et al., 2011) which is close to the maximum operating nitrogen loading rate used during the operation of this new multi zone wastewater treatment system.

Figure 4.17 shows that the total nitrogen removal efficiency correlated with COD/N ratio as it is the characteristics parameter for nitrogen removal (Benthum et al., 1998; Carerra et al., 2003). The COD/N ratio in this system changed from 5.23:1 to 28.28:1. According to Fu et al. (2008) the increased COD/N ratio supported the increased total nitrogen removal efficiency. The COD/P ratio also has a positive effect on nitrogen removal which is shown in Figures 4.18 and 4.19.

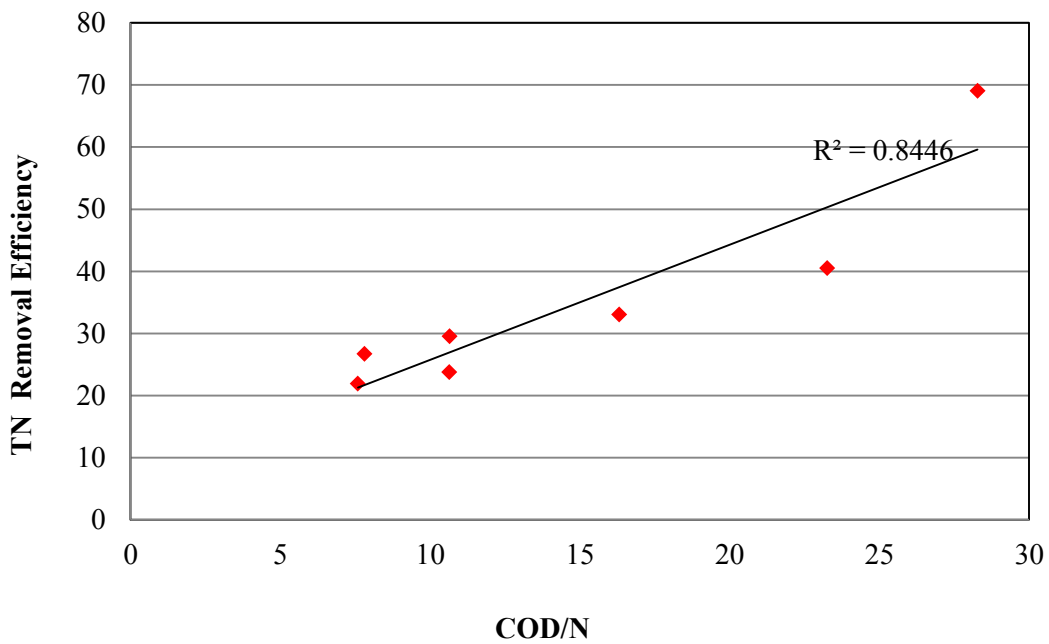


Figure 4.17: Dependence of percentage nitrogen removal on the COD/N ratio

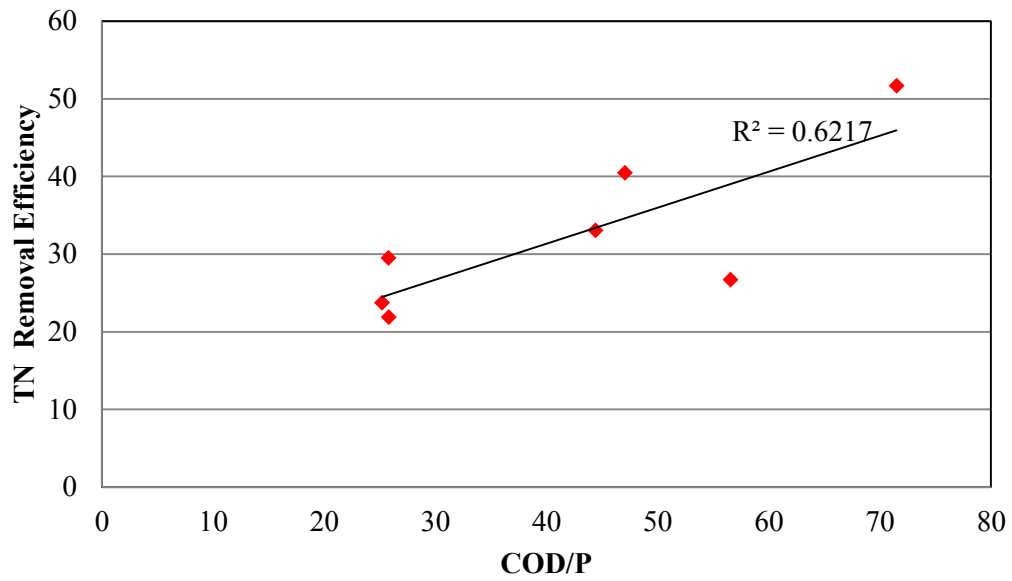


Figure 4.18: Relationship between TN removal efficiency and COD/P ratio

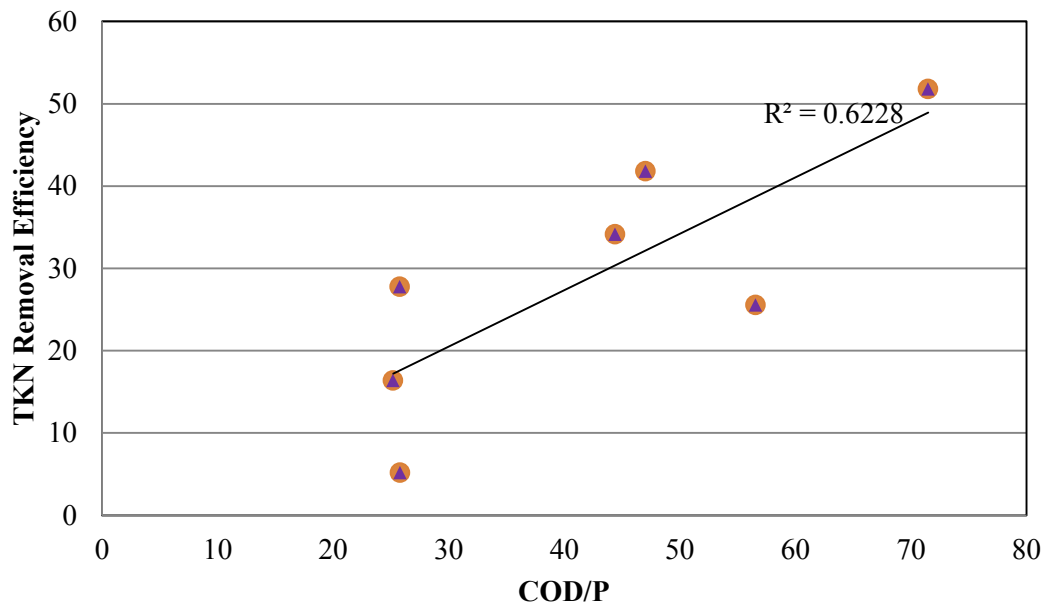


Figure 4.19: Relationship between TKN removal efficiency and COD/P ratio

The low concentrations of nitrite and nitrate in the effluent represent the efficiency of this technology in terms of nitrogen removal. In addition to the nitrite and nitrate content of influent wastewater, additional NO_3 and NO_2 are produced in the system due to nitrification processes. The concentrations of nitrite and nitrate in the raw wastewater have been shown in the table 4.2.

Table 4.2: Concentrations of nitrate and nitrite in the influent

Concentration (mg/L) Type	Nitrate (mg/L)	Nitrite (mg/L)
Unfiltered	357	33
Filtered	147	23

Because of its unstable chemical structure and the presence of high concentrations of dissolved oxygen in the aerobic zone, NO_2 is oxidized to NO_3 . However, if the nitrifying microorganisms do not function properly, NO_2 accumulates in the system (Zeng et al., 2010). The removal of NO_3 is proportional to the respiration rate which further depends on the easily available carbon source for the denitrifying microorganisms in the anoxic zone (Jeill and Silverstein, 1999). The accumulation of NO_3 in the system occurs when the microorganisms have less biodegradable carbon source for denitrification. The presence of anaerobic digestion also influences the concentration of nitrogen in the system since digestion process produces nitrogen which is released into the mixed liquor during the recycling of sludge from the anaerobic zone.

