



Wastewater Treatment of Concentrated Latex Factory by Anaerobic and Oxidation Ponds

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Master of Science Thesis in Environmental Management
Prince of Songkla University

2003

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(mm) TD745 P37 2003 C.2
Bib Key..... 237334
..... 6 U.R. 2547

Thesis Title Wastewater Treatment of Concentrated Latex Factory
 by Anaerobic and Oxidation Ponds
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ชื่อวิทยานิพนธ์	การบำบัดน้ำเสียของโรงงานน้ำยางชั้นโดยใช้ระบบบ่อแบบไร้อากาศและบ่อฝั่
ผู้เขียน	นางสาวภัทรภรณ์ พิมลไทย
สาขาวิชา	การจัดการสิ่งแวดล้อม
ปีการศึกษา	2546

บทคัดย่อ

อุตสาหกรรมการผลิตน้ำยางชั้นเป็นอุตสาหกรรมที่มีความสำคัญต่ออุตสาหกรรมยางพาราในภาคใต้ของประเทศไทย แต่เนื่องจากน้ำเสียจากโรงงานน้ำยางชั้น และยางสกิม ประกอบด้วยปริมาณสารอินทรีย์และ ซัลเฟต ในปริมาณสูง ส่งผลให้ความสามารถในการบำบัดน้ำเสียของบ่อไร้อากาศในระบบบำบัดที่อยู่ของโรงงาน มีความสามารถในการกำจัดสารอินทรีย์ต่ำ

วัตถุประสงค์ของการศึกษา เพื่อทดลองหาเกณฑ์การออกแบบระบบบ่อน้ำบำบัดน้ำเสียแบบบ่อไร้อากาศและบ่อฝั่ของโรงงานผลิตน้ำยางชั้น โดยพิจารณาจากตัวแปรที่ใช้ในการออกแบบและควบคุมระบบบ่อที่สำคัญ คือ ภาระบรรทุกสารอินทรีย์ (BOD_5 Loading)

ทั้งนี้การทดลองเริ่มจากการออกแบบค่าภาระบรรทุกสารอินทรีย์ที่แตกต่างกัน โดยบ่อไร้อากาศใช้ค่าภาระบรรทุกสารอินทรีย์ $100-400 \text{ g } BOD_5 / \text{m}^3 \cdot \text{d}$ และบ่อฝั่อยู่ในช่วง $7-13 \text{ g } BOD_5 / \text{m}^2 \cdot \text{d}$ จากนั้นทำการเก็บตัวอย่างน้ำเสียจากโรงงานน้ำยางชั้นแห่งหนึ่งในจังหวัดสงขลา เพื่อนำมาบำบัดในบ่อบำบัดจำลองที่ออกแบบไว้และศึกษาการทำงานของบ่อในห้องปฏิบัติการ

ผลการทดลองแสดงประสิทธิภาพการบำบัดที่เหมาะสมใกล้เคียงกันของบ่อน้ำบำบัดแบบไร้อากาศในการบำบัดน้ำเสียจากโรงงานน้ำยางชั้น โดยมีประสิทธิภาพการบำบัด BOD_5 และ COD มีค่าเฉลี่ยอยู่ในช่วง 67-83 และ 50-77 เปอร์เซ็นต์ ตามลำดับ ประสิทธิภาพการบำบัด TKN และ NH_3-N แสดงค่าไม่แตกต่างกัน และประสิทธิภาพการบำบัดของแฉ่งแขวนลอย และซัลเฟต มีค่าเฉลี่ยอยู่ในช่วง 29-42 และ 19-24 เปอร์เซ็นต์ ตามลำดับ สำหรับประสิทธิภาพการบำบัดซัลเฟตของบ่อน้ำบำบัดแบบไร้อากาศนั้นค่อนข้างต่ำเนื่องจาก ปริมาณความเข้มข้นของซัลเฟตที่สูงมาก ผลที่ได้จากการทดลองแสดงประสิทธิภาพการบำบัดสารอินทรีย์ของบ่อน้ำบำบัดแบบไร้อากาศที่เหมาะสม คือ ภาระบรรทุกสารอินทรีย์เท่ากับ $200 \text{ g } BOD_5 / \text{m}^3 \cdot \text{d}$

บ่อฝิ่งมีประสิทธิภาพการบำบัด BOD₅ และ COD มีค่าเฉลี่ยอยู่ในช่วง 53-46 และ 88-77 เปอร์เซ็นต์ ตามลำดับ ประสิทธิภาพการบำบัด TKN และ NH₃-N มีค่าเฉลี่ยอยู่ในช่วง 88-95 และ 90-96 เปอร์เซ็นต์ ตามลำดับ ประสิทธิภาพการบำบัดของแข็งแขวนลอย และซัลเฟต มีค่าเฉลี่ยอยู่ในช่วง 64-89 and 61-74 เปอร์เซ็นต์ ตามลำดับ พบว่าความสามารถในการบำบัดซัลเฟตของบ่อฝิ่ง มีประสิทธิภาพสูงกว่าบ่อหมักไร้อากาศ ที่ภาระบรรทุกสารอินทรีย์ 7 g BOD₅/m².d สามารถบำบัดปริมาณซัลเฟตได้เหมาะสม

ในแง่ของเทคโนโลยีการบำบัดน้ำเสียโดยอาศัยระบบบ่อไร้อากาศและบ่อฝิ่งนี้ ผลที่ได้จากการทดลองสามารถนำไปเป็นแนวทางในการออกแบบและควบคุมระบบบ่อแบบไร้อากาศและบ่อฝิ่งสำหรับการบำบัดน้ำเสียของโรงงานน้ำยางชั้นที่เหมาะสมได้ต่อไป

Thesis title	Wastewater Treatment of Concentrated Latex Factory by Anaerobic and Oxidation Ponds
Author	Ms. Pattaraporn Pimolthai
Major Program	Environmental Management
Academic Year	2003

Abstract

Concentrated latex industries are an important part of the rubber industry in southern Thailand. However, the wastewater from concentrated latex factories contains high levels of organic matter and sulfate concentration. These high levels of sulfate concentration caused a low efficiency of wastewater treatment by anaerobic system in rubber factories.

The objective for this study was to find a suitable criteria for the design and operation of anaerobic and oxidation ponds for treatment of the concentrated latex wastewater based on BOD₅ loading.

The experimental units for anaerobic and oxidation ponds were set up and operated at 100-400 g BOD₅/m³.d and 7-13 g BOD₅/m².d, respectively. Wastewater from a selected concentrated latex factory in Songkhla, Thailand was used as a feed in this experimental units.

The achieved results presented that the similar treatment efficiencies of anaerobic ponds in the range of organic loading at 100-400 g BOD₅/m³.d were very good in terms of BOD₅ and suspended solids removal efficiency. Average BOD₅ and COD removal efficiency in anaerobic pond were found to be in a range of 67-83%, and 50-77%, respectively. There was not much difference in TKN and NH₃-N removal efficiency. Suspended solids and sulfate removal efficiency were found to be in a range of 29-42% and 19-24%, respectively. The sulfate removal efficiency presented low, because of very high sulfate concentrations in the wastewater. The optimum criteria for operating anaerobic pond was 200 g BOD₅/m³.d.

Average BOD₅ and COD removal efficiency in oxidation pond were found to be in a range of 53-46%, and 62-79%, respectively. Average TKN and NH₃-N removal efficiency were found to be in a range of 88-95% and 90-96%, respectively. Suspended solids and sulfate removal efficiency were found to be in a range of 64-89% and 61-74%, respectively. The wastewater treatment of oxidation ponds presented significantly higher in sulfate removal efficiency at 7 g BOD₅/m².d.

The anaerobic-aerobic wastewater system technologies, with the acceptable levels of removal efficiency from the experiment, can be used in the future as a guideline for appropriate criteria for the design and operation of anaerobic and oxidation ponds for treatment of wastewater from concentrated latex factory.

ACKNOWLEDGEMENT

First of all, the author would like to express her gratitude profound appreciation to Asst. Prof. Dr. Udomphon Peutpaiboon, the author's adviser, for his benevolent guidance, concerns and great helps throughout this study. By his attitudes and actions; honesty, gentleness, patience, generosity and encouragement in his life are valuable for creating the memories about the great performer in the author's life.

The author is grateful for Asst. Prof. Dr. Somtip Danteravanich for her valuable suggestions, constructive comments, helpful criticism, insightful support and encouragement, as well as the author is grateful for the committees including, Asst. Prof. Dr. Gallaya Srisuwan and Asst. Prof. Dr. Veerasak Thonglimp who contributed generously of their time and talents to the substance and texture of this thesis.

Furthermore, sincere thanks are due to the manager and the head of wastewater treatment unit the selected concentrated latex factory in Songkhla for their kindness to the permission.

Special appreciation must be extended to the graduate students of the Faculty of Environmental Management, Prince of Songkla University, including Mr. Narong Bensa-ard, Mr. Prasert Pan-in, Mr. Anan Mudor, Mr. Naruthep Bunreaukhaw, Ms. Patraporn Kristsanapun, Mr. Phongpat Sontamino, Ms. Fareda Karang, Mr. Sirisak Phuttasit, Mr. Kritsana Sangkato, and Mr. Sawai Kalapun for their extensive help in the field. In addition, gratitude is expressed to Mr. Weerachart In-thong, for his assistance in the analytical laboratory, Ms. Supaporn Jariyuwat and Ms. Tittaya Sae-Tung for their assistance with the analytical procedure.

Special thanks go to Mrs. June Ferguson for her helpful English and Mr. Erik Heyer for his helpful comments.

This Thesis was funded by Thai Royal Government, with related granted from Graduated School, Prince of Songkla University.

Finally the author would like to express her profound gratitude to the author's parents, sister, brother and the Christians family at Hope Church. Many thanks for their loves and being always the strength and the source of the best encouragement.

P. Pimolthai

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LIST OF ABBREVIATIONS

BOD ₅	= 5- days biochemical oxygen demand
CaO	= Lime
CH ₄	= Methane
CL	= Concentrated latex
COD	= Chemical oxygen demand
DAHP	= Diammonium hydrogen phosphate
DRC	= Dry rubber content
HRT	= Hydraulic retention time
NH ₃ -N	= Ammonia nitrogen
RE	= Removal efficiency
PSU	= Prince of Songkla University
SO ₄ ²⁻	= Sulfate ion
SS	= Suspended solids
STR	= Standard thai rubber
TKN	= Total kjeldahl nitrogen
TMTD	= Tetramethyl thiuram disulfide
VFA	= Volatile fatty acid
WSP	= Waste stabilization pond
WW	= Wastewater

CHAPTER 1

INTRODUCTION

1.1. Introduction

At present, Thailand is recognized as the world's leading in natural rubber producer and exporter. Natural rubber is an important crop with high commercial value especially in the South. However, the effluent from rubber production particularly that containing high organic matter that often pollutes the environment.

In October 2002 recently, Thailand exported 43,197.70 tons of concentrated latex, in the number of 1,004.83 million Baht of foreign currency earnings. (The Thai rubber association news, 2002). Rubber production in Thailand mainly consists of ribbed smoke sheet, STR, fresh latex, concentrated latex, crepe rubber, with the remainder consisting of cup lump and etc. More information about Thailand rubber industry can be found at www.THAINR.com.

Concentrated latex factories are an important part of the rubber industry in southern Thailand. The trend in investment in the rubber industry is currently positive and the Thai Government believes that there is great potential due to the strong and stable quality of Thai rubber.

Songkhla has the largest rubber plantation area, approximately 1.65 million rai or 18.5% of the rubber plantation areas in southern Thailand. The availability of many raw materials in Songkhla and very convenient transportation to other provinces ensure good prospects of further investment. List of concentrated Latex factories in Songkhla in 2002 was shown in Table 1.

The most critical source of water pollution from rubber factories derives from the effluent, which causes high organic matter and unpleasant odors from the wastewater treatment system. Most of the rubber factories use anaerobic and oxidation ponds systems to treat their wastewater.

Nowadays, the wastewater treatment system from concentrated latex factories in southern Thailand does not function well, combined with a lack of new development systems. This can cause water pollution problems in many areas in the future.

The purpose of this study was to find the suitable operating criteria for waste stabilization pond systems, treating wastewater from concentrated latex factories. The results from the experiment could be useful to rubber factories for developing and implementing wastewater treatment systems.

Table 1. List of concentrated latex factories in Songkhla province, 2002

Factories	Manpower (persons)	Production types	CL produced volumes (tons/day)
<u>Songkhla</u>			
<u>Amphoe Natawee</u>			
1.Safeskin Latex (Thailand) Ltd	191	CL, Skim rubber	200-300
<u>Amphoe Bangklum</u>			
2.Southland Latex Ltd.	93	CL, Rubber sheets	65
3.Chaiyaporn Latex Co.Ltd.	60	STR 10,20	17-20
4.Thaima Rubber Product Ltd.	50	CL, Skim rubber	67
5.Thai Hau Para Co.Ltd.	94	CL, Rubber sheets, STR 5L, STR 20	120
<u>Amphoe Rattaphum</u>			
6.Feltex Ltd.	68	CL, Skim rubber	15
<u>Amphoe Sadao</u>			
7.Thavon Para Industrial Ltd.	400	CL, Skim rubber, STR	80-90
8.Hee Hub Haud Ltd.	120	CL, Crepe	60-70
9.Maltex Rubber Ltd.	120	CL, Skim rubber	78
10.Sadao Para Industrial (1998) Co.Ltd.	18	CL, Crepe	20-30
11.Numhau Rubber Ltd.		CL, Smoked sheets	
12.Saabmee Latex Ltd.	65	CL, Smoked sheets	105
<u>Amphoe Chana</u>			
13.Chana Rubber Ltd.	130	CL, Skim rubber, STR 5L, STR 20	40
14.Chalong CL Industrial Co.Ltd.	113	CL, Skim rubber, STR XL, 5L, 5CV 50, 58, 60	70-100
<u>Amphoe HatYai</u>			
15.Haadsin Rubber Ltd.	46	CL, Skim rubber	125
16.Rubberland Product Ltd.	52	CL, Skim rubber	30
17.Excel Rubber Co.Ltd.	75	CL, Skim rubber, TTR 5L	40
<u>Amphoe Sabayoi</u>			
18.Feltex Ltd.	69	CL, Skim rubber	25

Source: Department of Industrial works (<http://www.diw.go.th>), 2002

1.2. Review of Literatures

1.2.1. Latex Composition

Many plants, including dandelions, which produce a milky white liquid known as latex. The reasons for producing this liquid are unclear, but it might be as a means of helping wounds to heal quickly or as an energy store. But whatever the reasons, the really interesting thing is that these lattices contain a hydrocarbon polymer - natural rubber.

The latex is obtained from the tree by tapping. This is done by wounding the tree by cutting out a thin strip of bark, usually in the form of a part spiral. The latex extrudes from the cut and is collected in a cup. This process is repeated every day or so, moving down the bark, until a whole panel of bark has been removed. Luckily it grows back whilst another panel is used.

Latex is an emulsion of small rubber particles in a serum (mainly water), where each particle is coated with a layer of protein which enables it to stay in suspension. It is very similar to milk, which is an emulsion of coated fat globules in whey (mainly water), although latex is slightly thicker than milk.

Pure crude rubber is a white or colorless hydrocarbon. The simplest unit of rubber is isoprene, which has the chemical formula C_5H_8 . At the temperature of liquid air, which is about $-195\text{ }^\circ\text{C}$, crude rubber is a hard, transparent solid; from $0\text{ }^\circ\text{C}$ to $10\text{ }^\circ\text{C}$, it is brittle and opaque, and above $20\text{ }^\circ\text{C}$, it becomes soft, resilient, and translucent. When rubber is mechanically kneaded, or is heated above $50\text{ }^\circ\text{C}$, it becomes plastic and sticky; more than $200\text{ }^\circ\text{C}$, it decomposes. Crude rubber is insoluble in water, alkali, and weak acid; it is soluble in benzene, gasoline, chlorinated hydrocarbons, and carbon disulfide. It is oxidized readily by chemical oxidizing agents, and slowly by atmospheric oxygen.

(S.C. Heuston, 2000, <http://www.heustonline.com/intro%20to%20rubber.htm>)

Latex is in fact of cytoplasm structure and contains i.e. ribosomes but seldom nuclei. Apart from rubber particles very freshly tapped latex also contains so-called lutoid particles which can be separated by centrifuging at low speed.

The composition of the fresh latex is rather complex due to its origin and the relative proportions of certain constituents (e.g. proteins and minerals) can show important variations depending on many factors (season, tapping system). The mainly composition is water, which is approximate 58.5% and the dry rubber content is approximate 36%. A typical fresh latex composition was shown in Table 2.