However, the proper performance of a treatment system should produce adequate nitrification and denitrification and near zero concentrations of NO_3 and NO_2 in the effluent. The concentrations of nitrate and nitrite in the effluent samples are given in Table 4.3.

Table 4.3: Average concentrations of nitrite and nitrate in the effluent of the treatment system

Time	Nitrate (mg/L)	Nitrite (mg/L)
Month 1	2.37	0.12
Month 2	3.3	0.12
Month 3	2.4	0.28
Month 4	1.09	0.10
Month 5	1.19	0.07
Month 6	2.91	0.15
Month 7	2.36	0.14

4.2.3 Phosphorus Removal:

Phosphorus removal by biological processes is accomplished by the enhanced biological phosphorus removal (EBPR) process. This process is economically advantageous compared to chemical processes due to lower sludge production (Metcalf and Eddy, 2003). Phosphorus is removed by the accumulation of phosphorus in the intracellular spaces, which is further removed by the waste sludge. The overall phosphorus removal during the treatment of hog waste is shown in Figure 4.20.

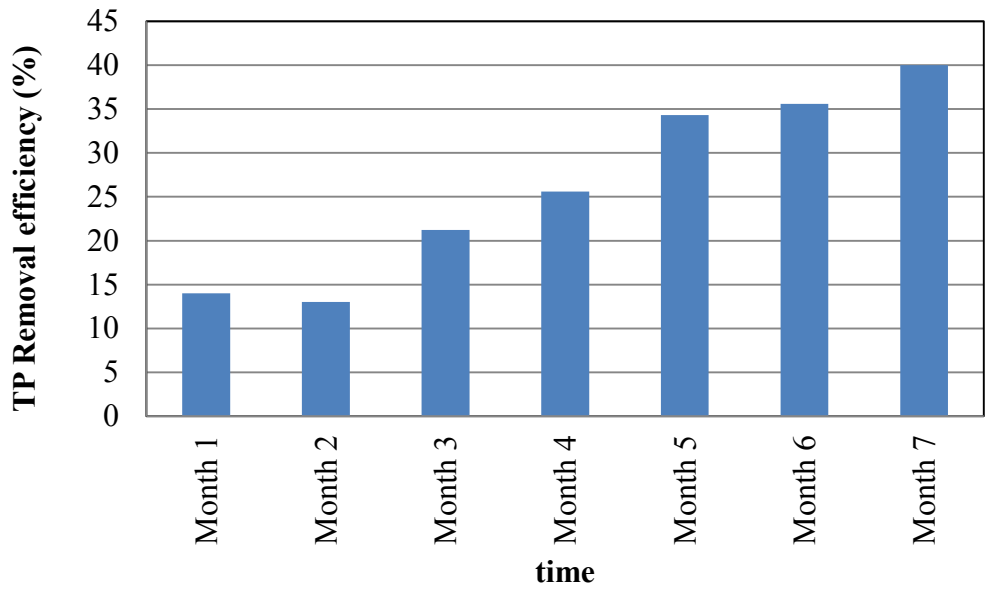


Figure 4.20: Percentage removal of phosphorus with time

The removal of phosphorus increased from 14% to 40% from Month 1 to Month 7 (Figure 4.20). The phosphorus loading rate increased from 0.015 to 0.035 kg/m³.d. In order to increase the activity of PAOs, PLR was kept almost constant during the operation period. In this study, it was found that phosphorus removal efficiency increased significantly with the increase of COD/N which is shown in figure 4.21.

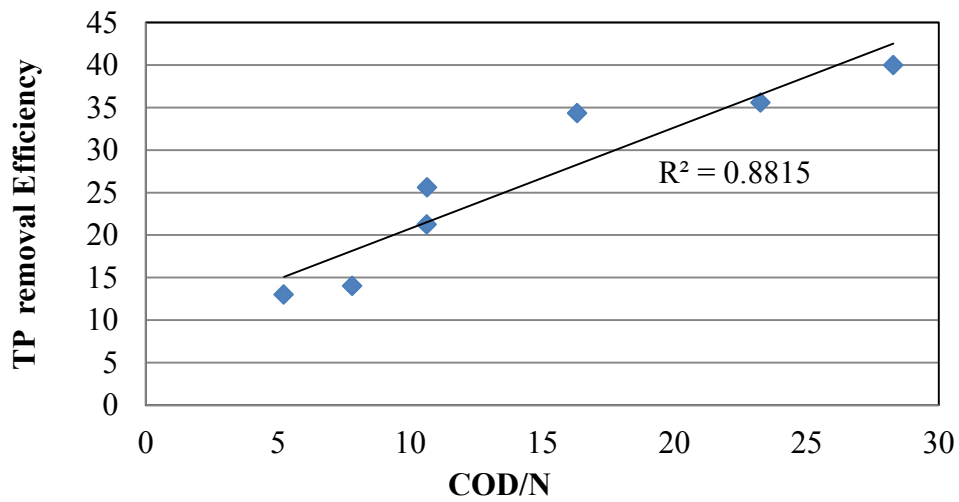


Figure 4.21: Relationship between phosphorus removal and COD/N ratio in the system

The phosphorus removal efficiency increased with the increase of COD/N ratio from 5.23:1 to 28.28:1. Initially, with the COD/N ratio between 5.23:1 and 7.81:1, this ratio did not have a significant impact on phosphorus removal as the microorganisms were acclimating to the wastewater. After this period, the COD/N ratio exhibited a positive correlation with the phosphorus removal efficiency. This may be due to the decrease of nitrogen concentration in the system and the lower competition between the nitrifiers and PAOs in the mix liquor. Organic loading rate showed an impact on phosphorus removal which is presented in Figure 4.22.

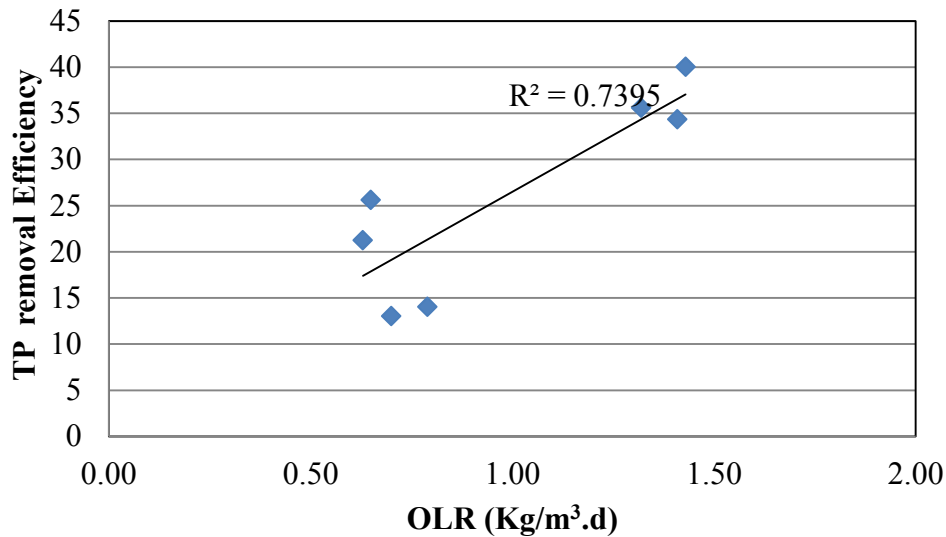


Figure 4.22: Dependence of phosphorus removal efficiency on organic loading rate

Due to anaerobic digestion in the anaerobic zone, short chain fatty acids are produced in this zone in addition to acetic acid which was added to the influent. Acetic acid is a suitable source of carbon for phosphorus removing organisms. Also, other carbon sources i.e. amino acids and sugars can be taken up by the PAOs (Wentzel et al., 1991).

4.3 Mixed Liquor Characteristics and Sludge Yield:

The observed biomass yield was estimated from the mixed liquor solids concentration data collected during the treatment of real hog waste (Table 4.4). Figure 4.23 shows that the observed biomass yield ranged from 0.04953 to 0.1239 mg VSS/mg COD, and presented a decreasing trend during the course of operation. In this figure, the solids data have been normalized by the total amount of COD entering the reactor per day. Hence, the slopes of the linear regression lines correspond to the observed sludge yields. Figure 4.23 shows that the biomass yield decreased with the progress of operation.