Table 2. Typical Fresh Latex Composition

Composition	%
Dry Rubber Content	36.0
Amino Acids and N-Bases	0.3
Neutral lipids	1.0
Proteins	1.6
Phospholipids	0.6
Carbohydrates	1.5
Salts (mainly K,P and Mg)	0.5
Water	58.5

Source: (Dr. W. Rensing. <http://www.rubber-stichting.ind.tno.nl/art2nr17.html>), 2001

1.2.2. Latex Processing Process

As soon as possible the latex is temporarily preserved with ammonia, the quantity depending on the transportation time to the factory and filling into field latex in order to prevent bacterial contamination or at least to limit its effects.

The concentrated latex processing and the wastewater originating points were shown in Figure 1. Ammonia is added into the fresh latex in an approximate wet weight fraction of 0.2% while zinc oxide and TMTD count for about 0.013% each. After entering at the highest point of the factory, diammonium hydrogen phosphate (DAHP) is added to the natural rubber latex to precipitate magnesium in a storage tank over night. Per ton of received natural rubber latex 1.5 kg DAHP is added.

Following precipitation, the latex flows to the CL production centrifuges, where a DRC of 60% is obtained and then adding ammonia for 0.6-0.7% by weight. The production of one ton of CL consumes 2.2 tons of both natural rubber latex and process water. The production of CL results in two wastewater streams, each containing some rubber residues. The centrifugal by-product, called skim latex, has a DRC of 3%, while the stream originating from the washing of the centrifuges has a DRC of 1%. These two are separated at this point. The skim latex flows to the skim block production and the wastewater flows to the wastewater treatment system.

Coagulation of the rubber residues in the skim latex in several long basins of sulfuric acid produces the skim rubber. The skim coagulum is collected for production, by scraping it from the top of the basins. Before entering the basins, the skim latex is stirred in a holding tank, which in addition to mixing also brings down the ammonia concentration from 0.20-0.25% to app. 0.20-0.22% wet weight. (Bochdam *et al.*, 2001). The wastewater from the skim block process flows to the same wastewater treatment system.

In addition, the commercial product is nowadays mainly prepared by centrifuge. Most concentrated latex factories in Songkhla also use centrifuge; and there are only two types made on a large scale:

- HA (*high-ammonia*) latex, preserved with 0.7% ammonia
- LA-TZ (*low ammonia*) latex, preserved with 0.2% ammonia + 0.025% TMTD/ZnO + 0.04 - 0.05% lauric acid as ammonium laurate

In addition, other types are available as follows:

PV latex: The Pre-Vulcanized latex is in wide spread use. Natural latex can be readily vulcanised in the liquid state and the product retains most of the good-processing characteristics of raw-latex concentrate.

Creamed Latex, latices of 65% DRC prepared by adding a Creaming Agent such as Sodium alginate. Locust Bean Gum makes bigger rubber particles and less protein but is too complicated and require too much preparation time.

Evaporated Latex, latices of 66% DRC is produced, well - preserved for long distance transport.

Zero Protein Cream Latex (new). Contains virtually no extracted proteins.
(Bonega *et al.*, 2001)

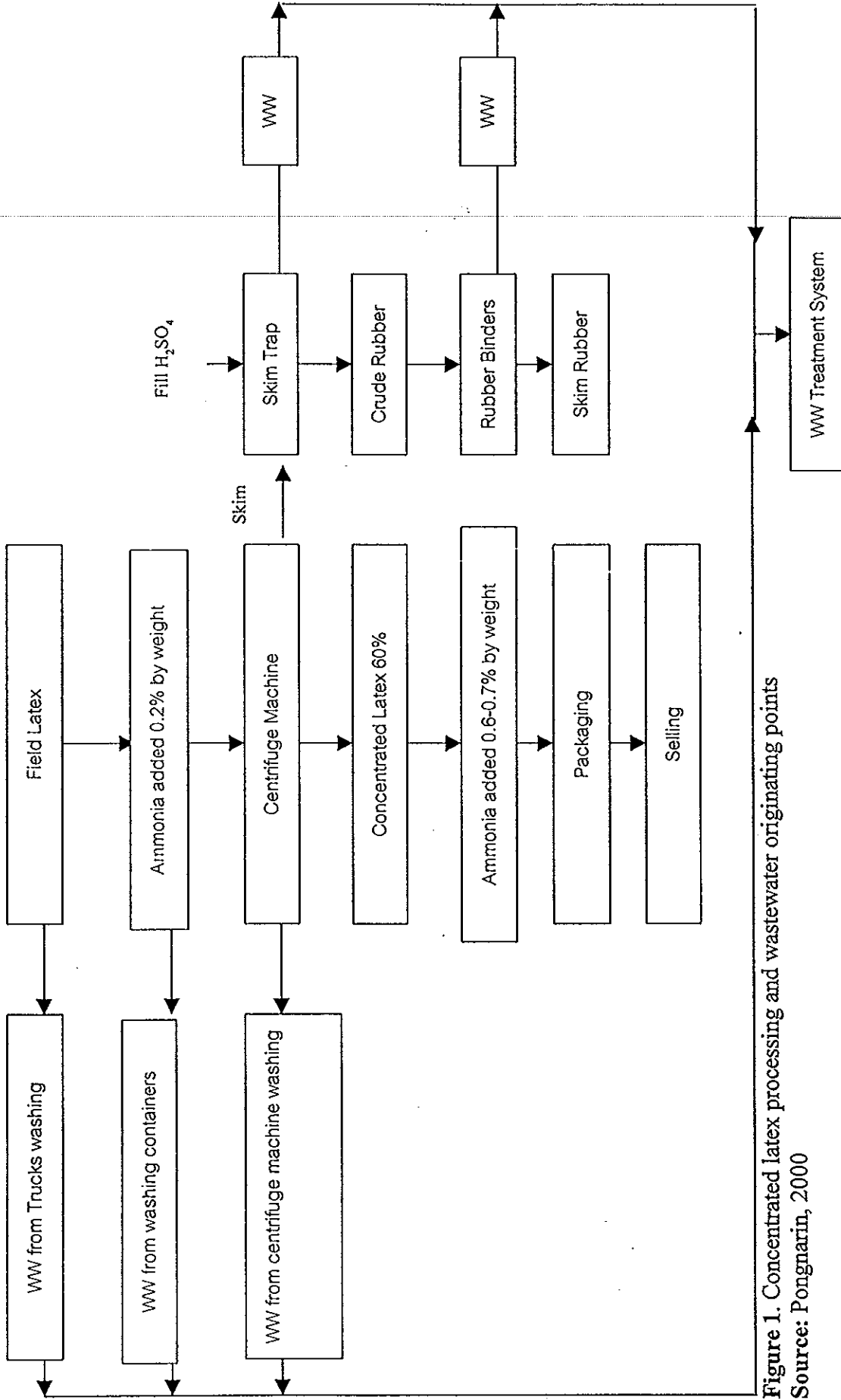


Figure 1. Concentrated latex processing and wastewater originating points
 Source: Pongnarin, 2000

1.2.3. Wastewater Composition from Concentrated Latex Factories

The data in Table 3 presented the wastewater composition from concentrated latex factories in Songkhla.

Most of the wastewater compositions were explained in terms of pH, COD, BOD₅, SS, TKN, NH₃-N and Sulfate.

Table 3. Wastewater compositions from concentrated latex factories in Songkhla

Parameters	Factory A	Factory B	Factory C*	Factory D
pH	8.76	5.20	3.72	8.06
COD (mg/l)	15,401	5,119	9,405	8,640
BOD ₅ (mg/l)	1,463	2,500	5,325	2,610
SS (mg/l)	2,059	800	350	2,020
TKN (mg/l)	455	754	-	-
NH ₃ -N (mg/l)	354	624	-	-
Sulfate (mg/l)	-	-	2,262	1,010

Sources: Arporn, 1998, Pongnarin, 2000 and *Pattanawan, 2001

1.2.4. Waste Stabilization Ponds

Waste Stabilization Ponds (WSP) are a common wastewater treatment system. They are easy to prepare and maintain, and very efficient in removing both organic matter and the wide range of excreted pathogens present in wastewater. The operation of suitable waste stabilization ponds depends on their design and operation systems for well-treated effluent.

- **Advantages of Waste Stabilization Ponds**

- **Simplicity**

WSP are simple to construct: earthmoving is the principal activity; other civil works are minimal- preliminary treatment, inlets and outlets, pond embankment protection. They are also simple to operate and maintain: routine tasks comprise cutting the embankment grass, removing scum and any floating vegetation from the pond surface, keeping the inlets and outlets clear, and repairing any damage to the embankments.

- Low Cost

WSP are normally less expensive than other wastewater treatment processes. There is no need for high-cost, electromechanical equipment, or for a high annual consumption of electrical energy. The latter point is well illustrated by the following data was shown in Table 4 for a flow of 10 million US gallons per day (37,800 m³/d) of sewage in the United States (Middlebrooks *et al.*, 1982)

Table 4. Energy Consumption in Treatment Process in USA

Treatment process	Energy consumption (kWh/yr)
Activated sludge	10,000,000
Aerated lagoons	8,000,000
Biodiscs	1,200,000
Waste stabilization ponds	nil

The cost advantages of WSP were analysed in detail by Arthur (1983) in the World Bank Technical Paper. WSP systems were the cheapest treatment process at land costs of US\$ 50,000-150,000 (1,983 \$ per hectare), depending on the discount rate (opportunity cost of capital; range: 5-15%.)

- High Efficiency

According to Duncan Mara, modern WSP design procedures ensure high efficiency wastewater treatment, by more than 90% of BOD₅ Removal, 70-90% of Total Nitrogen Removal and 30-45% of Total Phosphorus Removal (Council of the European Communities, 1991)

WSP are particularly efficient in removing excreted pathogens, whereas in contrast all other treatment processes are very inefficient in this. Due to their long hydraulic retention time, they are more resilient to both organic and hydraulic shock loads than other wastewater treatment processes. Strong wastewater from agro-industrial processes are easily treated in WSP. Moreover, WSP are the only secondary treatment process that can readily and reliably produce effluents safe for reuse in agriculture and aqua culture and also water tourism.

- **Types of WSP**

- **Anaerobic Ponds**

Anaerobic Ponds are commonly 2-5 m deep and receive such a high organic loading. Usually their primary function is BOD₅ removal and that they contain no dissolved oxygen and no algae, although occasionally a thin film of mainly anaerobic bacteria can be seen at the surface.

The biochemical reaction in anaerobic pond in Figure 2 can be explained that the organic matter in wastewater is digested by acid forming bacteria to become organic acid such as acetic acid, propionic acid. Some of hydrogen sulfide, methane and carbon dioxide gases are produced from this step. After that, the organic acid is transferred as methane and carbon dioxide gases by methane forming bacteria in the secondary step. COD and BOD₅ concentration decreased in this step. Anaerobic pond can cause odor from hydrogen sulfide and need a propiate control condition.

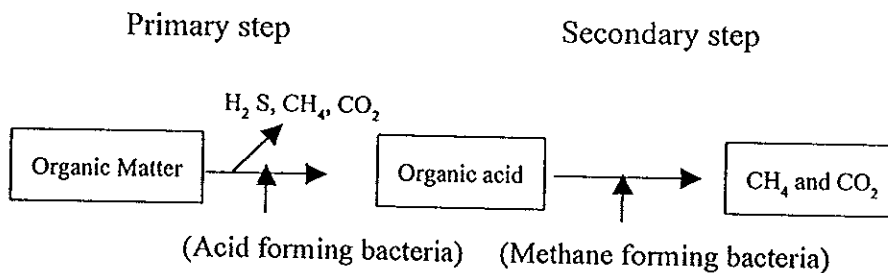


Figure 2. Biochemical Reaction in Anaerobic Pond

- **Oxidation Ponds**

Oxidation ponds usually function as secondary wastewater treatment ponds, which receive low surface organic loading rate. The pond bacteria are mostly generated by algal photosynthesis. Due to the algae being colored dark green, they are sometime called green ponds.

Oxidation pond contains bacteria and algae in suspension; aerobic conditions (the presence of dissolved oxygen) prevail throughout its depth. There are two types of aerobic ponds:

(a) Shallow oxidation ponds obtain their dissolved oxygen via two phenomena: oxygen transfer between air and water surface, and oxygen produced by photosynthetic algae.

(b) An aerated pond is similar to an oxidation pond except that it is deeper and mechanical aeration devices are used to transfer oxygen into the wastewater.

The relationship between bacteria and algae in oxidation pond was shown in Figure 3. Following the figure explained that a result of the photosynthesis activities, which use CO_2 , NH_3 , PO_4 , and H_2O as substances of the pond algae, is produced oxygen and their new cell algae. Bacteria will use oxygen for organic matter digestion and for new cell bacteria reproduction and other composition, as substances for photosynthesis later.

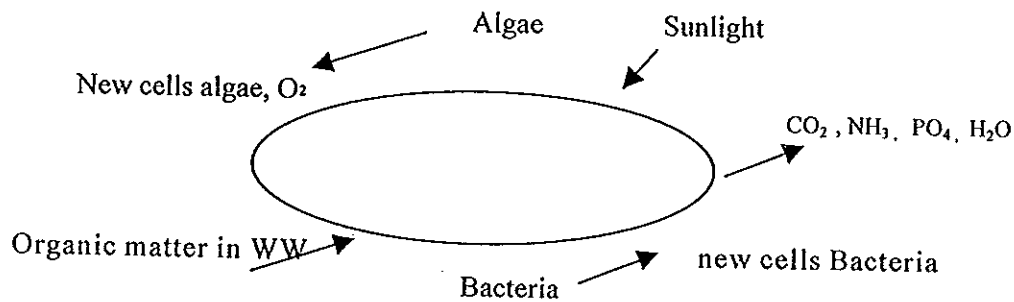


Figure 3. Relationship between Bacteria and Algae in Oxidation Pond

- Facultative Ponds

Facultative ponds are approximately 1.2-2 m in depth, and the principal bacteria are facultative bacteria which work in both anaerobic and aerobic zones. In an aerobic zone, there is dissolved oxygen in the upper level and in the anaerobic zone, there is accumulated settle organic matter in lower level.

- Polishing Ponds

Their functions similarly work as oxidation ponds in organic matter removing (1-1.5 m deep) but with less surface organic loading rate usually located in the last series of ponds, to adjust wastewater conditions before discharge and also further removal of excreted pathogens.

1.2.5. Process Design of WSP

Design parameters of WSP are BOD₅ Loading and Hydraulic Retention Time. Usually BOD₅ Loading per surface pond area and Hydraulic Retention Time can be calculated from the following equation:

$$\text{Surface BOD}_5 \text{ Loading} = \frac{Q \times \text{BOD}_5}{A} \quad \text{g. BOD}_5 / \text{m}^2 \cdot \text{d}$$

$$\text{Hydraulic Retention Time} = \frac{V}{Q} \quad \text{d}$$

The common WSP design parameters in each of WSP by Metcalf and Eddy, 1991 was shown in Table 5, which based on surface BOD₅ Loading.

Table 5. WSP Design Parameters

WSP Types	Depth (m)	Retention Time (days)	BOD ₅ Loading (g BOD ₅ / m ² .d)	BOD ₅ Removal (%)	Suspended Solids in Effluent(mg/l)
Polishing Pond	1.0-1.5	5-20	≤2	60-80	10-30
Oxidation Pond	1.0-1.2	10-40	7-13	80-95	80-140
Facultative Pond	1.2-2.0	5-30	5-20	80-95	40-60
Anaerobic Pond	2.5-5.0	20-50	22-56	50-85	80-160
Aerated Pond	2.0-6.0	3-10	-	80-95	80-250

Source: Metcalf and Eddy, 1991

In addition, design criteria for WSP based on volumetric BOD₅ Loading, can be calculated from the following equation:

$$\text{Volumetric BOD}_5 \text{ Loading} = \frac{Q \times \text{BOD}_5}{V} \quad \text{g. BOD}_5 / \text{m}^3 \cdot \text{d}$$

Where Q = Wastewater flow (m³ /d)
 BOD₅ = Influent BOD₅ (mg/l)
 A = Surface area of pond (m²)
 V = Pond volume (m³)

Examples of design criteria for anaerobic pond based on Volumetric loading rate were shown in Tables 6 and 7.

▪ Process Design in other Countries

There were researches on WSP design and usage in Mediterranean Europe by Duncan Mara 1997, which reported various usages of ponds in wastewater treating from communities and agriculture.

In Portugal, a municipal WSP system at Vidiquerira serves a population of 6,000 and comprises an anaerobic pond (0.7 ha, 3 m deep) and a facultative pond (2.4 ha, 1.5 m deep). BOD₅ removal was approximately 85%.