Table 4.4: Characteristics of mixed liquor

Time	TS (mg/L)	TSS (mg/L)	VSS (mg/L)	TCOD (mg/L)
Month 1	1370	591	506	1148
Month 2	1275	680	503	1230
Month 3	1178	780	509	1448
Month 4	1265	803	540	1620
Month 5	2550	1340	986	2420
Month 6	2157	1150	940	1930
Month 7	1948	903	550	1264

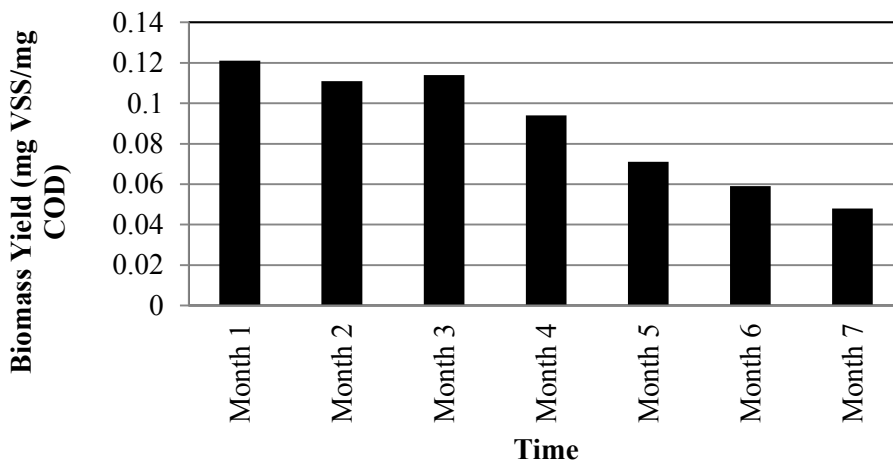


Figure 4.23: Biomass yield in the system

The specific utilization rates of carbon, nitrogen and phosphorus are presented in Table 4.5.

Table 4.5: Specific utilization rate of contaminants

Specific utilization rate Time	COD ($\text{kg/m}^3 \cdot \text{d/kg}$ VSS)	N ($\text{kg/m}^3 \cdot \text{d/kg}$ VSS)	P ($\text{kg/m}^3 \cdot \text{d/kg}$ VSS)
Month 1	13.72	0.46	0.04
Month 2	8.55	0.24	0.19
Month 3	9.91	0.64	0.10
Month 4	8.60	0.80	0.08
Month 5	12.58	0.57	0.07
Month 6	12.59	0.50	0.07
Month 7	13.10	0.56	0.82

4.4 Composition of Sludge in Anoxic and Anaerobic Zones

The production of sludge in the system occurs due to the accumulation of active microorganisms, as well as the presence of non-biodegradable inert matter and their settlement in the system. Sludge is commonly characterized by its content of total solids (TS), total suspended solids (TSS) and volatile suspended solids (VSS). The sludge composition in the anoxic and anaerobic zones is presented in Table 4.6.

Table 4.6: Characteristics of sludge

Zone	Time	TS (mg/L)	TSS (mg/L)	VSS (mg/L)	TSS/TS	VSS/TS
Anoxic	Month 1	4033	3200	1919	0.79	0.48
	Month 2	29140	28860	23690	0.99	0.81
	Month 3	31880	30570	21697	0.96	0.68
	Month 4	31294	30415	24303	0.97	0.78
	Month 5	27755	26381	20677	0.95	0.74
	Month 6	30644	28067	21795	0.92	0.71
	Month 7	31206	30066	23863	0.96	0.76
Anaerobic	Month 1	14221	11250	9336	0.79	0.66
	Month 2	33903	31718	26405	0.94	0.78
	Month 3	51951	44911	36461	0.86	0.70
	Month 4	38526	37525	29353	0.97	0.76
	Month 5	43246	29026	21966	0.67	0.51
	Month 6	35709	31512	22667	0.88	0.63
	Month 7	35419	34973	25397	0.99	0.72

4.5 Comparing the results with the previous work:

Westerman et al. (2000) operated an up flow biological aerated biofilter for the treatment of pig manure with organic loading rate of $5.7 \text{ kg/m}^3\cdot\text{d}$ at average temperature 27°C for 12 months. The obtained BOD and COD removal efficiencies were 88% and 75%, respectively. Lower temperatures close to 10°C and the increase in organic loading rate to $9 \text{ kg/m}^3\cdot\text{d}$ decreased the removal efficiency of COD to 56%. The COD removal efficiency showed a linear relationship with the organic loading rate (OLR) ranging from 2-12 $\text{kg/m}^3\cdot\text{d}$. The removal efficiencies of TKN, NH_3 and total nitrogen were 84%, 94% and 61%, respectively. The reactor was filled with calcareous or siliceous gravel as the support material with an intermittent aeration to the reactor. The biofilter was aerated by an air browser below the filter. Despite the higher removal efficiencies, this treatment system showed to be greatly temperature-sensitive in terms of contaminant removal which is a big disadvantage of this system. In our study, the treatment system was operated at room temperature. Another drawback of Westerman et al. (2000) is that it does not remove phosphorus, and the operation of system requires high maintenance. For example, the biofilters required frequent cleaning, normally four times every day. The integrated wastewater treatment system used in the present study used a custom-built support material for the biofilm which did not clog during the entire operation of the system and it is advantageous compared to the calcareous or siliceous support in terms of materials, maintenance and operation used in this system.

Zhu et al. (2006) treated the liquid swine manure in laboratory-scale sequencing batch reactors, by altering anaerobic-aerobic-anoxic-aerobic phases in the same reactor. This technology removed the COD up to 100% and BOD up to almost 97.4%. Nitrogen and phosphorus removals

were 99% and 89%, respectively. The solid retention time and hydraulic retention time were maintained at 15 and 3 days, respectively, at a constant temperature of 19-21°C at a pH of 7.45 operating for 3 months. This system had a high footprint and required high maintenance and control.

Karakashev et al. (2008) introduced a different process for the removal of carbon, nitrogen and phosphorus which contained a USAB (Upflow Anaerobic Sludge Blanket), an OLAND (Oxygen-Limited Autotrophic Nitrification/Denitrification) and a PRS (Phosphorus removal by precipitation). These processes were performed at laboratory-scale and full-scale basis for the removal of contaminants from pig manure. This is a hybrid technology where the combination of physical, chemical and biological processes have been used to remove the contaminants from pig manure with the removal efficiencies of 96%, 88% and 81% for carbon, nitrogen and phosphorus, respectively. The combination of the processes which was called the PIGMAN has an innovative concept, but it requires a large footprint and high maintenance, as well as high energy and control, making the system uneconomical. The integrated multi-zone treatment system examined in this study uses only biological processes for the removal of contaminants which is the most economical process in this field. If the examined system could be operated for a longer period, it could produce higher efficiencies of removal (as the trend shows) which along with lower footprint, easier operation and maintenance present the superior performance of the examined treatment system compared to the conventional technologies.

The environmentally superior technology (EST) is developed in North Carolina (Vanotti et al., 2009) to treat pig manure and to meet the environmental quality. The removal efficiencies for COD, BOD, TKN, $\text{NH}_4^+\text{-N}$, TN and TP were 90.9%, 99.4%, 95.5%, 96.6%, 88.1% and 77.1%,

respectively. The influent flow rate was maintained between 10 to 60 m³/d, with the temperature ranging between -2.5 to 31 °C. Nitrogen is removed by the biological nutrient removal process which is called NDN process in an aeration tank with high performance bacteria adapted with high strength wastewater. This process removes COD and BOD₅ with high efficiencies of 87% and 98%. The removal of phosphorus by this system is mainly accomplished by the chemical process of calcium phosphate precipitation, and also by solid-liquid separation (Garcia et al., 2007). For the phosphorus removal process, a high pH of 9.5 is required. The main advantage of this system is the low cost due to the on-farm implementation and engineering improvements, and contribution to a cleaner environment. But the operation of this system is very complicated compared to the system examined in this study. The phosphorus is not removed biologically by the system but by chemical process which requires large amounts of chemicals and produces chemically-rich precipitates.

Kunz et al. (2008) presented technologies for manure management which constituted mainly of solid-liquid separation in lagoons. The separated solids are spread on the agricultural land as fertilizers. However, nutrients, in excess of the land capacity, have to be removed by appropriate swine manure treatment in order to prevent soil and groundwater contamination. To improve the solid-liquid separation, easily biodegradable synthetic organic polymers (polyacrylamide) are used for coagulation and flocculation prior to biological treatment. These processes are not pH-dependent and they are more practical. This technology can remove 80-95% of total solids and around 90% of chemical oxygen demand. The removal efficiencies of BOD, COD, TKN and TP are reported to be 98%, 95%, 82% and 85% respectively. This process is commonly used for manure management, but it requires large foot print and high maintenance.

Chao et al. (2008) studied the treatment performance of a plug flow polyethylene bag bioreactor in the removal of contaminants from swine manure, producing 71% removal of COD at the temperature of 24.7 °C. The hydraulic retention time (HRT) was 15.9 days. This technology also resulted in the removal of total solids (TS) and volatile solids (VS) with efficiencies of 74% and 69%, respectively. The effluent pH was between 7-7.5 which is similar to the values obtained in our study. There is no significant nutrient removal by this system. This system produces biogas, unlike the multi-zone system of this study which did not produce biogas since VFA was needed for biological nutrient removal processes and methanogenesis was not supported.

The BIOSOR technology (Buelna et al., 2007) is used globally and has been studied in the removal of BOD₅ in the range of 10000-20000 mg/L, TKN, 2000-3800 mg/L, TP, 500-900mg/L and suspended solids, 10000-20000 mg/L. This technology has shown the removal of more than 97% BOD, 95% suspended solids, 75% TKN, and 87% phosphorus. This technology is effective enough to remove around 95% of odor. The settled sludge is deodorized by anaerobic digestion which is performed in this study. The supernatant is first pre-filtered and then passes through biofilters.

Frijters et al. (2007) examined the Circox airlift reactor for the removal of COD and nitrogen from wastewater. The nitrogen loading rate was 0.45 kg/m³.d and the initial ammonia concentration was 500 mg/L. Granular biomass was produced in this technology and air was introduced to nitrify 50% of the nitrogen introduced to the system. In the Circox technology, the nitrogen concentration and air flow rate can vary to further control the removal efficiencies. The pH of wastewater was maintained at 8.3 with the operating temperature of 32 °C. In our study,

pH ranged from 7 to 8.5 and the operating temperature was room temperature. The Circox process also removes sulphates which are not considered in our study. The dissolved oxygen concentration was 1-2 mg/L in the mixed liquor of Circox technology which was 3-6 mg/L in our system. There is no phosphorus removal by the Circox system due to the absence of proper anaerobic zone.

Molinuevo et al. (2009) used upflow anaerobic sludge bed (UASB) technology for the treatment of effluent which was digested at 55 °C prior to the treatment with hydraulic retention time (HRT) of 15 days and organic loading rate of 4.6 kg COD/ m³.d. This system used constant organic loading rate and higher HRT for the treatment. But in our system, both parameters were varied during the course of operation. In the UASB-post digested effluent technology, the removal of nitrogen and COD is carried out by anaerobic oxidation of predigested effluent only, resulting in partial removal of COD. Ammonium removal ranged from 83% to 86%. There is no significant phosphorus removal. In our treatment system, aerobic, anoxic and anaerobic utilization of carbon source occurs under different operating conditions. Also, ammonia is oxidized by the aerobic oxidation in the mixed liquor.

Dosta et al. (2008) conducted a treatment process with sequencing batch reactor to treat the hog wastewater. This treatment system used three aerobic/anoxic periods with the coagulation/flocculation process in the last 15 minutes of anoxic process which required extra maintenance and chemical compounds and control. The temperature, HRT, and SRT were 30 °C, 2.7 days and 12 days, respectively, with a controlled pH range of 8 to 8.8. . The temperature, HRT, SRT in our system was in the range of 19-23 °C, 1.43 -1.74 days, and 17-33 days, respectively, and pH was controlled by maintaining the influent pH. In our system, the oxidation

of ammonium produces nitrite but requires a high air flow rate and DO concentrations of 3-6 mg/L. The coagulation-flocculation process in the technology of Dosta et al. (2008) used FeCl_3 which is not performed in our system. Also our system is removing 40% of phosphorus with 86% BOD, 89% COD and 69% nitrogen, while the treatment system of Dosta et al. (2008) removes 66% of COD and 98% of nitrogen without any phosphorus removal.

Figuera et al. (2011) presented a study of aerobic granular sequencing batch reactor (GSBR) for the removal of COD and nitrogen by 87% and 70%, respectively. The raw slurry of pig waste was treated without dilution in this system. The organic loading rate was $4.4 \text{ kg/m}^3\cdot\text{d}$ and nitrogen loading rate was $0.83 \text{ kg/m}^3\cdot\text{d}$ which were kept constant over the operation period. The system worked with 1.5L of reactor volume and air flow rate of 3.5 L/min. Our reactor volume was 100 L, while using varying OLR, PLR and NLR. The raw wastewater was kept at a temperature of 19-23 °C for pre-fermentation. The feast and famine regime was introduced to the treatment system of Figuera et al. (2011) in order to produce aerobic granules, and resulted in a different mixed liquor dissolved oxygen concentration trend with air flow rate 6-8 L/min. The nitrogen removal by this system was done by simultaneous nitrification and denitrification processes.

Lee et al. (1996) presented a sequencing batch reactor to treat the swine waste where pre-fermentation was conducted for 10 days at room temperature. The removal efficiency of nitrogen was 90% and phosphorus was 89%. The sludge phosphorus content was reported to be 7%, while in our system, it ranged from 3%-5%. The preparation of substrate required 10 days for fermentation, coagulation with FeCl_3 , centrifugation and filtration. In our system, the pre-fermentation was done on a continuous basis and raw wastewater was diluted and used directly

to the system without coagulation, centrifugation and filtration. Table 4.7 shows the comparison of some previous treatment technologies with this new integrated multi-zone treatment system:

Table 4.7: Comparison between Integrated Multi-Zone Wastewater Treatment System and reported work in literature

Parameters	Integrated System	Westerman et al.(2000)	Zhu et al.(2000)	Dosta et al. (2008)	Figuera et al. (2011)
COD removal (%)	89	75	100	66	87
BOD removal (%)	89	88	97.4	-	-
TN removal (%)	69	50	99	98	70
TP removal (%)	40	26	89	-	-
COD concentration(mg/L)	1000-2400	500-1900	8800	4100	500-14500
TN concentration (mg/L)	200-230	140-274	2100	2300	100-2100
TP concentration (mg/L)	40-48	63-85	600		-
SRT(d)	12-33	-	15	12	-
HRT(d)	1.43-1.74	-	3.3	2.7	-
pH	7.5-8.5	-	7.45	7.1-9.3	7-7.7
Temp (°C)	19-22	27	19-21	32	
DO (mg/L)	3-6	4-11	0	>1	3-7

The integrated treatment system examined in this study was compact, economical, and used biological processes for the removal of contaminants. Certain technologies use the combination of different processes (physical, chemical, biological) which is uneconomical, requires large footprint and high maintenance. In our system, the microorganisms required additional time to adapt to the hog waste after operation with the synthetic wastewater. Therefore, it is plausible that higher removal efficiencies would be achieved if the treatment system had operated for a longer period.

CHAPTER 5 : RESULTS AND DISCUSSION-SYNTHETIC WASTEWATER

5.1 Operating Conditions:

The influent concentrations of carbon, nitrogen and phosphorus during the reported experiments were in the range of 500 to 4000 mg/L, 42 to 200 mg/L, and 16 to 40 mg/L, respectively. The treatment system operated with food-to microorganisms (F/M) ratio of 0.95 to 3.4 (d^{-1}) and SRT of 10-200 days, The organic loading rate was maintained in the range of 0.95 to 2.5 $kg\ COD/m^3.d$, nitrogen loading rate was in the range of 0.51 to 0.135 $kg\ N/m^3.d$, and phosphorus loading rate changed from 0.041 to 0.049 $kg\ TP/m^3.d$, as shown in Figure 5.1.