In Spain, most WSP systems are in the southeast of the country and many of these systems have odor problems due to high organic loading and high sulfate concentrations in the wastewater. The former, arise as a result of seasonal fluctuations in organic load, mainly agro-industrial wastewater (from fruit processing plants, other food factories), but also due to a high tourist population in summer. The high sulfate concentration occurs as a result of saltwater intrusion into the sewer in many coastal towns, but also because the drinking water has very high sulfate concentrations, generally in the range 350-1,200 mg SO₄²⁻/l. These ponds were designed for a population equivalent to 27,500. The organic loading, are up to 3,500-5,600 g BOD₅/m³.d. The design value per volume is 1,650 g BOD₅/m³.d. Sulfate concentrations are high 400-1,100 mg SO₄²⁻/l. Odor is consequently a problem and effluent quality is poor, although this overloaded system still achieves a BOD₅ removal of 75% in winter and 84% in summer.

Mara and Pearson (1986) and Mara *et al.* (1998) recommend the design values of anaerobic ponds, which may be safely used for design purposes in a region with a Mediterranean climate. These recommendations were based on those of Meiring *et al.* (1968) that the volumetric BOD₅ loading should lie between 100 and 400 g BOD₅/m³.d. The former in order to maintain anaerobic conditions and the latter to avoid odor release. However, the upper limit for design is set at 350 g BOD₅/m³.d in order to provide an adequate margin of safety with respect to odor. This is appropriate for normal domestic or municipal wastewater, which contains less than 300 mg SO₄²⁻/l.

The performance of anaerobic ponds increases significantly with temperature, and the design assumption for BOD₅ removal as experienced with anaerobic ponds in Germany in winter (Table 6). In northeast Brazil at 25 °C where conditions are very similar to those in the Eastern Mediterranean and North Africa in summer, show variation of BOD₅ removal with retention time, for finding suitable BOD₅ removal as given in Table 7.

Table 6. Design values of permissible volumetric BOD₅ Loading on and percentage of BOD₅ removal in anaerobic ponds at various temperatures

Temperature (°C)	Volumetric loading (g BOD ₅ /m ³ .d)	BOD removal (%)
<10	100	40
10-20	20T-100	2T+20
20-25	10T+100	2T+20
>25	350	70

T = Temperature (°C)

Source: Mara and Pearson (1986) and Mara *et al.* (1997).

Table 7. Variation of BOD₅ removal with retention time in anaerobic ponds in northeast Brazil at 25 °C

Retention time (d)	Volumetric loading rate (g BOD ₅ /m ³ .d)	BOD ₅ removal (%)
0.8	306	76
1.0	215	76
1.9	129	80
2.0	116	75
4.0	72	68
6.8	35	74

Source: Silva (1982).

1.2.6. Potential of using WSP for Concentrated Latex Factory

Arporn, (1998) investigated the removal efficiency of wastewater treatment system (Stabilization Pond) of 3 selected concentrated latex factories in Songkhla based on their effluent characteristics.

The average of BOD₅, COD, SS removal efficiency was found to be 97-99%, 96-99%, 86-96% respectively.

BOD₅, COD and SS concentrations in effluent of each factory are represented as given in Table 8.

Table 8. BOD₅, COD and Suspended Solids Concentration in Effluent from Concentrated Latex Factories in Songkhla

Parameters	Factory A	Factory B	Factory C	% Removal Efficiency
BOD ₅ (mg/l)	50-55	26-32	63-78	97-99
COD (mg/l)	228-247	119-184	192-546	96-99
SS (mg/l)	117-122	80-92	124-316	86-96

Industrial Effluent standard of Thailand (1996) for BOD₅, COD and Suspended Solids Concentration maximum values were 20, 120 and 50 mg/l, respectively.

1.2.7. Effect of Sulfate in Anaerobic Reactors

The wastewater from concentrated latex factories with skim block production contains high sulfate concentration, which can cause water pollution and foul smell. There are various wastewater treatment systems to reduce the high sulfate concentration.

Anaerobic pond is a biological wastewater treatment system for wastewater from industrial factories. However, anaerobic treatment can cause some problems for implementing wastewater treatment system.

In anaerobic pond, the main sulfate reduction took place. The sulfate reduction to become sulfide by *desulfuricants* bacteria. The sulfate is as terminal electron acceptor.

The reaction for sulfate reduction as follows:



The sulfur reduction to become hydrogen sulfide by *Desulfuromonas acetoxidans* bacteria. Their function is reducing sulfur to hydrogen sulfide and carbon dioxide.

In fact, sulfate concentration can effect organic matter digestion process in anaerobic condition. The reasons are:

1. Sulfate in wastewater can be reduced to become sulfide, which is the main inhibitor for Methane Producing Bacteria. (MPB)
2. Sulfide cause increased oxygen demand in the effluent
3. The competition between Sulfate Reducing Bacteria (SRB) and Methane Producing Bacteria (MPB) in substance digestion process, less methane is produced.

Mizuno, *et.al*, (1998) investigated the behavior of Sulfate Reducing Bacteria (SRB) in acidogenic phase in anaerobic condition, by setting the different conditions of HRT and sulfate concentration. The result can be concluded as following:

(a) The substance was metabolized to Volatile Fatty Acid (VFA), lactate, Ethanol, H₂ and CO₂, at the low level of HRT and low sulfate concentration. Because there was not enough of sulfate for sulfate reducing bacteria and the period of time was too short for methane producing bacteria.

(b) At low sulfate concentration and the high level of HRT, H₂ and CO₂ can be transferred as methane gas by methane producing bacteria.

(c) At low level of HRT but high sulfate concentration supported sulfate reducing bacteria in sulfide producing process.

(d) There was competition between methane producing bacteria and sulfate reducing bacteria, using H₂ in methane or H₂S producing process, depending on sulfate concentration.

Mizuno, *et.al*, (1994) investigated the effect of sulfate concentration and COD: SO₄²⁻ ratio to anaerobic digestion. By setting COD: SO₄²⁻ ratio was in the range of 1.5-148. COD concentration was in the range of 2,500-10,000 mg/l and sulfate concentration was in the range of 68-1,667 mg/l. The result shown that approximate 80% of methane gas, was mainly produced by MPB at COD: SO₄²⁻ ratio, which was more than 6.

The Sulfate Reducing Bacteria (SRB) was well functioning, more than 50% in low sulfate concentration condition (Sulfate depleted) at COD: SO₄²⁻ ratio of 1.5. Acetate and hydrogen were transferred as methane gas by MPB. In the other hand, high sulfate concentration, butyrate was digested to become sulphide and acetate by sulfate reducing bacteria and they inhibit methane producing bacteria.

Pattanawan, (2001) conducted a study of latex rubber wastewater treatment in terms of organic matter and sulfate, and to adapt anaerobic pond and biofiltration system to reduce sulfate and hydrogen sulfide. The experimental investigation of anaerobic pond system with different HRT was at 20 and 40 days. This ability in reducing organic matter in terms of SCOD and Sulfate at HRT 20 days was approximate 24% and 54% respectively. At HRT 40 days, the average organic matter and sulfate removal was 33% and 94% respectively.

1.3. Objectives

The objectives of this study were as follows:

1. To find a suitable design criteria of anaerobic and oxidation ponds for treatment of concentrated latex wastewater based on BOD₅ loading.
2. To find a suitable operation conditions for anaerobic and oxidation ponds for treatment of concentrated latex wastewater.

CHAPTER 2

METHOD OF STUDY

2.1. Sample Collection and Preservation

The wastewater samples were taken from a selected concentrated latex factory in Songkhla. Combined wastewater samples which were from concentrated latex and skim latex productions were collected at the point of untreated wastewater streams (the outlet from the rubber trap) and analyzed for pH, BOD₅, COD, TKN, NH₃-N, SS, and Sulfate in the Laboratory of Environmental Management Faculty, PSU- HatYai.

The small amounts of wastewater were first collected in June 2002 for preliminary analysis. The wastewater was preserved constantly in the cool room with a temperature 4 °C at the Environmental Management Faculty.

The average pH value of wastewater samples is very low due to the addition of sulfuric acid in the skim block production process, but it should be further raised to 7 ± 0.3 (Bochdam *et al.*, 2001) by addition of lime (CaO) prior to entering the reactors.

2.2. Wastewater Quality Analysis

In the laboratory, the wastewater samples were analyzed for various parameters using the procedures described in the 20th edition of "Standard Methods for the Examination of Water and Wastewater" APHA, AWWA and WEF (1992).

The methods of analysis were shown in Table 9 while the analytical technique and principles will be described in Appendix.

Table 9. Methods of analysis

Parameters	Methods of analysis
-pH	-pH meter
-SS	-Gravimetric method
-BOD ₅	-Azide Modification method
-COD	-Dichromatic Open Reflux method
-Total Kjeldahl Nitrogen	-Macro Kjeldahl method
-Ammonia Nitrogen	-Tritimetric method
-Sulfate	-Turbidimetric method

Source: adapted from APHA, AWWA and WEF, 1992

2.3. Experimental set up

The reactors are divided into two types: anaerobic and oxidation ponds. The anaerobic ponds were situated on the 8th floor of the environmental management faculty at room temperature. The oxidation ponds, which came after the anaerobic reactors, were situated on the open roof of the building under ambient condition.

The experimental units for both anaerobic and oxidation ponds made by acrylic plate with a dimension in Figure 4 as follows. The effective volume of anaerobic pond was 0.225 m³.

1. Anaerobic ponds 0.3 x 1.0 x 1.0 m³ (width x length x depth)
2. Oxidation ponds 0.5 x 1.2 x 0.6 m³ (width x length x depth)

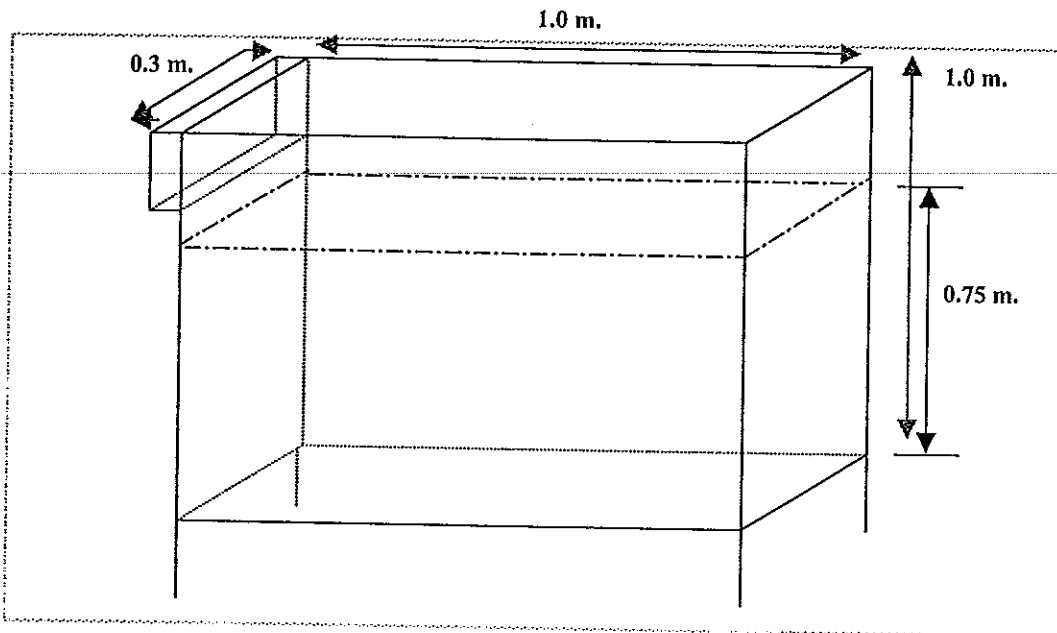


Figure 4. Dimension of anaerobic ponds set up

2.4. Experimental Running

▪ Anaerobic Ponds

Variation of four BOD₅ loading and hydraulic retention time following recommended design criteria for anaerobic pond was shown in Table 10.

When the anaerobic ponds were filled with the wastewater, the systems were started up and kept running until the steady state of the ponds was achieved. Then the influent and effluents were sampled and analyzed for every three days in laboratory. The suitable BOD₅ loading and hydraulic retention time for anaerobic ponds was selected for further treatment with oxidation pond.

Table 10. BOD₅ loading and HRT in anaerobic ponds

No	BOD ₅ loading (g BOD ₅ /m ³ .d)	HRT (d)
1	100	74.4
2	200	37.2
3	300	24.8
4	400	18.6

Condition: Average BOD₅ concentration in wastewater = 7,430±914 mg/l

▪ **Oxidation Ponds**

After the suitable BOD₅ loading for wastewater treatment from anaerobic ponds was achieved, further treatment of the wastewater in oxidation ponds was continued with the experimental running as shown in Table 11.

Table 11. BOD₅ loading and HRT in oxidation ponds

No	BOD ₅ loading (g BOD ₅ / m ² .d)	HRT (d)
5	7	74.2
6	10	51.9
7	13	39.9

Condition: Average BOD₅ concentration in wastewater = 1,483±125 mg/l

CHAPTER 3

RESULTS and DISCUSSION

3.1. Preliminary Analysis Results

The small amounts of wastewater from the selected concentrated latex factory were collected at the outlet from the rubber trap in June, 2002 for the preliminary analysis, as described in Chapter 2.

Experimental parameters were pH, BOD₅, COD, TKN, NH₃-N, SS and Sulfate. The analysis results were shown in Table 12.

Table 12. Wastewater characteristic from the selected concentrated latex factory

Parameters	Average values
pH	4.58±0.06
BOD ₅ (mg/l)	6,557±586
COD (mg/l)	10,877±455
TKN (mg/l)	1,076±109
NH ₃ -N (mg/l)	912±250
SS (mg/l)	1,041±422
Sulfate (mg/l)	4,824±164

The average pH value of wastewater sample was 4.58±0.06. The average of BOD₅, COD, SS concentrations were found to be 6,557±586 mg/l, 10,877±455 mg/l, and 1,041±422 mg/l, respectively. As the results, the organic matter in wastewater was very high.

The average TKN and NH₃-N concentrations were found to be 1,076±109 mg/l, and 912±250 mg/l, respectively. The sulfate concentration was 4,824±164 mg/l.

According to the production and water use data in year 2002 of the selected concentrated latex factory, the total wastewater from concentrated latex and skim latex production was approximately 350 m³/d.

3.2. Anaerobic Pond

As described in Chapter 2, the experimental running for anaerobic ponds were done from 1st July 2002 to 15th October 2002, (included the steady state). Experimental results can be described as follows:

The range and average results for all parameters at different volumetric BOD₅ loadings for anaerobic ponds were summarized in Table 13.

3.2.1. pH

Figure 5 presented the average pH in effluent at different volumetric organic loadings for anaerobic ponds. The designs for BOD₅ loading were 100, 200, 300 and 400 g BOD₅/m³.d.

The influent pH after adjustment with CaO was 7.13±0.09. In each BOD₅ loading, the pH tendency was increased but no evident significant differences. The increase in pH could possibly be due to the pH adjustment with CaO at the inlet to the ponds.

The pH of the wastewater associated with the rubber production is generally low, to the addition of sulfuric acid. Therefore, pH adjustment of the wastewater is necessary.

Accordingly, the advantage of the pH adjustment in influent to anaerobic pond is to keep constant condition of the effluent from anaerobic ponds. As a result of pH values, which are in the optimal range not higher than 9, indicated the efficient functional bacteria.

When the pond processes are stable, the pH adjustment can possibly be phased out due to the reactor's buffer capacity and microbial adaptation (Ejby Schmidt, 2002)

Under anaerobic conditions, pH value is associated with reduction of sulfate to sulfide. At the usual pH level, most of the sulfide is converted to H₂S and some of it escapes into the atmosphere above the wastewater. (Chemistry for environmental engineering, 1994)

Scum, which covered on rubber wastewater surface, caused a poorly anaerobic condition. Due to H₂S can not escape into the atmosphere, so that H₂S dissolves in wastewater and being more acidity in the wastewater.