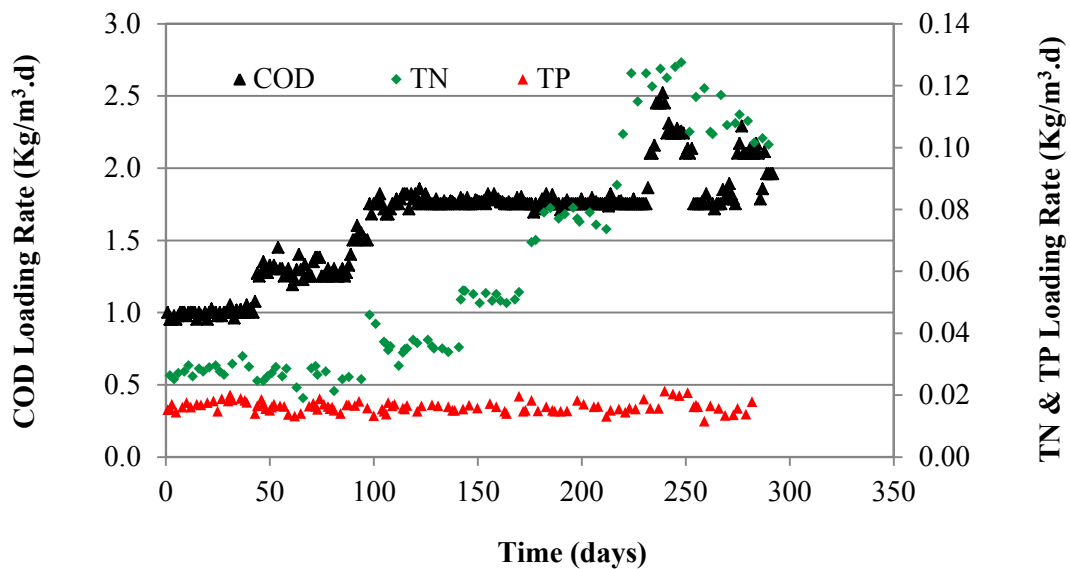


Figure 5.1: Loading rates of carbon, nitrogen and phosphorus in the system during the treatment of synthetic wastewater

5.2 Removal Efficiencies:

The removal efficiencies of COD and nitrogen were in the range of 83.3% to 99% and 65.9% to 85% respectively. Phosphorus removal efficiency gradually improved with the increase of nitrogen loading rate, reaching 100%. The efficiency of contaminant (carbon, nitrogen, and phosphorus) removal is calculated from the following equation:

$$\% \text{ Removal} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

where: C_{in} (mg/L) = Concentration of the contaminant in the influent and C_{out} (mg/L) = Concentration of contaminant in the effluent

Table 5.1: Operating conditions and optimum removal efficiencies for the treatment of synthetic wastewater.

Operating Conditions		Influent Concentration(mg/L)			Removal efficiency		
OLR(kg COD/m ³ .d)	0.95-2.5	COD	N	P	COD	N	P
NLR(kg TN/m ³ .d)	0.051-0.135	500-4000	42-200	16-40	99%	85%	100%
PLR(kg TP/m ³ .d)	0.041-0.049						
C/N/P	49.2:7.1:1						
SRT(d)	10-200						
F/M(d ⁻¹)	0.95 to 3.4						
HRT(d)	1.43						

5.2.1 Chemical Oxygen Demand:

Figure 5.2 shows the concentration of COD in the influent and effluent streams. It is clear that most of the COD from the wastewater is removed by the system. The removal efficiency of COD is calculated by the following Equation:

$$\% \text{ Removal} = \frac{COD_{in} - COD_{out}}{COD_{in}} \times 100\%$$

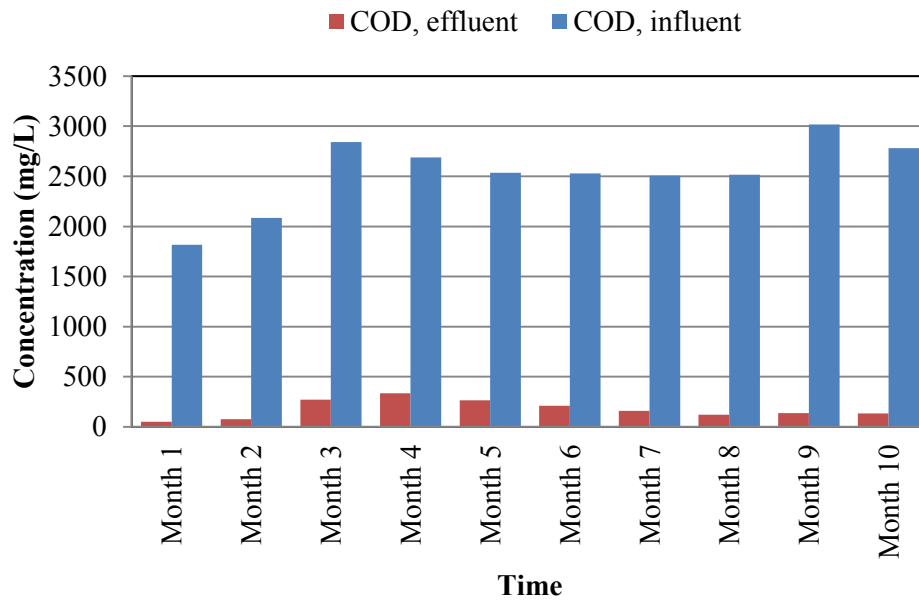


Figure 5.2: Overall COD concentration in the influent and effluent samples

The average COD concentrations in the influent and effluent for ten operation months are presented in Figure 5.2, demonstrating that the average COD concentrations in the influent and effluent were maintained in the range of 800 to 3000 mg/L, and 52 to 250 mg/L, respectively.

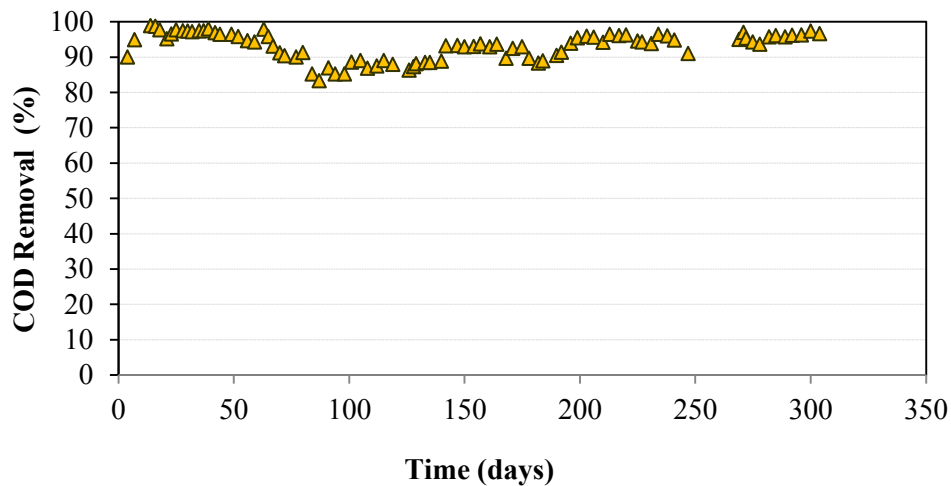


Figure 5.3: Variations of the COD removal efficiency with time

Figure 5.3 shows that the COD removal efficiency increased from 90% to 97% during the days 0 to 50 and decreased from 97% to 80% during the days 50 to 150. The system then showed continuous increase of COD from days 150 to 310 of operation.

5.2.2 Total Nitrogen, TN:

The removal of nitrogenous compounds in the multi-zone integrated treatment system is achieved by the simultaneous nitrification and denitrification processes. The nitrifiers in the mix liquor (aerobic zone) transform the ammonium nitrogen to nitrite and further to nitrate. Nitrate serves as an electron acceptor by microorganisms in the anoxic zone, resulting in the production of nitrogen gas which escapes to the atmosphere since it has a low solubility in water. The removal of total nitrogen and ammonia-nitrogen are given in Figure 5.4.