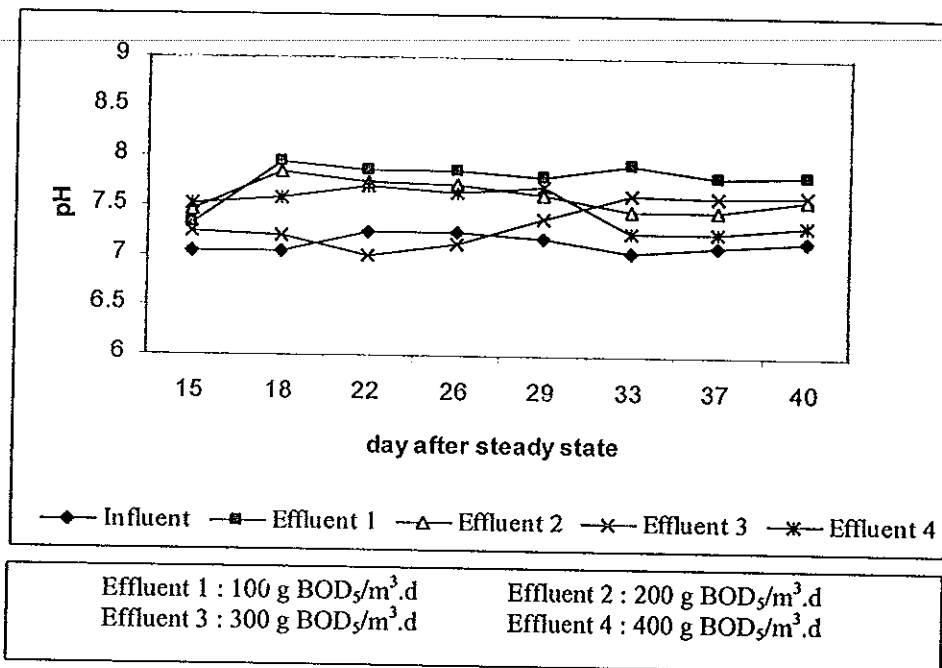


Figure 5. Average pH at different volumetric organic loadings for anaerobic ponds

3.2.2. BOD₅ and COD

The average BOD₅ in effluent at different volumetric organic loadings for anaerobic ponds were shown in Figure 6.

The influent BOD₅ concentration was 7,430±914 mg/l. In fact, the high content of organic matter in wastewater, the anaerobic ponds reduced much organic matter. The decrease of BOD₅ from the day 26 to 33 presented no evident significant differences. As the results, there is no correlation between HRT and BOD₅ removal efficiency seems evident.

All above, the consideration for removal of BOD₅, the anaerobic ponds converted about 67-83% of organic matter efficiently. The BOD₅ removal efficiency for anaerobic ponds at 200 g BOD₅/m³.d was better than the others. The average BOD₅ concentration in effluent was about 1,258±184 mg/l.

This is particularly intense at the consisting high temperature of a tropical region. The possibility of the ponds temperature were being mesophilic, which running at temperature of 30-40 °C

Following in the Figure 7 presented the average COD at different volumetric organic loading for anaerobic ponds. The influent COD concentration was 9,571±509 mg/l. The average COD removal efficiency in anaerobic pond was found in a range of 50-77%.

The decrease of COD tendency resembles to the BOD₅, as well as the BOD:COD ratio is in the usual ranges for the rubber wastewater, the ratio varies between approximately 0.5-0.7.

The major advantage of the COD test is the short time required for evaluation. The determination can be made in about 3 hours rather than the 5 days required for the measurement of BOD. For this reason it is used as a substitute for the BOD test in many instances. COD data can often be interpreted in terms of BOD values after sufficient experience has been accumulated to establish reliable correlation factors. (Chemistry for environmental engineering, 1994)

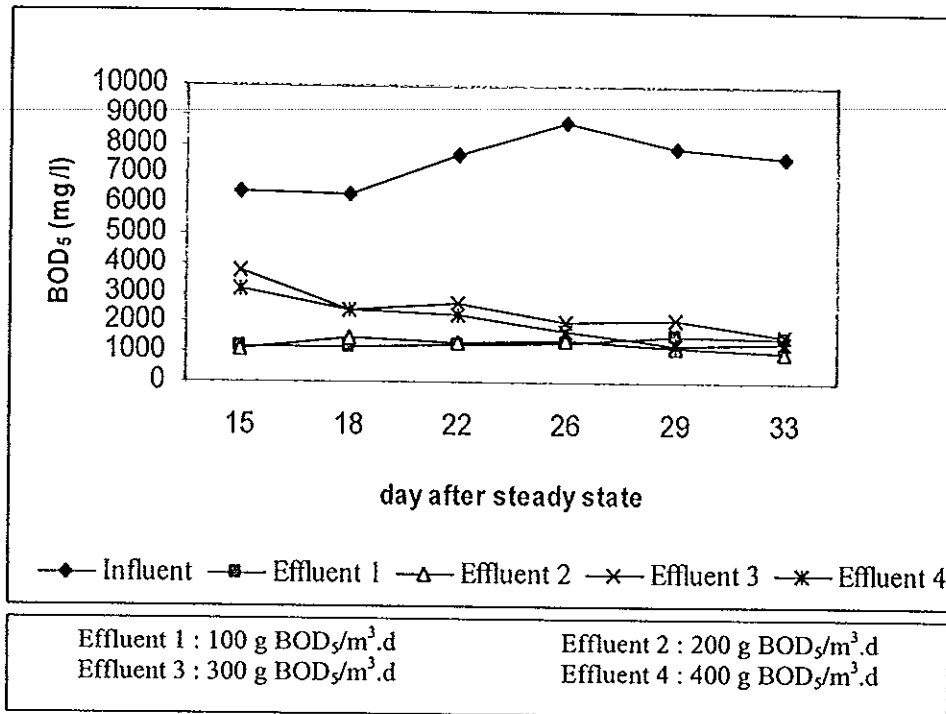


Figure 6. Average BOD₅ at different volumetric organic loadings for anaerobic ponds

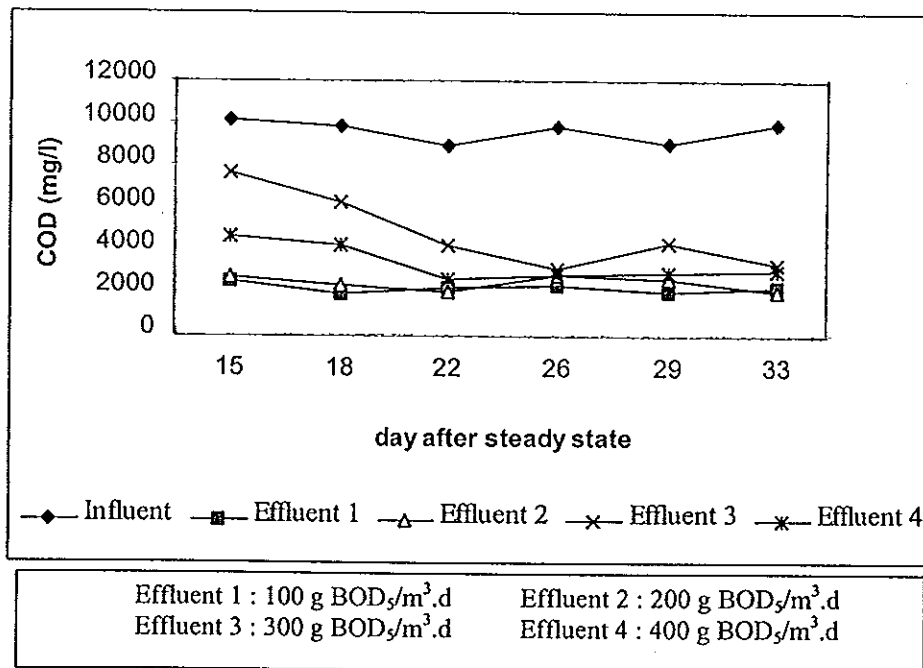


Figure 7. Average COD at different volumetric organic loadings for anaerobic ponds

3.2.3. TKN and NH₃-N

The average TKN at different volumetric organic loading for anaerobic ponds were shown in Figure 8. The influent TKN concentration was approximately 1,330±25 mg/l.

The TKN tendency in anaerobic ponds was not much decreased. The TKN removal efficiency at 200 g BOD₅/m³.d presented better than the others, with approximately TKN concentration of 1,036±129.19 mg/l. The TKN removal efficiency at 400 g BOD₅/m³.d was not well functioned, as the removal tendency presented very low.

The source of high TKN amounts in the rubber wastewater are expected from account of the addition of NH₃ and DAHP ((NH₄)₂ HPO₄) for preservation and precipitation purposes.

In anaerobic ponds, organic nitrogen is hydrolyzed to ammonia, so ammonia concentrations in anaerobic pond effluents are generally higher than in the raw wastewater. (Duncan Mara, 1997)

The results from NH₃-N analysis of anaerobic ponds were shown in Figure 9. The influent NH₃-N concentration was approximately 1,219±27.38 mg/l. The NH₃-N removal tendency resembles to the TKN. The organic matter is degraded in anaerobic ponds, appeared an increase of ammonia nitrogen.

Under anaerobic condition, nitrates and nitrites are both reduced by process called denitrification. Presumably nitrates are reduced to nitrites and the reduction of nitrites occurs. Reduction of nitrites is carried all the way to ammonia by bacteria, most of them carry the reduction to N₂, which escapes to the atmosphere.

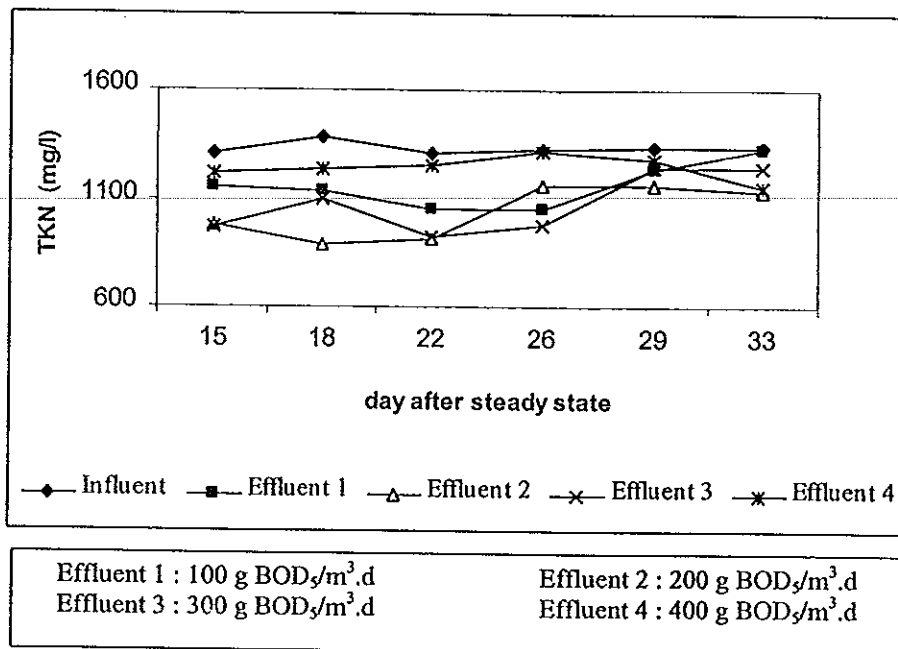


Figure 8. Average TKN at different volumetric organic loadings for anaerobic ponds

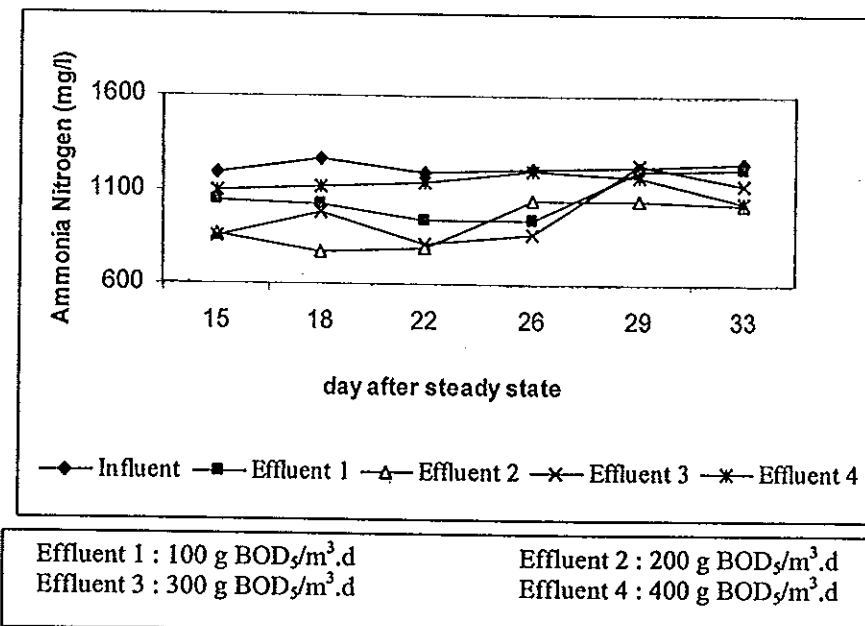


Figure 9. Average NH₃-N at different volumetric organic loadings for anaerobic ponds

3.2.4 Suspended Solids

Figure 10 presented the average SS in effluent at different volumetric organic loadings for anaerobic ponds. The influent SS concentration was approximately 996 ± 88 mg/l. In each BOD_5 loading, the removal tendency was gradually decreased.

In rubber wastewater contains most non-easy biodegradable suspended solids. The SS tendency at $200 \text{ g } BOD_5/m^3.d$ presented more decrease than the others.

The measured SS concentration indicated a general decreasing tendency through the system, which is to be expected as the total retention time increase and gradually more of SS settle.

It was found that SS removal efficiency presented in anaerobic ponds were in a range of 29-42% by sedimentation of settleable solid and subsequent anaerobic digestion.

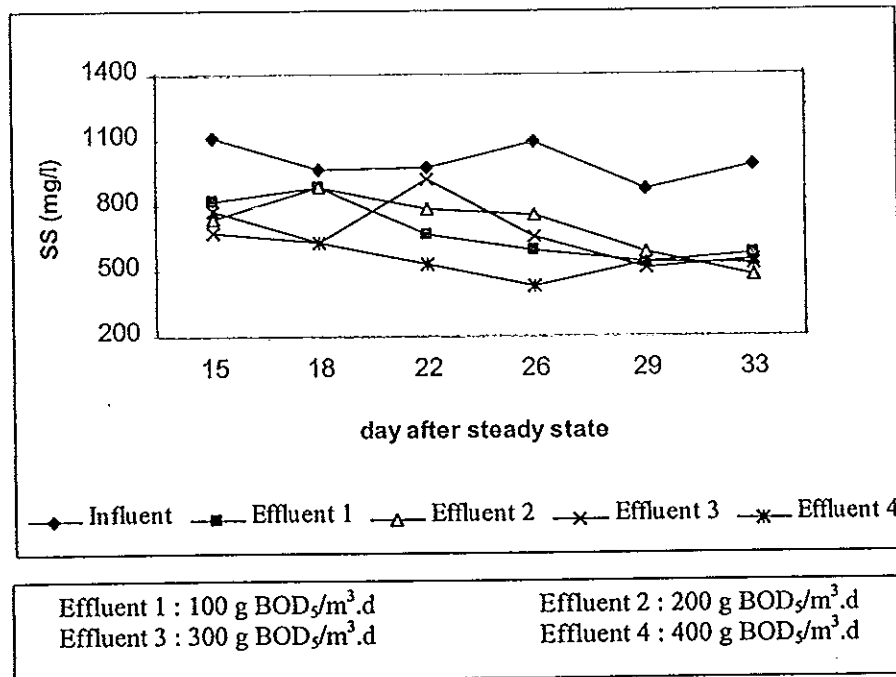


Figure 10. Average SS at different volumetric organic loadings for anaerobic ponds

3.2.5. SO_4^{2-}

The average SO_4^{2-} in effluent at different volumetric organic loadings for anaerobic ponds were shown in Figure 11. The influent SO_4^{2-} concentration was approximately $4,936 \pm 209$ mg/l. The decrease of SO_4^{2-} tendency for anaerobic ponds was not much. As the results, the optimal sulfate removal efficiency at about 24% was achieved at $200 \text{ g BOD}_5/\text{m}^3 \cdot \text{d}$. The average sulfate concentration was $3,733 \pm 213$ mg/l.

As the result, the sulfate removal efficiency is quite low. The most likely explanation for this is the measured sulfate concentration is extremely high, which is a result of the extensive use of sulfuric acid for coagulation in the skim block production. The addition of an approximate 2,000 kg of H_2SO_4 per day for producing the skim block was reported by the selected concentrated latex factory.

Even though, the anaerobic conditions can efficiently reduce sulfate concentration, but as the result, the sulfate content could be slightly decreasing. Due to the fact that the high content of sulfate possible blocked the sulfate-reducing bacteria functions. (Mizuno, 1994)

The recommended design of sulfate loading should not exceeded than $500 \text{ mg SO}_4^{2-}/\text{l}$ and also a small amount of sulfide is beneficial as it reacts with heavy metals to form insoluble metal sulfides which precipitate out but concentrations of 50-150 mg/l can inhibit methanogenesis. (Pfeffer, 1970)

Sulfate (SO_4^{2-}) is reduced to sulfide (S^{2-}), typically in the form of hydrogen sulfide (H_2S). Eight electrons are added to sulfate to make sulfide. Below is the reduction of sulfate to sulfide during growth on acetate. (Timothy, 2000)



The sulfate ion is reduced to sulfide ion, under anaerobic conditions. The relationship existing between H_2S , HS^- and S^{2-} associated with pH levels are at pH values of 8 and above, most of the reduced sulfur exists in solution as HS^- and S^{2-} ions, and the amount of free H_2S is so small that its partial pressure is insignificant, and at pH levels below 8, the equilibrium shifts rapidly toward the formation of unionized H_2S and is about 80% complete at pH 7. (Chemistry for environmental engineering, 1994)

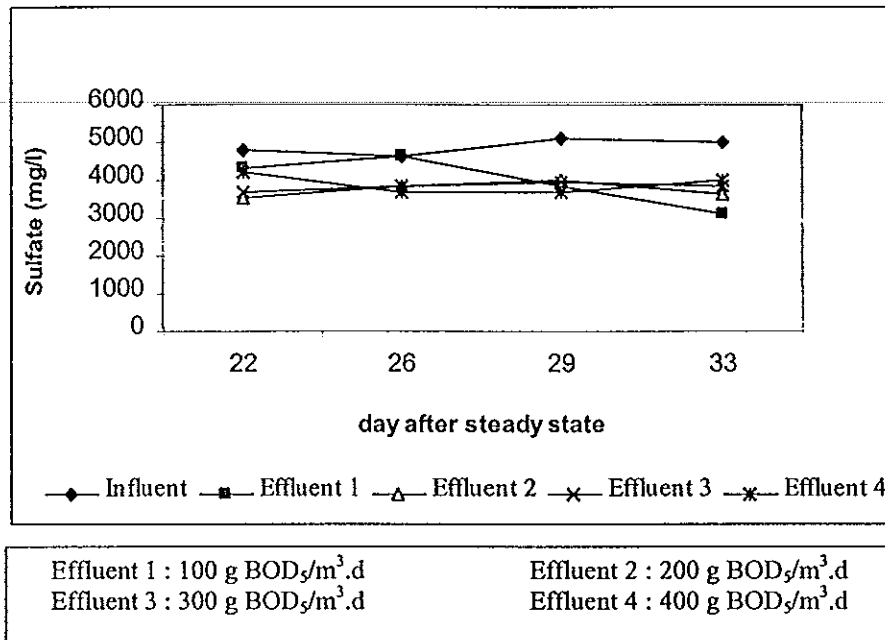


Figure 11. Average SO_4^{2-} at different volumetric organic loadings for anaerobic ponds

From the experimental results, optimum of criteria for operating anaerobic pond is found to be at 200 g BOD₅ /m³.d because the consideration of removal efficiency from anaerobic ponds presented satisfactory decrease better than the others. The decrease of organic matter tendency was most constantly. The effluent BOD₅ concentration was 1,258±184 mg/l.

As the result, the organic matter removal efficiency for anaerobic ponds at 200 g BOD₅ /m³.d was about 83 % and the SS removal efficiency was about 29 %, also bringing the decrease of TKN and NH₃-N concentrations. Due to the appropriate design BOD₅ loading and hydraulic retention time. The operating system maintains constant conditions.

When the focus was on sulfate removal efficiency, the optimal sulfate removal for anaerobic ponds was at 200 g BOD₅ /m³.d. The low sulfate removal efficiency was about 24%. Since the concentration of sulfate in the influent far exceeds the acceptable limit at 4,936±209 mg/l. The sulfate reduction process in anaerobic could probably be blocked.

Table 13. The range and average results for all parameters at different volumetric BOD₅ loading for anaerobic ponds

Parameters	Effluent														
	Influent			100			200			300			400		
	Range	Average		Range	Average	% RE	Range	Average	% RE	Range	Average	% RE	Range	Average	% RE
pH	7.05-7.24	7.13 ± 0.09		7.33-7.94	7.78 ± 0.16	-	7.45-7.85	7.64 ± 0.16	-	7.01-7.62	7.26 ± 0.21	-	7.25-7.71	7.56 ± 0.16	-
BOD ₅ (mg/l)	6.325-8.725	7.430 ± 0.14		1.150-1.550	1.310 ± 0.164	82 ± 1	1.050-1.500	1.258 ± 0.184	83 ± 3	1.600-3.775	2.425 ± 0.750	67 ± 12	1.250-3.125	2.020 ± 0.734	72 ± 12
COD (mg/l)	8,900-10,120	9,571 ± 509		1,920-2,480	2,190 ± 209	77 ± 1	2,040-2,740	2,415 ± 342	74 ± 3	3,080-7,620	4,783 ± 1,775	50 ± 15	3,000-4,640	3,356 ± 845	64 ± 6
NH ₃ -N (mg/l)	1.191-1.260	1.219 ± 0.2738		934-1,214	1,057 ± 125.36	13 ± 8	766-1,046	920 ± 129.19	18 ± 11	809-1,228	977 ± 169.12	13 ± 9	1,031-1,020	1,124 ± 58.7	14.1 ± 5
TKN (mg/l)	1.307-1.376	1.330 ± 0.25		1,050-1,328	1,158 ± 107.76	12 ± 7	908-1,162	1,036 ± 129.19	17 ± 9	925-1,344	1,093 ± 169.12	12 ± 9	1,212-1,318	1,24 ± 58.7	6.8 ± 4
SS (mg/l)	872-1,110	996 ± 88		540-880	677 ± 140	32 ± 12	475-885	702 ± 148	29 ± 13	510-920	656 ± 143	34 ± 13	430-770	570 ± 115	42 ± 9
SO ₄ ²⁻ (mg/l)	4,645-5,120	4,936 ± 209		3,101-4,622	3,975 ± 661	19 ± 14	3,513-3,997	3,733 ± 213	24 ± 4	3,838-3,936	3,818 ± 115	22 ± 2	3,668-4,192	3,885 ± 259	21 ± 5

RE = Average Removal Efficiency

3.3. Oxidation Pond

The effluent from anaerobic ponds at the BOD₅ loading 200 g BOD₅/m³.d was further treated by oxidation ponds. The oxidation pond is a second step of wastewater treatment. The sufficient dissolved oxygen, which is transferred from winds, the photosynthetic algae might be influential factors in improving the quality of the wastewater.

The experiment for oxidation ponds system was conducted from 15th October 2002 to 31st December 2002, about 76 days. This period of time was the rainy season.

The range and average results for all parameters at different surface loading for oxidation ponds were summarized in Table 15.

3.3.1. pH

The average pH in effluent at different surface organic loadings for oxidation ponds was shown in Figure 12. The influent pH was approximately 7.15 ± 0.19 . Within this average pH value, the pond conditions are buffered. It was found that the increase of pH effluent in each BOD₅ loading.

Normally, the pH values from the effluent of well-designed oxidation ponds should be increased and it will produce quite acceptable pond conditions.

In wastewater treatment employing biological processes, pH must be controlled within a range favorable to the particular organisms involved. Chemical processes used to coagulate wastewater require that the pH be controlled within rather narrow limits. Based on the theoretical concept of pH mentioned the relationships between pH and acidity, the pH lower than 8.5 contains acidity and at pH 7.0 considerable carbon dioxide remains to be neutralized.

Throughout the acidity conditions in wastewater, due to the amount of sulfuric acid or salt of sulfuric acid. Conversion of these materials to sulfuric acid and sulfates is brought about by sulfur-oxidizing bacteria under aerobic conditions. (Chemistry environmental engineering, 1994)

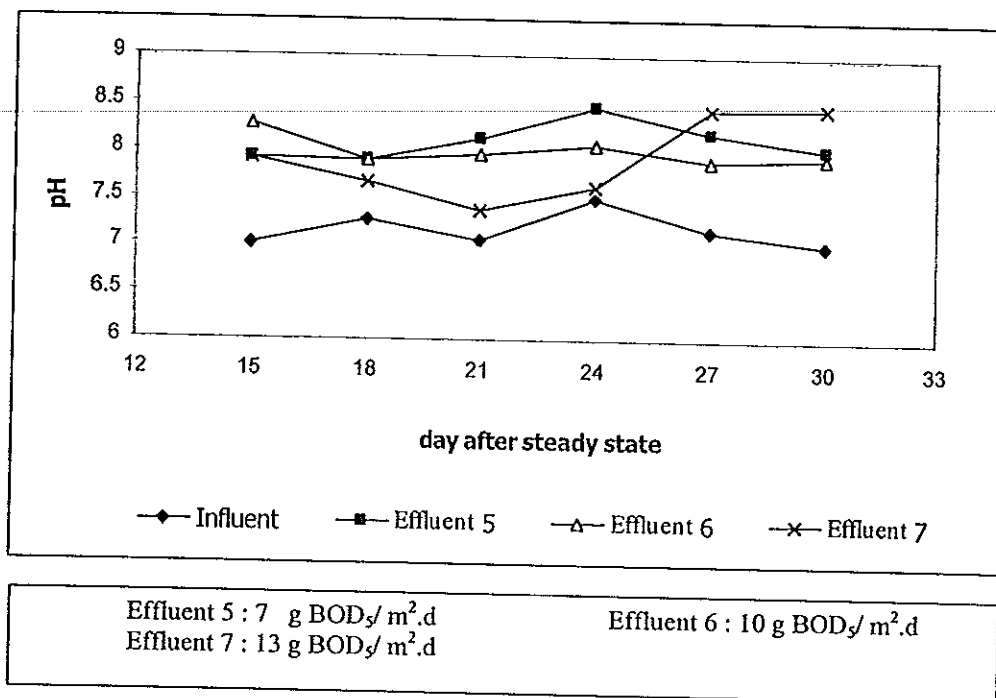


Figure 12. Average pH at different surface organic loadings for oxidation ponds

3.3.2. BOD₅ and COD

The average BOD₅ in effluent at different surface organic loadings for oxidation ponds were shown in Figure 13.

The influent BOD₅ concentration was approximately 1,483±125 mg/l. The designs of different surface organic loading for oxidation ponds were 7, 10, and 13 g BOD₅/ m².d.

It was found from the experimental results that average BOD₅ removal efficiency of about 53-46% can be achieved in oxidation ponds.

The wastewater in oxidation ponds, which are designed for BOD₅ removal on the basis of a relatively low surface loading 10-40 g BOD₅/ m².d to permit the development of a healthy algae population as the oxygen for BOD₅ removal by the pond bacteria is mostly generated by algae photosynthesis. (Duncan Mara, 1997)

Figure 14 showed the results of average COD in effluent from oxidation ponds. The decrease of COD resembles to the BOD₅. The completed results showed that the organic matter was decreased, because organic compounds in wastewater may be used as food for bacteria which can biochemically digest or oxidise the organic compounds to produce energy for growth.

By supplying enough oxygen, an aerobic condition is developed. Bacteria that obtain their energy aerobically are much more efficient. The same organic waste food supply supports a much larger bacterial flora by aerobiosis than anaerobiosis, and therefore, aerobic decomposition of organic matter is much more rapid. (Oxidation ponds: <http://ponce.sdsu.edu>)

The wind has an important effect on the behavior of an aerobic zone, as it induces vertical mixing of the pond liquid, good mixing within the pond aerobic layer ensures a more uniform distribution of BOD₅, bacteria and algae and hence a better degree of waste stabilization. (Duncan Mara, 1997)

In oxidation ponds, algal production of oxygen occurs near the surface of ponds, in a euphotic zone limited by the depth of light penetration into the pond. A small amount of oxygen also enters the pond by surface diffusion.

Furthermore, there was a report by U.S. Army corps of engineers showing the increase of the percentage of BOD₅ removal efficiency in oxidation pond, of the longest retention time at the temperature above 30 °C, which resembles the temperature here.

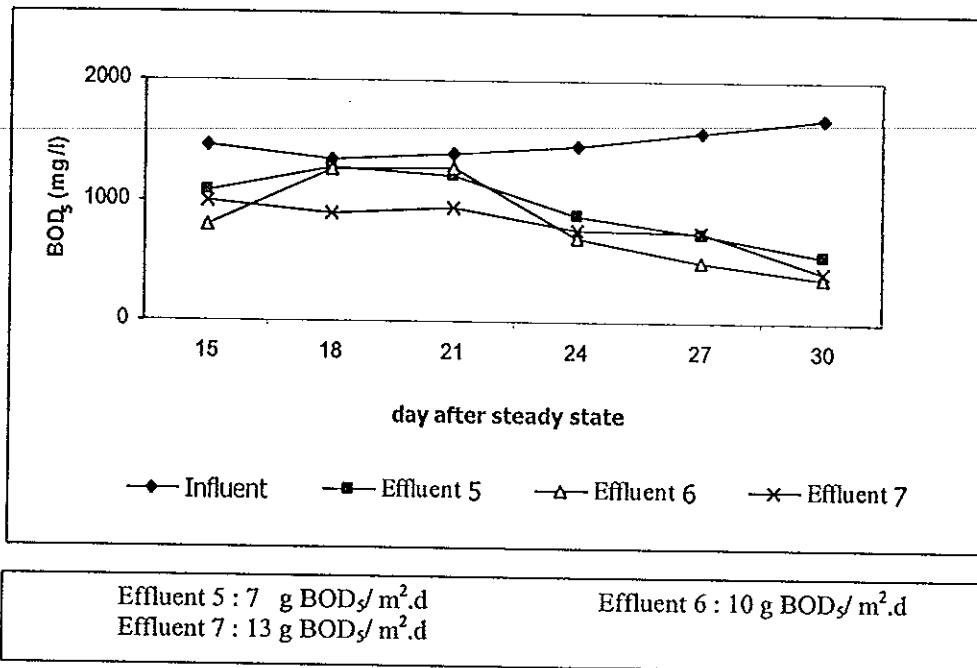


Figure 13. Average BOD₅ at different surface organic loadings for oxidation ponds

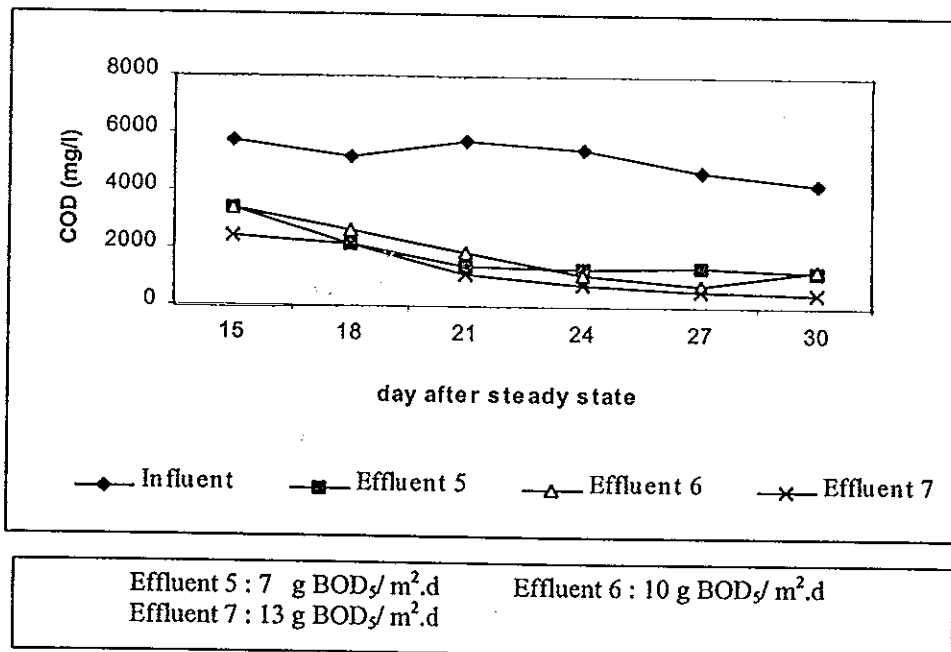


Figure 14. Average COD at different surface organic loadings for oxidation ponds

3.3.3. TKN and NH₃-N

The average TKN in effluent at different surface organic loadings for oxidation ponds were shown in Figure 15. The average TKN in influent was 1,230±136 mg/l. The decrease of TKN was greatly. Average TKN removal efficiency of about 88-95% was achieved.

Even though, the removal efficiency in each surface BOD₅ loading presented not much difference. As the experimental result, the best TKN removal efficiency was achieved at 7 g BOD₅/ m².d.