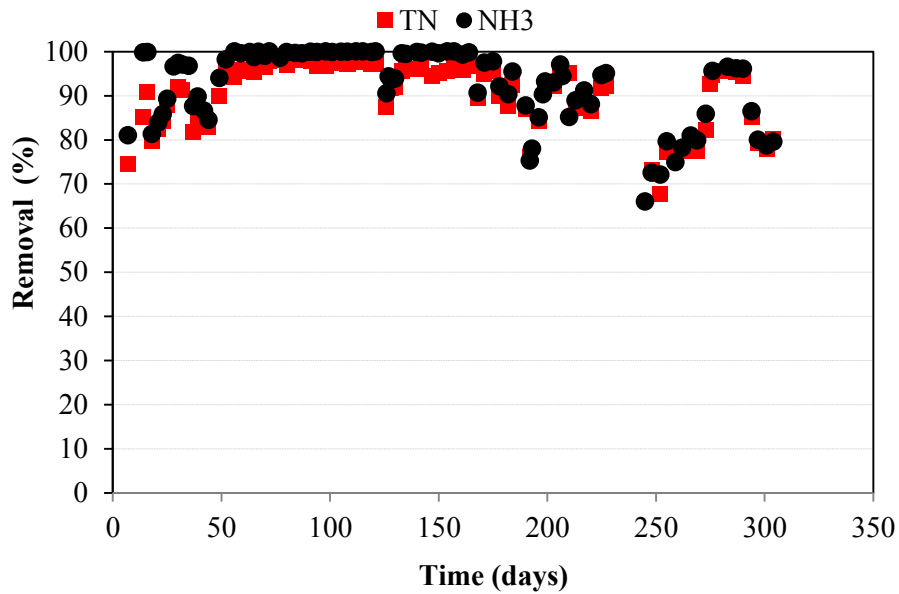


Figure 5.4: Total nitrogen and ammonia removal efficiencies with time

This figure shows that the percentage removal of total nitrogen and ammonia-nitrogen increased with the increased loading rate of nitrogen, until day 200. After that time, the system started accumulating nitrite in the mix liquor and it showed reduced removal of nitrogen from 91% to 65% when the loading rate of nitrogen was at maximum. In order to increase the removal efficiency of nitrogen, its loading rate was reduced to 0.11 kg TN/m³.d, resulting in the increase of nitrogen removal efficiency to 99% after 300 days.

Nitrite and nitrate do not exist in synthetic influent but they were produced in the system during the nitrogen removal processes. The produced nitrite and nitrate should be removed during the nitrification and denitrification processes. An adequate wastewater treatment technology shows 100% removal of nitrite and nitrate. The average concentrations of nitrite and nitrate in the effluent are shown in Table 5.2. The very low concentrations of nitrite and nitrate in the effluent demonstrate the proper performance of the integrated system.

Table 5.2: Nitrite and nitrate concentrations in effluent of the system

Time	Nitrate(mg/L)	Nitrite(mg/L)
Month 1	0.2667	0.0572
Month 2	0.1956	0.0202
Month 3	0.4360	0.0585
Month 4	0.2472	0.0236
Month 5	0.2110	0.0215
Month 6	0.1991	0.0092
Month 7	0.229	0.0126
Month 8	0.2710	0.0215
Month 9	0.322	0.012

5.2.3 Total Phosphorus, TP:

The increase of nitrogen loading rate to the system increased the removal of phosphorus. However, further increase of nitrogen loading rate was detrimental to phosphorus removal and reduced the efficiency of phosphorus removal. Figure 5.5 shows the changes in the efficiency of phosphorus removal with time.

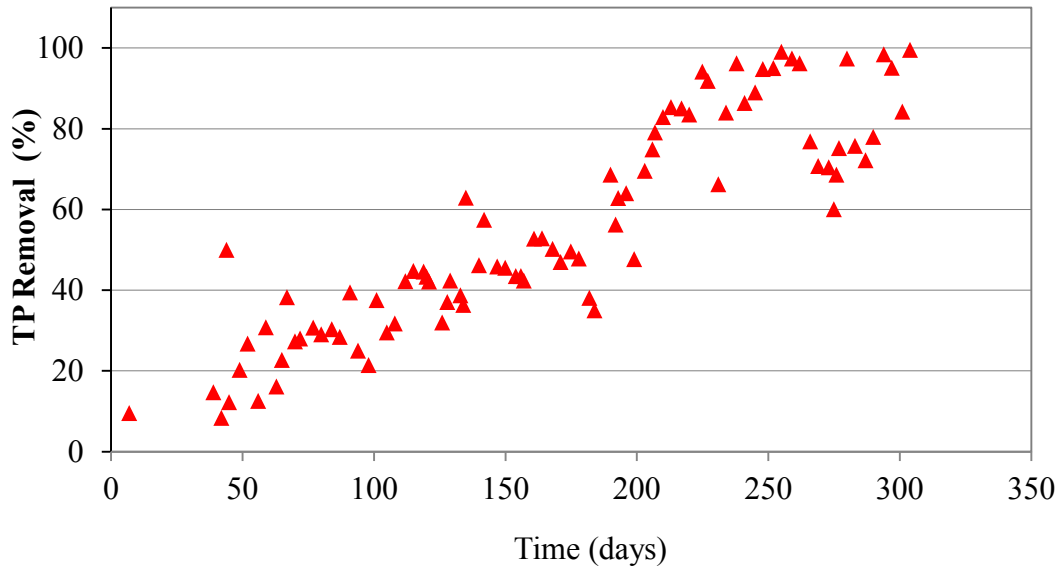


Figure 5.5: Variations of phosphorus removal efficiency with time

Figure 5.5 shows that the phosphorus removal efficiency increased from 10% to 100%. After 250 days of operation, the removal efficiency of nitrogen decreased from 91% to 65%. In addition, the accumulation of extracellular polymeric substances (EPS) increased in the effluent stream. In response to these operational problems, the influent carbon concentration was reduced to 2800 mg/L from 4000 mg/L. The optimum C/N/P ratio for maximum efficiency of contaminant removal was found to be 49.2:7.1:1. At the end of operation, the integrated multi-zone treatment system produced 99% carbon removal, 100% phosphorus removal and 85% nitrogen removal which indicate the superior performance of the new multi-zone integrated wastewater treatment system.

5.2.4 Influence of N/P ratio on TN and TP removal:

The overall results for TP and TN removal showed dependence on N/P ratio. From Figure 5.6, it is clear that with the increase of N/P ratio the removal efficiency of total phosphorus increased while the total nitrogen removal efficiency decreased.

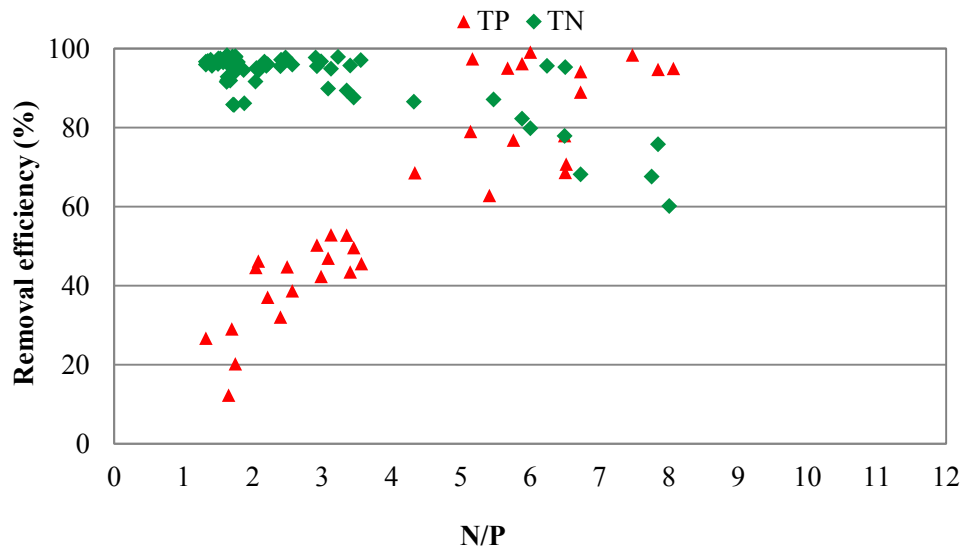


Figure 5.6: Removal efficiencies of total nitrogen and total phosphorus versus N/P ratio

With the increase of N/P ratio from 1.5 to 8.2, the total phosphorus removal increased from 10% to 100% while the total nitrogen removal efficiency decreased from 97% to 60%.