Algae, though the process of photosynthesis, produce oxygen. Algae also consume nitrogen and phosphorous, two common nutrients found in wastewater. (Oxidation ponds: <http://ponce.sdsu.edu>)

One of the end products of aerobic bacteria is ammonia, which is not given off as a gas, and is nitrified by the aerobes Nitrosomonas, oxidizing the ammonia into nitrite, and Nitrobacter, oxidizing the nitrite into non-toxic nitrate. Nitrates are directly plant usable and will not harm fish. The only gas given off by aerobic bacteria is odorless carbon dioxide, thereby eliminating any offensive odor. (Aerob-A-Jet™ & Aerobic Bacteria: <http://www.aerob-a-jet.com/AerobicBacteria.htm>)

Results of NH₃-N in effluent for oxidation ponds were shown in Figure 16. The decrease of NH₃-N resembles the TKN. The average NH₃-N removal efficiency was found to be in a range of 90-96%. Surface BOD₅ loading at 7 g BOD₅/ m².d provided the best removal efficiency.

Ammonia is incorporated into new algal biomass. Eventually the algae become moribund and settle to the bottom of the pond; around 20 percent of the algae cell mass is non-biodegradable and the nitrogen associated with this fraction remains immobilized in the pond sediment. That associated with the biodegradable fraction eventually diffuses back into the pond liquid and is recycled back into algal cells to start the process again. At high pH, some of the ammonia will leave the pond by volatilization. (Duncan Mara, 1997)

Although the total nitrogen removal in WSP systems can reach 80 percent or more, and ammonia removal can be as high as 95 percent. (Duncan Mara, 1997)

The aerobic bacteria also require oxygen to convert ammonia to nitrite (known as nitrification) and from nitrite to nitrate, if oxygen is depleted the bacteria will die off, the process stopped; concentration of nitrite and ammonia will increase. (Frank Chong, 2002)

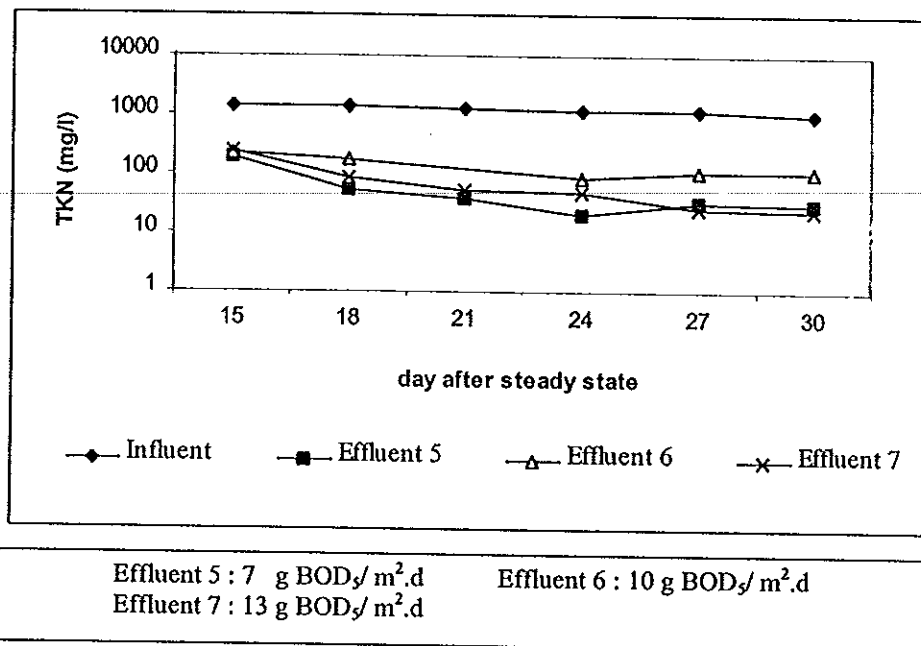


Figure 15. Average TKN at different surface organic loadings for oxidation ponds

Remark: The result at 10 g BOD₅/m².d on the day 21 could not be used.

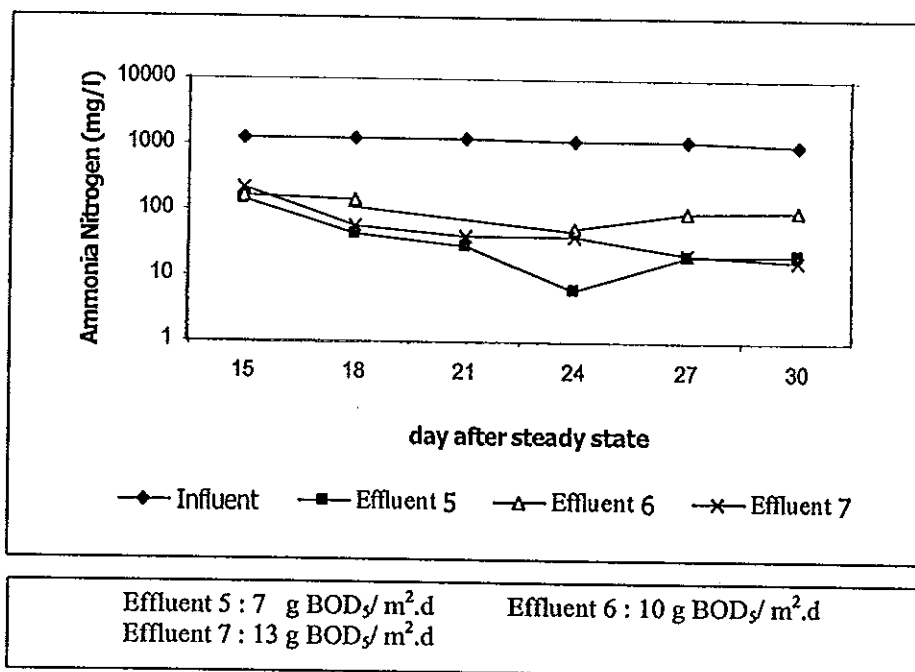


Figure 16. Average NH₃-N at different surface organic loadings for oxidation ponds

Remark: The result at 10 g BOD₅/m².d on the day 21 could not be used.

3.3.4. Suspended Solids

Figure 17 presented the average SS in influent at different surface organic loadings for oxidation ponds. The average SS in the influent was 444 mg/l. The decrease of SS tendency was greatly and constantly at 7 and 13 g BOD₅/ m².d.

The SS tendency at 10 g BOD₅/ m².d presented quite high concentration. Due to the amount of algae was very much in this oxidation pond. However, the decrease of SS after the day 27 appeared constant in the oxidation pond at 10 g BOD₅/ m².d.

Approximately half of the solid waste left after primary treatment settles in the oxidation ponds. Breakdown of the floating and sinking organic matter in the sewage is aided by algal growth and bacteria activities in the ponds. (Oxidation ponds: <http://ponce.sdsu.edu>)

Oxygen in the top aerobic zone is provided by wind and is used by aerobic bacteria to stabilize the waste in this region of the pond. The top aerobic layer also serves to reduce the odors while the waste is being anaerobically stabilized in the bottom layer. The intermediate zone, which is partly aerobic and partly anaerobic, is where the facultative bacteria degrade the suspended organic matter. (Fedler, *et al*, 1993)

Though the aerobic condition supported photosynthetic algae. An algae population consisting of a lot of highly colored algae and bacteria was observed in the oxidation ponds.

By the influent of winds, Sunlight and the rainy season, so even more and more solids were packed and could settle down to the bottom and these solids that have settled out sink to the bottom where microbes continue to break them down.

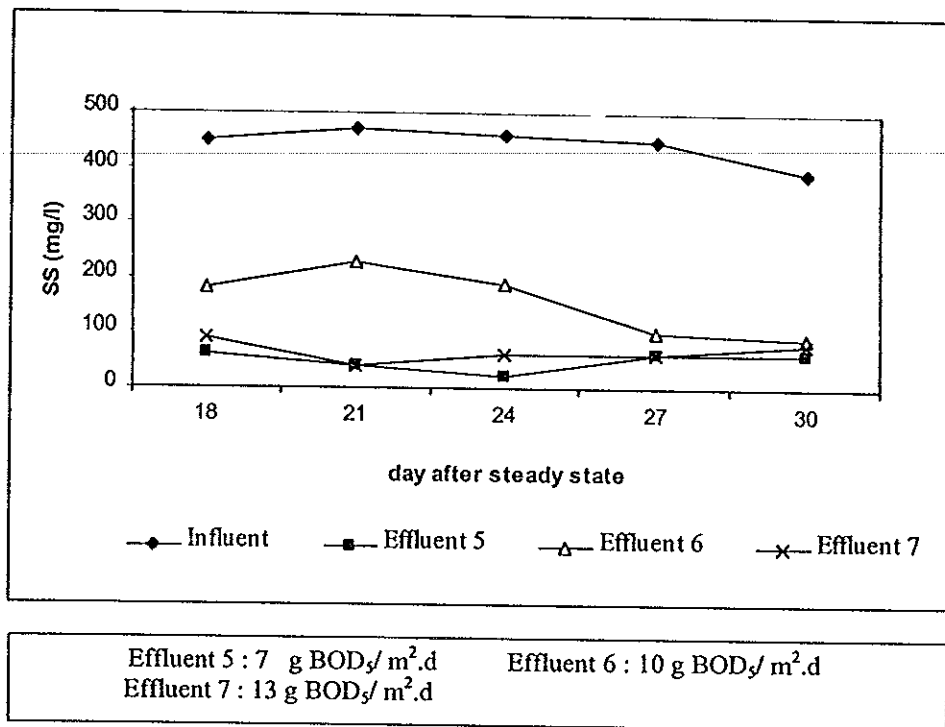


Figure 17. Average SS at different surface organic loadings for oxidation ponds

3.3.5. SO₄²⁻

Figure 18 presented the average SO₄²⁻ in effluent at the differences of surface organic loading for oxidation ponds. The influent sulfate concentration was app. 2,316±114 mg/l. As the results, the sulfate removal efficiency at 7 g BOD₅/m².d presented better performance than the others.

The sulfate removal efficiency in oxidation ponds was very much reduced, though this decrease of sulfate in the oxidation ponds is rather surprising, instead of the more efficiency removal, taking place in the anaerobic ponds.

For this event, there is some reason to think that at first the sulfate concentration has been partially decreased in the anaerobic ponds.

The second reason is, since the aerobic process could only occur on the surface of thick waste within the waste itself. In the absence of oxygen, anaerobic process occurs, as the depth of a pond is greater than the euphotic zone. Wind mixing does not mix the near-surface oxygenated water the full depth of the pond.

The amount of oxygen produced or transferred to deeper water is less than is needed by bacterial respiration there, then an anaerobic zone develops at the bottom of the pond. (General description of oxidation pond function: www.maf.govt.nz/.../rural-nz/sustainable-resource-use/resource-management/dairy-shed-astewater/dairyef4.htm)

For the reason above the sulfate reduction by the sulfate reducing bacteria under the anaerobic zone in the bottom continues to be generated. Furthermore, sulfate is an end product of aerobic bacteria through their metabolism and as well as the aerobic bacteria (especially chemotrophic bacteria eg. *Thiobacillus*), through their process oxidized sulfide (HS^-) to elemental sulfur (S^0), which is insoluble, probably both of sulfate amount and elemental sulfur have been washed out by the heavy rainfall in the rainy season as mentioned. (Wastewater Treatment Pond: <http://www.me.cc.va.us>)

All above, the consideration of removal efficiency from oxidation ponds presented a satisfactory decrease for all parameters. Due to the suitable design BOD_5 loading and hydraulic retention time supported the condition in oxidation ponds, as well as seasonal influencing factor was from rainfalls. The optimum of criteria for operating oxidation ponds was $7 \text{ g BOD}_5/\text{m}^2\cdot\text{d}$. Because as the results presented the great of organic matter removal efficiency and an appropriate sulfate removal efficiency.

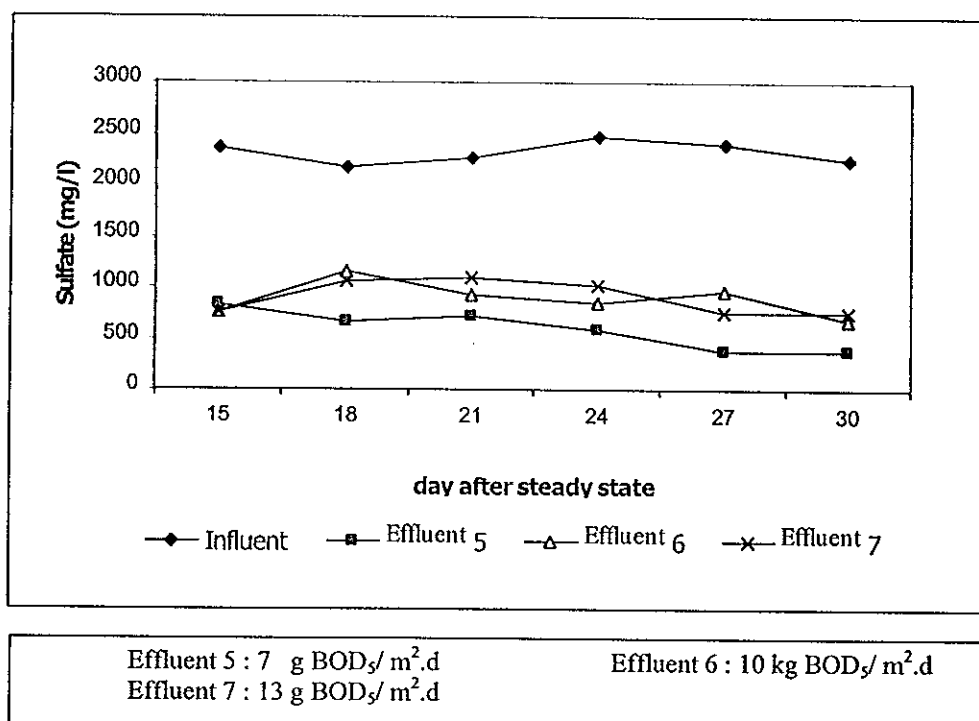


Figure 18. Average SO_4^{2-} at different surface organic loadings for oxidation ponds

Table 14. The range and average results for all parameters at different surface BOD₅ loading for oxidation ponds

Parameters	Influent		Effluent											
			BOD ₅ loading rate (g.BOD ₅ / m ² .d)											
	Range	Average	7			10			13					
			Range	Average	% RE	Range	Average	% RE	Range	Average	% RE	Range	Average	% RE
pH	7-7.5	7.15±0.19	7.9-8.45	8.09±0.21	-	7.89-8.27	7.99±0.14	-	7.37-8.46	7.9±0.45	-			
BOD ₅ (mg/l)	1,340-1,684	1,483±125	550-1,275	877±259	53±21	360-1,275	712±311	51±27	420-995	734±190	46±15			
COD (mg/l)	4,270-5,720	5,180±532	540-2,160	1,229±472	62±7	747-2,640	1,404±606	68±10	480-2,120	843±579	79±9			
NH ₃ -N (mg/l)	966-1,260	1,159±107	6-142	43±49.81	96±3	54-168	111±44.9	90±3	18-212	64±73.45	94±5			
TKN (mg/l)	988-1,375	1,230±136	20-187	60±63.02	95±4	84-487	139±57.58	88±3	24-240	78±81.84	93±5			
SS (mg/l)	390-470	444±31	20-60	48±17	89±4	90-230	158±60	64±10	40-90	66±19	85±4			
SO ₄ ²⁻ (mg/l)	2,161-2,478	2,316±114	380-822	589±174	74±7	680-1,143	886±164	61±7	750-1,090	903±166	61±7			

RE = Average Removal Efficiency

CHAPTER 4

CONCLUSION

Anaerobic-oxidation ponds systems are suitable for use in treating very strong organic matter from concentrated and skim block latex wastewater. These systems appear especially beneficial because of their simplicity, low cost and high efficiency and suitability for hot climates as shown by the presented results.

Based on the experimental results following conclusions can be drawn:

1. The optimum criteria for operating of anaerobic pond was found to be at 200 g BOD₅/ m³.d
2. The optimum criteria for operating of oxidation pond was found to be at 7 g BOD₅/ m².d
3. The low sulfate removal efficiency in anaerobic pond was notified, which may resulted from very high sulfate concentration in wastewater.
4. Sulfate removal efficiency can be enhanced by utilizing lower concentration of sulfate in wastewater.

In anaerobic ponds, the principal biological reactions are acid formation and methane fermentation. From the experimental results, it can be concluded that in the demonstration system presented the designs of BOD₅ loading for anaerobic ponds, as calculated from Table 10 in Chapter 2, were acceptable levels of wastewater treatment.

When the focus was on BOD₅ and SS reduction, the achieved results show that the similar treatment efficiencies of anaerobic ponds were very good in the range of 100-400 g BOD₅ loading/m³.d, with 83% and 42% of BOD₅ and SS removal efficiencies, respectively.

The sulfate removal efficiency was not found to be suitable, due to very high sulfate concentration. Therefore, sulfate removal efficiency was reduced and also was the main obstacle for biogas production.

In the oxidation ponds, also known as secondary treatment, aerobic bacteria decompose organic matter and algae, through photosynthetic reactions, providing sufficient oxygen for an aerobic environment. The main seasonal influencing factor is from rainfall, bringing higher removal efficiency for all parameters. The result of oxidation ponds significantly presented an appropriate sulfate removal efficiency; 7 g BOD₅/ m².d.

The acceptable levels of removal efficiency from this experiment can be used in the future as a guideline for appropriate design and operation for waste stabilization ponds to treat wastewater from concentrated latex and skim block wastewater.

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APPENDIX A

Experimental Results

Anaerobic Ponds

day	BOD ₅ loading (g BOD ₅ /m ³ .d)	pH	BOD ₅ (mg/l)	COD (mg/l)	TKN (mg/l)	NH ₃ -N (mg/l)	SS (mg/l)	SO ₄ ²⁻ (mg/l)	
15	Influent	7.05	6,425	10,120	1,309	1,193	1,110	-	
	Effluent	100	7.33	1,150	2,480	1,153	1,037	820	-
		200	7.45	1,100	2,740	977	861	740	-
		300	7.23	3,775	7,620	971	855	675	-
		400	7.52	3,125	4,640	1,212	1,096	770	-
18	Influent	7.05	6,325	9,800	1,376	1,260	960	-	
	Effluent	100	7.94	1,140	1,920	1,136	1,020	880	-
		200	7.85	1,500	2,260	882	766	885	-
		300	7.19	2,400	6,200	1,100	984	625	-
		400	7.57	2,450	4,200	1,236	1,120	625	-
22	Influent	7.23	7,660	8,900	1,307	1,191	970	4,792	
	Effluent	100	7.86	1,250	2,240	1,050	934	660	4,317
		200	7.74	1,325	2,040	908	792	780	3,513
		300	7.01	2,650	4,240	925	809	920	3,659
		400	7.69	2,300	2,600	1,250	1,134	530	4,192
26	Influent	7.24	8,725	9,760	1,326	1,210	1,087	4,645	
	Effluent	100	7.86	1,320	2,340	1,050	934	595	4,622
		200	7.72	1,425	2,800	1,162	1,046	755	3,825
		300	7.13	2,030	3,080	977	861	657	3,838
		400	7.64	1,700	2,820	1,318	1,202	430	3,668
29	Influent	7.18	7,878	8,970	1,335	1,219	872	5,120	
	Effluent	100	7.80	1,550	2,000	1,312	1,205	540	3,861
		200	7.63	1,150	2,600	1,156	1,040	580	3,987
		300	7.39	2,100	4,280	1,344	1,228	510	3,936
		400	7.71	1,250	2,880	1,280	1,164	540	3,672
33	Influent	7.05	7,568	9,875	1,330	1,242	980	5,007	
	Effluent	100	7.92	1,450	2,160	1,328	1,214	570	3,101
		200	7.46	1,050	2,050	1,134	1,018	475	3,608
		300	7.62	1,600	3,280	1,246	1,130	550	3,840
		400	7.25	1,300	3,000	1,147	1,031	525	4,011

Oxidation Ponds

day	BOD ₅ loading (g BOD ₅ /m ² .d)	pH	BOD ₅ (mg/l)	COD (mg/l)	TKN (mg/l)	NH ₃ -N (mg/l)	SS (mg/l)	SO ₄ ²⁻ (mg/l)	
15	Influent	7	1,460	5,700	1,336	1,260	-	2,351	
	Effluent	7	1,075	2,160	187	142	-	822	
		10	8.27	800	2,640	224	168	-	753
		13	7.9	995	2,120	240	212	-	757
18	Influent	7.25	1,340	5,200	1,375	1,246	450	2,161	
	Effluent	7	1,275	1,387	53	43	60	661	
		10	7.89	1,250	1,880	172	144	180	1,143
		13	7.66	900	1,080	82	57	90	1,055
21	Influent	7.04	1,385	5,720	1,271	1,198	470	2,263	
	Effluent	7	1,200	1,280	40	28	40	710	
		10	7.95	1,275	1,120	-	-	230	924
		13	7.37	937	760	51	40	40	1,090
24	Influent	7.5	1,460	5,480	1,215	1,162	460	2,478	
	Effluent	7	877	1,387	20	6	20	576	
		10	8.05	700	747	84	54	190	853
		13	7.61	767	560	50	40	60	1,018
27	Influent	7.15	1,570	4,710	1,196	1,126	450	2,396	
	Effluent	7	725	1,240	32	20	60	386	
		10	7.89	500	1,300	109	92	100	965
		13	8.43	750	480	25	22	60	753
30	Influent	7.01	1,684	4,270	988	966	390	2,248	
	Effluent	7	550	540	30	21	60	380	
		10	7.93	360	1,440	107	100	90	680
		13	8.46	420	480	24	18	80	750

APPENDIX B

Analytical Techniques

1. pH

Principle: The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode.

Apparatus:

pH Meter: pH meter consisting of potentiometer, a glass electrode, a reference electrode, and a temperature compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in the test solution.

2. Biochemical Oxygen Demand (BOD₅)

Principle: The biological O₂-consumption is determined by measuring of DO₀ and DO₅ after 5 days of incubation at 20 °C

Apparatus:

a. Incubation bottles, 250 to 300 ml capacity, clean bottles with a detergent, rinse thoroughly and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use a waterseal. Obtain satisfactory water seals by inventing bottles in a water bath or by adding water to the flared mouth of special BOD bottles. Place a paper or plastic cup or foil cap over flared mouth of bottle to reduce evaporation of the water seal during incubation.

b. Air incubation or water bath, thermostatically controlled at 20±1 °C. Exclude all light to prevent possibility of photosynthetic production of DO.

Reagents:

a. *Manganous sulfate solution:* Dissolve 480 g MnSO₄·4H₂O, 400 g MnSO₄·2H₂O, or 364 g MgSO₄·H₂O in distilled water, filter, and dilute to 1 litre. The MnSO₄ Solution should not give a color with starch when added to an acidified potassium iodide (KI) solution.

b. *Alkali-iodide-azide reagents:*

1) For saturated or less-than-saturated samples, dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI (or 150 g KI) in distilled water and dilute to 1 litre. Add 10 g NaN₃, dissolved

in 40 ml distilled water. Potassium and sodium salts may be used interchangeable. This reagent should not give a color with starch solution when diluted and acidified.

2) For supersaturated samples- Dissolve 10 g NaN_3 in 500 ml distilled water. Add 480 g sodium hydroxide (NaOH) and 750 g sodium iodide (NaI), and stir until dissolved. There will be a white turbidity due to sodium carbonate (Na_2CO_3), but this will do no harm.

c. Sulfuric acid, conc H_2SO_4 : One milliliter is equivalent to about 3 ml alkali-iodide-azide reagent.

d. Starch: Use either an aqueous solution or soluble starch power mixtures. To prepare an aqueous solution, dissolve 2 g laboratory-grade soluble starch and 0.2 g salicylic acid, as a preservative, in 100 ml hot distilled water.

e. Standard sodium thiosulfate titrant: Dissolve 6.205 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water. Add 1.5 ml 6 N NaOH or 0.4 g solid NaOH and dilute to 1,000 ml. Standardize with bi-iodate solution.

f. Standard potassium bi-iodate solution, 0.0021 M: Dissolve 812.4 mg $\text{KH}(\text{IO}_3)_2$ in distilled water and dilute to 1000 ml.

Standardization- Dissolve approximately 2 g KI , free from iodate, in an Erlenmeyer flask with 100 to 150 ml distilled water. Add 1 ml 6 N H_2SO_4 or a few drops of conc H_2SO_4 and 20 ml standard biiodate solution. Dilute to 200 ml and titrate liberated iodine with thiosulfate titrant, adding starch toward end of titration, when a pale straw color is reached. When the solutions are of equal strength, 20 ml 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ should be required. If not, adjust the $\text{Na}_2\text{S}_2\text{O}_3$ solution to 0.025 M.

g. Potassium fluoride solution: Dissolve 40 g $\text{KF} \cdot 2\text{H}_2\text{O}$ in distilled water and dilute to 100 ml.

Method: Azide Modification of Idometric method

Sample analysis: To the sample collected in a 250 to 300 ml bottle, add 1 ml MnSO_4 solution, followed by 1 ml alkali-iodide-azide reagent. If pipets are dipped into sample, rinse them before returning them to reagent bottles. Alternatively, hold pipet tips just above liquid surface when adding reagents, stopper carefully to exclude air bubbles and mix by inverting bottle a few times. When precipitate has settled sufficiently (to approximately half the bottle volume) to leave clear supernate above the manganese hydroxide floc, add 1 ml conc H_2SO_4 .

Restopper and mix by inverting several times until dissolution is complete. Titrate a volume corresponding to 200 ml original sample after correction for sample loss by displacement with reagents. Thus, for a total of 2 ml (1 ml each) of MnSO_4 and alkali-iodide-azide reagents in a 300 ml bottle, titrate $200 \times 300 / (300 - 2) = 201$ ml.

Titrate with 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ solution to a pale straw color. As a few drops of starch solution and continue titration to first disappearance of blue color. If end point is overrun,

back-titrate with 0.0021M bi-iodate solution added dropwise, or by adding a measured volume of treated sample. Correct for amount of bi-iodate solution or sample. Disregard subsequent recolorations due to the catalytic effect of nitrite or to traces of ferric salts that have not been complexed with fluoride.

Table 15. Range of BOD_5 values and percent of sample dilution

BOD_5 Range	% Samples
20,000-70,000	0.01
10,000-25,000	0.02
4,000-14,000	0.05
2,000-7,000	0.1
1,000-3,500	0.2
400-1,400	0.5
200-700	1.0
100-350	2.0
40-140	5.0
20-70	10.0
10-35	20.0
4-14	50.0
0-7	100.00

Calculation:

a. For titration of 200 ml sample, 1 ml 0.025 $\text{Na}_2\text{S}_2\text{O}_3$ = 1 ml/l DO.

b. BOD_5 BOD_5 (mg/l) = $(D_1 - D_2)/P$

Where D_1 = Dissolved Oxygen number in first day (mg/l)

D_2 = Dissolved Oxygen number in the 5th day (mg/l)

P = ratio of sample dilution

3. Chemical Oxygen Demand (COD)

Principle: The organic matter is oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ under acidic conditions. The excess oxidiser is titrated by ferrous ammonium sulfate, whereby the consumed dichromate can be calculated in term of oxygen equivalent.

Apparatus:

Reflux apparatus, consisting of 500 or 250 ml erlenmeyer flasks with ground glass 24/40 neck and 300 mm jacket Liebig, West, or equivalent condenser with 24/40 ground glass joint and a hot plate having sufficient power to produce at least 1.4 KW/cm² of heating surface, or equivalent.

Reagents:

a. *Standard potassium dichromate solution, 0.0417 M:* Dissolve 12.259 g K₂Cr₂O₇, primary standard grade, previously dried at 103 °C for 2 h, in distilled water and dilute to 1,000 ml.

b. *Sulfuric acid reagent:* Add Ag₂SO₄, reagent or technical grade, crystals or powder, to conc. H₂SO₄ at the rate of 5.5g Ag₂SO₄/kg H₂SO₄. Let stand 1 to 2 days to dissolve Ag₂SO₄

c. *Ferriin indicator solution:* Dissolve 1.485 g 1,10-phenanthroline monohydrate and 695 mg FeSO₄·7H₂O in distilled water and dilute to 100 ml. This indicator solution may be purchased already prepared.

d. *Standard ferrous ammonium sulfate (FAS) titrant, approximately 0.25 M:* Distilled water. Add 20 ml conc H₂SO₄, cool, and dilute to 1000 ml. Standardize this solution daily against standard K₂Cr₂O₇ solution as follows:

Method: Dichromate Open Reflux Method

Table 16. Concentrations of Chemicals used for sample size

Sample Size (ml)	0.25 N Standard Dichromate (ml)	Conc. H ₂ SO ₄ with Ag ₂ SO ₄ (ml)	Hg ₂ SO ₄ (ml)	Normality of Fe(NH ₄) ₂ (SO ₄) ₂	Final volume before titration (ml)
10.0	5.0	15	0.2	0.05	70
20.0	10.0	30	0.4	0.1	140
30.0	15.0	45	0.6	0.15	210
40.0	20.0	60	0.8	0.2	280
50.0	25.0	75	1.0	0.25	350

Calculation:

$$1. \text{ Molarity of FAS} = \frac{\text{Volume K}_2\text{Cr}_2\text{O}_7 \text{ (ml)} \times 0.25}{\text{Volume FAS used in titration (ml)}}$$

$$2. \text{ COD (mg O}_2\text{/l)} = \frac{(\text{A}-\text{B}) \times \text{N} \times 8000}{\text{ml Sample}}$$

where A = ml FAS used for Blank
 B = ml FAS used for Sample and
 M = molarity of FAS

4. Sulfate

Principle: Sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride (BaCl_2) so as to form barium sulfate (BaSO_4) crystals of uniform size. Light absorbance of the BaSO_4 suspension is measured by a photometer and the SO_4 concentration is determined by comparison of the reading with a standard curve.

Apparatus:

a. Magnetic stirrer: Use a constant stirring speed. It is convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate stirring speed. Use magnets of identical shape and size. The exact speed of stirring is not critical, but keep it constant for each run of samples and standards and adjust it to prevent splashing.

b. Photometer: One of the following is required, with preference in the order given:

- 1) Nephelometer.
- 2) Spectrophotometer, for use at 420 nm, providing a light path of 2.5 to 10 cm
- 3) Filter photometer, equipped with a violet filter having maximum transmittance near 420 nm and providing a light path of 2.5 to 10 cm.

c. Stopwatch or electric timer

d. Measuring spoon, capacity 0.2 to 0.3 ml.

Reagents:

a. *Buffer solution A:* Dissolve 30 g magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 5 g sodium acetate, $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 1 g potassium nitrate, KNO_3 , and 20 ml acetic acid, CH_3COOH (99%), in 500 ml distilled water and make up to 1000 ml.

b. *Buffer solution B* (required when the sample SO_4^{2-} concentration is less than 10 mg/l): Dissolve 30 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 5 g $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 1 g KNO_3 , 0.111 g sodium sulfate, Na_2SO_4 , and 20 ml acetic acid (99%) in 500 ml distilled water and make up to 1,000 ml.

c. *Barium chloride*: BaCl_2 , crystals, 20 to 30 mesh. In standardization, uniform turbidity is produced with this mesh range and the appropriate buffer.

d. *Standard sulfate solution*: Prepare a standard sulfate solution as described in (1 or 2) below; 1 ml = 100 $\mu\text{g SO}_4^{2-}$

1) Dilute 10.4 ml standard 0.0200N H_2SO_4 titrant specified in Alkalinity to 100 ml with distilled water.

2) Dissolve 0.1479 g anhydrous Na_2SO_4 in distilled water and dilute to 1,000 ml.

Method: Turbidimetric method

a. Formation of barium sulfate turbidity: Measure 100 ml sample, or a suitable portion made up to 100 ml, into a 250 ml erlenmeyer flask. Add 20 ml buffer solution and mix in stirring apparatus. While stirring, add a spoonful of BaCl_2 , crystals and begin timing immediately. Stir for 60 s at constant speed.

b. Measurement of barium sulfate turbidity: After stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at 5 mins.

c. Preparation of calibration curve: Estimate SO_4^{2-} concentration in sample by comparing turbidity reading with a calibration curve prepared by carrying SO_4^{2-} standard through the entire procedure. Space standards at 5 mg/l increments in the 0 to 40 mg/l SO_4^{2-} range. Above 40 mg/l accuracy decreases and BaSO_4 suspensions lose stability. Check reliability of calibration curve by running a standard with every three or four samples.

d. Correction for sample color and turbidity: Correct for sample color and turbidity by running blanks to which BaCl_2 is not added.

Calculation:

$$\text{mg SO}_4^{2-}/\text{l} = \frac{\text{mg SO}_4^{2-} \times 1,000}{\text{ml sample}}$$

5. Suspended Solids (SS)

Principle: Sample is poured through a weighed filter, which is subsequently dried. The residue results in an increased weight that, after drying.

Apparatus:

- a. Evaporating dishes: Dishes of 10 ml capacity made of porcelain, 90 mm diam.
- b. Buchner funnel
- c. Suction pump
- d. Drying oven, for operation at 103 °C to 105 °C.
- e. Analytical balance, capable of weighing to 0.1 mg.
- f. Whiteman GF/C

Method: Gravimetric Method

Sample analysis: Assemble filtering apparatus and filter and suction. Wet filter with a small volume of distilled water to seat it. Filter a measured volume of well-mixed sample through the glass fiber filter. Wash with three successive 10-ml volumes of distilled water, allowing complete drainage between washings and continue suction for about 3 mins after from filtration is complete. Carefully remove filter from filtration apparatus and transfer to an aluminum or stainless steel planchet as a support. Alternatively, remove the crucible and filter combination from the crucible adaptor if a Gooch crucible is used. Dry for at least 1 h at 103 °C to 105 °C in an oven, cool in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight loss is less than 4 % of previous weight or 0.5 mg, which ever is less.