The results suggested that nitrogen and phosphorus loading rates greatly affect the removal efficiencies of nitrogen and phosphorus. As the loading rate of phosphorus was very low and nearly constant, phosphorus was removed by the heterotrophic microorganisms that grew at higher nitrogen loading rate, out-competing the slow growing nitrifiers in the system. Hence, at

increased nitrogen loading rate, the concentration of nitrifiers in the mix liquor was not sufficient (due to their slow rate of growth) to remove the high nitrogen concentrations.

5.2.5 Influence of C/N ratio on COD and TN removal:

The dependence of COD and TN removal efficiencies on the C/N ratio is illustrated in Figure 5.7.

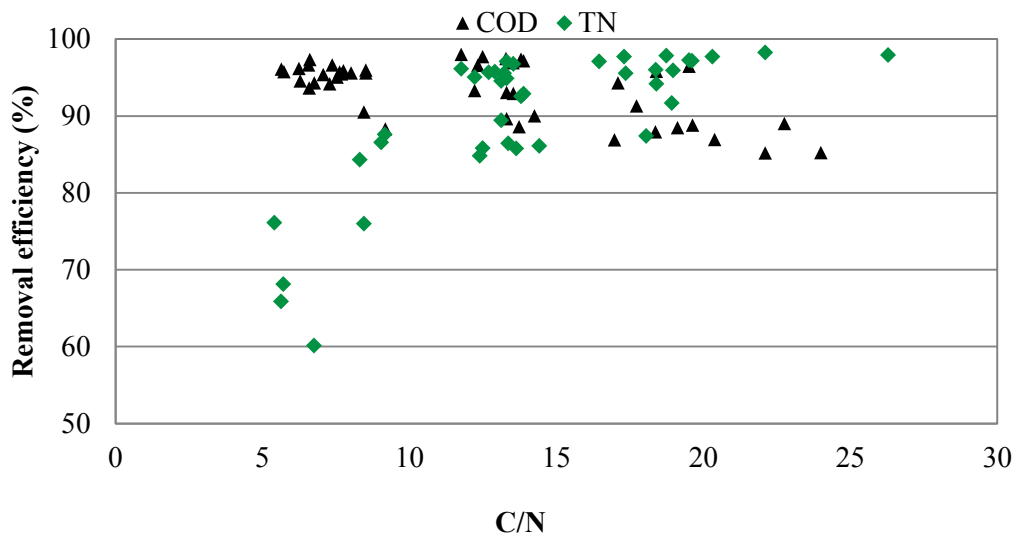


Figure 5.7: Dependence of percentage removal of COD and total phosphorus on the C/N ratio

With the increase of C/N ratio from 5 to 20, the removal efficiency of nitrogen increased from 60% to 97% while the removal efficiency of COD decreased from 98% to 85%. The relatively low reduction in the COD removal efficiency is due to the fact that both nitrifying and facultative microorganisms assimilate carbon source. Therefore, COD removal is accomplished not only by the nitrifiers in the aerobic zone, but also by other types of microorganisms present in all zones of the treatment system.

5.3 Total Chemical Oxygen Demand:

Total chemical oxygen demand is the requirement for the oxygen to chemically biodegrade the soluble and particulate organic/inorganic matter in the wastewater (Mullis and Schroeder, 1971). In this study, the total chemical oxygen demand in the mixed liquor, effluent, anoxic and anaerobic zones were determined. The fraction of total COD in the respective zones of the treatment system is given in Table 5.3.

Table 5.3: TCOD concentrations in the system

Time	Aerobic(mg/L)	Effluent (mg/L)	Anoxic (mg/L)	Anaerobic (mg/L)
Month 1	2350	1230	16670	22650
Month 2	1963	1750	21500	29560
Month 3	1520	1457	14330	39650
Month 4	1200	1076	8370	41520
Month 5	1250	1138	9332	38520
Month 6	1348	1160	6770	30250
Month 7	1667	1436	8820	35770
Month 8	1532	1198	5620	28253

5.4 Process Parameters:

The food per microorganism ratio (F/M) is a measure of the substrate concentration available to the unit concentration of microorganisms in the system. The specific substrate utilization rate is a

measure of substrate utilized by the unit concentration of microorganisms. The major process parameters during the operation of the treatment system are given in Table 5.4.

Table 5.4: Parameters for biomass yield in mixed liquor

Time	F/M(d ⁻¹) Average	Specific Utilization Rate (kg/m ³ .d)/kg VSS			Observed Biomass Yield (mg VSS/mg COD)
		CO	TP	TN	
Month 1	1.84	18	0.36	0.03	0.6576
Month 2	1.21	17	0.43	0.05	0.6296
Month 3	1.47	13	0.24	0.05	0.5992
Month 4	2.1	14	0.31	0.05	0.5628
Month 5	2.5	19	0.38	0.08	0.5246
Month 6	1.5	20	0.57	0.10	0.5048
Month 7	2.0	24	0.94	0.15	0.4808
Month 8	2.2	17	0.71	0.14	0.4509
Month 9	2.5	23.	1.06	0.18	0.4402
Month 10	2.57	23.	1.96	0.17	0.4152

From Table 5.4 it is clear that the utilization of carbon by microorganisms is higher than the utilization of nitrogen and phosphorus as carbon is required for microorganisms in every zone of reactor for growth as well as for simultaneous removal of nitrogen and phosphorus. The concentrations of total solids (TS), total suspended solids (TSS) and volatile suspended solids (VSS) of the mix liquor are presented in Table 5.5.

Table 5.5: Components of mixed liquor

Time	TS(mg/L)	SS(mg/L)	VSS(mg/L)	TCOD(mg/L)	TCOD/VSS
Month 1	3200	620	530	2310	4.4
Month 2	3424	650	459	2707	5.9
Month 3	2430	1105	1099	1350	1.2
Month 4	2540	1320	1112	1540	1.4
Month 5	2250	1230	1060	1280	1.2
Month 6	2400	1000	800	1200	1.5
Month 7	2200	1100	850	1250	1.41
Month 8	1968	1032	983	1348	1.40
Month 9	2332	1135	1075	1667	1.55
Month10	2330	1210	986	1498	1.52

5.5 Characterization of sludge:

The sludge is quantified by its content of total solids, total suspended solids, volatile suspended solids and total COD. A fraction of total COD can be degraded by microorganisms present in the anoxic and anaerobic zones. Tables 5.6 and 5.7 show the characteristics of sludge in the anoxic and anaerobic zone.

Table 5.6: Characteristics of sludge in the anoxic zone

Time	TS	SS	VSS	TCOD	TCOD/VSS	% TPash
Month	(mg/L)	(mg/L)	(mg/L)	(mg/L)	-	-
Month 1	23560	12320	9620	18900	1.96	2.2
Month 2	21570	19582	11560	25360	2.13	1.44
Month 3	14600	11230	7368	18000	2.44	1.24
Month 4	17522	12300	9563	12356	1.29	3.4
Month 5	12536	10632	8369	11230	1.34	4.1
Month 6	7563	5633	4366	8120	1.86	3.8
Month 7	4853	41320	3256	11220	3.44	7.5
Month 8	5693	4532	3622	21323	5.89	9
Month 9	32563	18633	13655	7336	.59	3.7
Month 10	5353	3520	2561	7788	3.44	6.2

Table 5.7: Characteristics of sludge in the anaerobic zone

Time	TS	SS	VSS	TCOD	TCOD/VSS	% TPash
Month	(mg/L)	(mg/L)	(mg/L)	(mg/L)	-	-
Month 1	29350	37560	24023	44120	1.83	1.8
Month 2	38650	30660	21360	37682	1.76	1.39
Month 3	26350	21980	21632	21520	.99	1.8
Month 4	24563	21566	17233	31256	1.81	2.5
Month 5	26352	19356	11253	25320	2.25	3.2
Month 6	35211	32650	25362	42532	1.67	4.9
Month 7	27211	25633	20566	16353	.79	4.2
Month 8	9765	7563	6523	45232	6.93	4.5
Month 9	38522	32440	25300	27563	1.09	5.5
Month 10	15632	12699	11233	15622	1.39	5.2

5.6 Comparison with the previous work:

Hait and Mazumder (2011) evaluated the feasibility of the activated sludge process in removing contaminants from the synthetic wastewater. They found that the activated sludge system can only remove 80% COD without any substantial nitrogen and phosphorus removal. It is also proved that the activated sludge system is not adequate at increased organic loading rates since the COD removal efficiency may fall as low as 46%.

The performance of a sequencing batch airlift reactor has been studied by Hajiabadi et al. (2009) with high strength synthetic wastewater which had a similar influent composition that examined in this study. The treatment system of Hajiabadi et al. (2009) only removes carbon and does not remove nitrogen and phosphorus.

Chen et al. (2006) showed the performance of a three-stage net-like rotating biological contractor (NRBC). This system removes around 90% carbon and 62% nitrogen from synthetic wastewater

with HRT of 6-9 hours. The phosphate concentration of effluent was measured but showed no significant removal. The operating pH was around 7.3 to 7.8.

Delgene's et al. (2000) proposed an integrated system with two anaerobic reactors, i.e. two times anaerobic digestion for carbon removal and SBR for nutrient removal. This system removed 98% carbon, 75% nitrogen and 97% phosphorus simultaneously. The influent organic carbon was 2200 mg/L, nitrogen was 86 mg/L and phosphorus was 20 mg/L. The multi-zone treatment system examined in this study, used influent concentrations of 500-4000 mg/L COD, 42-200 mg/L nitrogen and 16-40 mg/L of phosphorus, and produced removal efficiencies up to 99%, 85% and 100% respectively. Delgene's et al. (2000) also used a methanogenic reactor while methane generation was prevented in the examined system of the present study to support VFA production from anaerobic digestion for luxury phosphorus uptake.

Tsuneda et al. (2005) studied aerobic, anoxic, and anaerobic systems for the treatment of synthetic wastewater which used low concentrations of carbon source (sodium acetate, 20–40 mg C/L) to enhance phosphorus and nitrogen removal. The removal of nitrogen and phosphorus by the system was found to be 92% and 83%, respectively. The volume of reactor was very small (2L) compared to our system.

Kargi et al. (2003) showed the performance of a sequencing batch reactor for the treatment of different carbon sources along with nitrogen and phosphorus removal, managing COD/N/P ratio of 100/5/1.5 while the optimum ratio used in our system was 49.2:7.1:1. The removal of COD, ammonia, nitrate and phosphorus was 96%, 87%, 81% and 90% respectively. They used a mixture of glucose and acetate which produced a COD concentration of 1200 mg/L in influent wastewater, our treatment system used 500-4000 mg/L COD in the influent with a removal

efficiency of 99% which is better than the proposed system. An airlift reactor with simultaneous nitrification and denitrification is proposed by Walters et al. (2001) which achieved only 75% nitrogen removal.

Zhang et al. (2005) used a sequencing batch loop biofilm reactor where the average influent concentrations were 300 to 312 mg COD/L, 105 to 127 mg N/L and 10 to 11 mg P/L. The removal efficiencies were 92% to 95%, 90% to 98%, and 65% to 83%, respectively. They used two separated zones for nitrification and denitrification which is more compact than our system. Although this system was operated for more than 200 days, it could not remove higher contaminant concentrations. FU et al. (2008) used an anoxic/oxic membrane bioreactor (A/O-MBR) which removes 84.6% of total nitrogen, 94.6% of COD and 90% of total phosphorus, respectively. But the net accumulation of nitrite and nitrate occurred in the system while they are almost completely removed by our system.

Andalib et al. (2010) used laboratory scale twine fluidized bed bioreactor by which the removal of carbon of 96%, nitrogen of 84% and phosphorus of 12% were achieved. The organic loading rate, nitrogen loading rate, and phosphorus loading rate were 1.3–2.5 kg COD/ m³.d, 0.14–0.28 kg N/ m³.d, and 0.024–0.041 kg P/ m³.d, respectively which is close to the results of our system. The phosphorus loading rate was changing in this system but we tried to keep it constant during the period of operation. Hydraulic retention time was 2.9 hour and SRT of 78-108 days. The operating parameters are self-controlled by the activities in the reactor.

Some of the parameters of previous studies have been compared with the integrated wastewater treatment system are given in Table 5.8.

Table 5.8: Comparison between Integrated Multi-Zone Wastewater Treatment System and reported work in literature

Parameters	Integrated System	Chen et al., (2006)	Kargi et al., (2003)	Zhang et al., (2005)	Andalib et al., (2010)
COD removal (%)	99	90	96	92-95	96
TN removal (%)	85	62	87	90-98	84
TP removal (%)	100	-	90	65-83	12
OLR (kg/m ³ .d)	0.95-2.5	0.084-15.3	-	1-4	1.3-2.3
NLR (kg/m ³ .d)	0.51-0.135	0.023-0.161	-	0.002-0.003	0.14-.28
PLR (kg/m ³ .d)	0.041-.049	-	-	0.0002	0.024-0.041
SRT	10-200 d	6- 9 hr	10d	-	78-108d
HRT	1.43d	5-9 hr		8-24hr	2.9h
pH aerobic	7.5-8.5	7.3-7.8	7-7.5	7.3	-
Temp (°C)	19-23	20-23	25	25-30	-
DO aerobic (mg/L)	2-4	2..9-6.8	2	4-5	-

The multi-zone integrated treatment system operated for treatment of synthetic wastewater and produced high removal efficiencies of carbon, nitrogen and phosphorus. Most of the influent COD was removed but the presence of extra polymeric substances (EPS) was found in the effluent. We found from the literature review that most wastewater treatment systems that are based on a single-vessel airlift reactor, such as the Circox system, remove nitrogen and carbon but not phosphorus. The examined treatment system is a modified airlift reactor (BioCAST) with a small second reactor which is designed for the simultaneous removal of carbon, nitrogen and phosphorus with low sludge generation.

CHAPTER 6: CONCLUSIONS

In this study, a new integrated multi-zone wastewater treatment technology has been introduced in order to investigate the removal efficiency of organic and inorganic contaminants. Basically, it is a modified airlift reactor with a small second reactor which serves for solids digestion and facilitates phosphorus removal by biological processes. The treatment system was operated for the treatment of synthetic wastewater for 310 days and real agricultural wastewater for 150 days. The results showed that the treatment system is a promising technology in the field of wastewater treatment that can simultaneously remove carbon, nitrogen and phosphorus from wastewaters. The technology uses a combination of attached growth and suspended growth microorganisms which addresses the problems and disadvantages of many previous technologies. The high-strength synthetic wastewater used in this system was composed of high concentrations of glucose ($C_6H_{12}O_6$) and inorganic salts which were successfully removed by the system with high efficiencies of 99%, 85% and 100% for carbon, nitrogen and phosphorus, respectively, after 310 days of operation. The real agricultural wastewater contained high concentrations of carbon, NH_3 , TN and TP, and produced around 89% COD and BOD removal, 69% ammonia removal, and 40% phosphorus removal. The treatment system contains an aerobic zone which operated based on the principle of airlift reactor which also provided adequate hydrodynamics characteristics, mass transfer, and mixing with less sludge production i.e. less sludge handling and less sludge decontamination. From the analysis of obtained results it can be concluded that this system is a promising technology in the field of wastewater treatment.

CHAPTER 7: RECOMMENDATIONS AND FUTURE WORKS

The following recommendations are made for future research:

- Effect of operating temperature on the efficiency of treatment.
- Impact of pretreatment condition in the influent tank during the treatment of hog waste on the efficiency of treatment.
- Impact of recycle flow rate from the anaerobic to aerobic zone on phosphorus removal efficiency.
- Impact of operating conditions on the generation of extracellular polymeric substances
- Investigation of the efficiency of treatment using alternative industrial wastewaters
- A detail parametric sensitivity analysis to investigate the impact of various parameters on the performance of treatment system

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