Calculation:

$$\text{Suspended Solid (mg/l)} = \{(B-A) \times 1,000\} / \text{Samples (ml)}$$

where A = weight of filter + dried residue, mg, and
 B = weight of filter, mg.

6. Total Kjeldahl Nitrogen and Ammonia Nitrogen

Principle: During acidic digestion, organic nitrogen is converted into free ammonium. After addition of base, all ammonia is distilled from the now alkaline medium, absorbed in boric acid, and titrated with H₂SO₄

Apparatus:

a. Digestion apparatus: Kjeldahl flasks with a total capacity of 800 ml yield the best results. Digest over a heating device adjusted so that 250 ml water at an initial temperature of 25 °C can be heated to a rolling boil in approximately 5 mins. For testing, preheat heaters for 30 mins electric. A heating device meeting this specification should provide the temperature range of 365 °C to 370 °C for effective digestion.

b. Distillation apparatus: Arrange a borosilicate glass flask of 800 to 2,000 ml capacity attached to a vertical condenser so that the outlet tip may be submerged below the surface of the receiving acid solution. Use an all borosilicate glass apparatus or one with condensing units constructed of block tin or aluminum tubes.

Reagents:

Prepare all reagents and dilutions in ammonia-free water.

a. *Mercuric sulfate solution*: Dissolve 8 g red mercuric oxide, HgO, in 100 ml 6 N H₂SO₄

b. *Digestion reagent*: Dissolve 134 g K₂SO₄ in 650 ml water and 200 ml conc H₂SO₄. Add, with stirring, 25 ml mercuric sulfate solution. Dilute the combined solution to 1 litre with water. Keep at a temperature close to 20 °C to prevent crystallization.

c. *Sodium hydroxide-sodium thiosulfate reagents*: Dissolve 500 g NaOH and 25 g Na₂S₂O₂·5H₂O in water and dilute to 1 litre.

d. *Sodium hydroxide*, NaOH, 6 N

Method: Macro Kjeldahl Method

a. Selection of sample volume and sample preparation: Place a measured volume of sample in an 800 ml, kjeldahl flask. Select sample size from the following tabulation: If necessary, dilute sample to 300 ml and neutralize to pH 7, and dechlorinate.

b. Ammonia removal: Add 25 ml borate buffer and then 6 N NaOH until pH 9.5 is reached. Add a few glass beads or boiling chips and boil off 300 ml. If desired, distill this fraction and determine ammonia nitrogen. Alternatively, if ammonia has been determined by the distillation method, use residue in distilling flask for organic nitrogen determination.

For sludge and sediment samples, weight wet sample in a crucible or weighing bottle, transfer contents to a kjeldahl flask, and determine kjeldahl nitrogen. Follow a similar procedure for ammonia nitrogen and organic nitrogen determined by difference. Determinations of organic and kjeldahl nitrogen on dried sludge and sediment samples are not accurate because drying results in loss of ammonia salts. Measure dry weight of sample on a separated portion.

c. Digestion: cool and add carefully 50 ml digestion reagent (or substitute 10 ml conc H_2SO_4 , 6.7 g K_2SO_4 , and 1.25 ml HgSO_4 solution) to distillation flask. Add a few glass beads and, after mixing, heat under a hood or with suitable ejection equipment to remove acid fumes. Boil briskly until the volume is greatly reduced (to about 25 to 50 ml) and copious white fumes are observed (fumes may be dark for samples high in organic matter). Then continue to digest for an additional 30 mins. As digestion continues, colored or turbid samples will turn clear or straw-colored. After digestion, let flask and contents cool, dilute to 300 ml with water, and mix. Tilt flask and carefully add 50 ml hydroxide-thiosulfate reagent to form an alkaline layer at flask bottom. Connect flask to steam out distillation apparatus and shake flask to insure complete mixing. A black precipitate, HgS , will form, and the pH should exceed 11.

d. Distillation: Distill and collect 200 ml distillate below surface of 50 ml absorbent solution. Use plain boric acid solution when ammonia is to be determined by nesslerization and use indicating boric acid for a titrimetric finish. Use 50 ml 0.04 N H_2SO_4 solution for collecting distillate for manual phenate, nesslerization or electrode methods. Extend tip of condenser well below level of absorbent solution and do not let temperature in condenser rise above 29 °C. Lower collected distillate free of contact with delivery tube and continue distillation during last 1 or 2 mins to cleanse condenser.

Table 17. Ammonia Nitrogen Sample dilution

Ammonia Nitrogen in Sample (mg/l)	Sample Volume (ml)
5-10	250
10-20	100
20-50	50
50-100	25

Calculation:

$$\text{mg/l NH}_3\text{-N} = [(A-B) \times 280] / \text{ml Sample}$$

where $\text{NH}_3\text{-N}$ = Ammonia Nitrogen
 A = ml sulfuric acid used for samples
 B = ml sulfuric acid used for blank

$$\text{mg/l TKN} = (\text{mg/l Org nitrogen}) + (\text{mg/l NH}_3\text{-N})$$

APPENDIX C



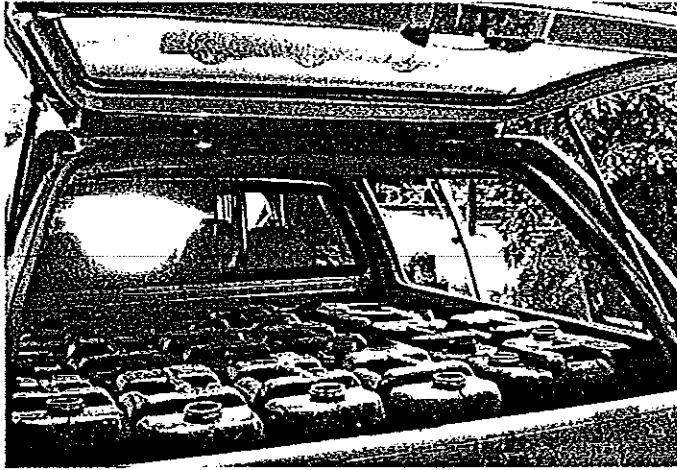
Picture C-1. The rubber trap at selected concentrated latex factory



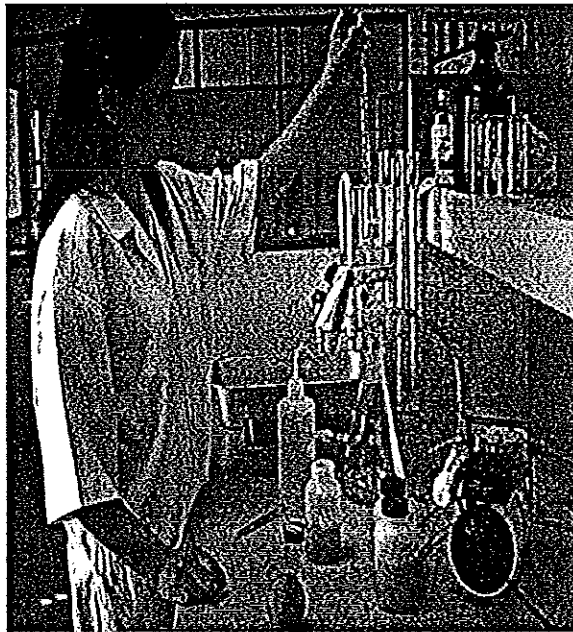
Picture C-2. The aeration pond at selected concentrated latex factory



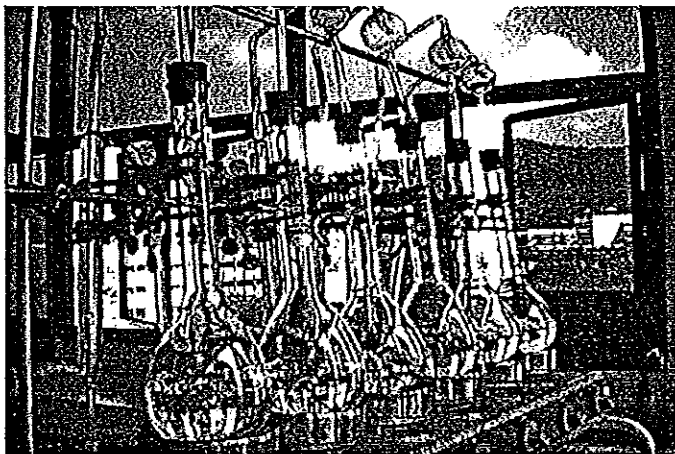
Picture C-3. Sampling point at selected concentrated latex factory



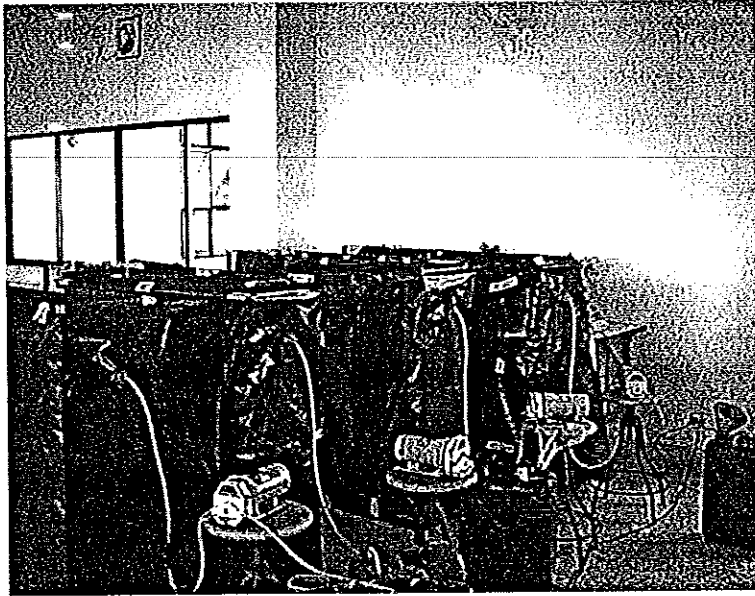
Picture C-4. Wastewater in tanks



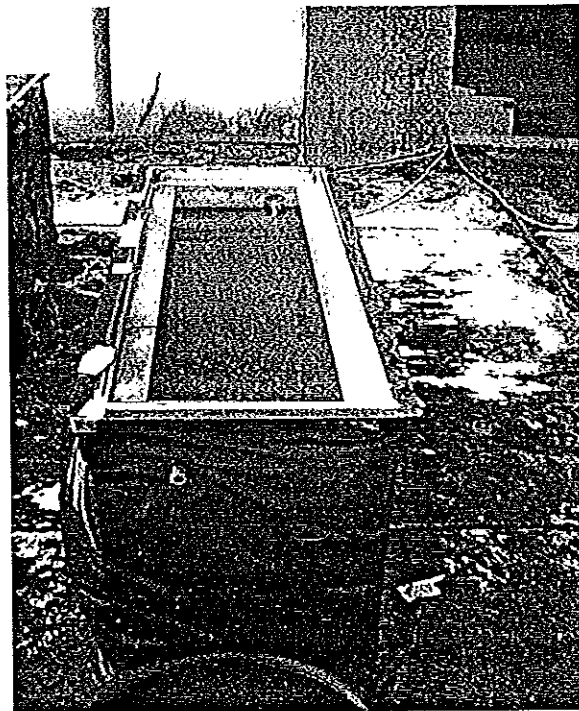
Picture C-5. Suspended solids analysis



Picture C-6. Ammonia nitrogen and TKN analytical device



Picture C-7. Experimental anaerobic ponds



Picture C-8. Experimental oxidation ponds

APPENDIX D

Glossary

- (1) **Aerobic** - having molecular oxygen present; growing in the presence of air.
- (2) **Anaerobic** - the absence of oxygen; able to live or grow in the absence of free oxygen.
- (3) **Biogas** - produced gas from the organic matter digestion by bacteria in anaerobic condition.
- (4) **BOD₅ loading** - a parameter in wastewater treatment system design, common units are (kg BOD/m³.d or kg BOD/m².d).
- (5) **Denitrification** - an anoxic process in which either an organic or inorganic electron-donating substrates are oxidized at the expense of reducing nitrate (NO₃⁻) or nitrite (NO₂⁻) to dinitrogen gas (N₂).
- (6) **Hydraulic Retention Time** - Time for liquid to pass through system.
- (7) **Nitrification** - biological oxidation of NH₄⁺ to NO₂⁻ and NO₃⁻, or a biologically induced increase in the oxidation state of nitrogen.
- (8) **Methanogens** - a type of anaerobic metabolism that results in methane production
- (9) **pH** - a measurement of the acidity or alkalinity of a solution
- (10) **Photosynthesis** - the formation of carbohydrates from carbon dioxide and water by the action of solar energy on green plants containing chlorophyll.
- (11) **Sludge** - the solid portion of sewage.
- (12) **Sulfate Reduction** - Sulfate reducing bacteria can be utilized to convert sulfate (SO₄²⁻) or sulfite (SO₃²⁻) to sulfide (S²⁻). The bacteria utilize electron-donating substrates present in wastewater or added substrates for the reduction of sulfate. The substrates are either partially oxidized (e.g. to acetate) or fully oxidized to carbon dioxide. Sulfate behaves as an alternative electron acceptor to support anaerobic respiration.
- (13) **WSP** - Waste Stabilization Ponds, Natural waste treatment systems are designed to obtain maximum benefit from the energy in wastewater, along with that provided by sunlight, wind, and gravity. They have been used for treating agricultural, municipal, and industrial wasteliquids and sludges and are often combined with conventional treatment systems to improve effluent quality. The feasibility of a natural treatment system depends mostly on the climate, soil conditions, available land, and waste characteristics.

APPENDIX E

Example of Calculation of Anaerobic and Oxidation Pond for Treatment of Wastewater from Concentrated Latex Factory

Assume	BOD ₅ of influent, L _i =	7,430 mg/l
	Q =	350 m ³ /d

Anaerobic Pond I

BOD ₅ of influent, L _i =	7,430 mg/l
BOD ₅ Loading =	200 g BOD ₅ /m ³ .d
Volume of pond required based on volumetric BOD Loading =	13,003 m ³
Assume Depth =	3.5 m
Surface area of pond required =	3,720 m ²
Assume BOD ₅ removal Efficiency =	83 %
BOD ₅ of Effluent from this pond =	1,263 mg/l

Anaerobic Pond II

BOD ₅ of influent, L _i =	1,263 mg/l
BOD ₅ Loading =	200 g BOD ₅ /m ³ .d
Volume of pond required based on volumetric BOD ₅ Loading =	2,210 m ³
Assume Depth =	3.5 m
Surface area of pond required =	631 m ²
Assume BOD ₅ removal Efficiency =	83 %
BOD ₅ of Effluent from this pond =	215 mg/l

Oxidation Pond I

BOD ₅ of influent, L _i =	215 mg/l
Surface BOD ₅ Loading =	7 g BOD ₅ / m ² .d
Surface area of pond required =	1,0750 m ²
Assume Depth =	1.3 m
Volume of pond =	13,975 m ³
Assume BOD ₅ removal Efficiency =	53 %
BOD ₅ of Effluent from this pond =	101 mg/l

Oxidation Pond II

BOD ₅ of influent, L _i =	101 mg/l
Surface BOD ₅ Loading =	7 g BOD ₅ / m ² .d
Surface area of pond required =	5,050 m ²
Assume Depth =	1.3 m
Volume of pond =	6,565 m ³
Assume BOD ₅ removal Efficiency =	53 %
BOD ₅ of Effluent from this pond =	48 mg/l

Oxidation Pond III

BOD ₅ of influent, L _i =	48 mg/l
Surface BOD ₅ Loading =	7 g BOD ₅ / m ² .d
Surface area of pond required =	2,400 m ²
Assume Depth =	1.3 m
Volume of pond =	3,120 m ³
Assume BOD ₅ removal Efficiency =	53 %
BOD ₅ of Effluent from this pond =	23 mg/l

Oxidation Pond IV

BOD ₅ of influent, L _i =	23 mg/l
Surface BOD ₅ Loading =	7 g BOD ₅ / m ² .d
Surface area of pond required =	1,150 m ²
Assume Depth =	1.3 m
Volume of pond =	1,495 m ³
Assume BOD ₅ removal Efficiency =	53 %
BOD ₅ of Effluent from this pond =	11 mg/l

Note: Assume BOD₅ removal efficiency is same as in the experiments.

VITAE

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Education Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Science (Biotechnology)	Prince of Songkla University	1997
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