SUSTAINABLE TREATMENT OF RUBBER LATEX PROCESSING WASTEWATER

The UASB-System Combined with Aerobic Post - Treatment

Nguyen Trung Viet

Promotor: Prof. dr. ir. G. Lettinga
bijzonder hoogleraar in de anaerobe zuiveringstechnologie en hergebruik

Nguyen Trung Viet

SUSTAINABLE TREATMENT OF RUBBER LATEX PROCESSING WASTEWATER

The UASB-System Combined with Aerobic Post - Treatment

Proefschift
ter verkrijging ven de graad van dotor
op gezag van de rector magnificus
van Wageningen Universiteit,
dr. C. M. Karssen
in het openbaar te verdedigen
op maandag 25 Oktober 1999
des namiddags te 16:00 uur in de Aula

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Nguyen Trung Viet

Sustainable treatment of rubber latex processing wastewater/Nguyen Trung Viet. – [S.I : S.n.]
Thesis Wageningen University. With ref. – With summary in Ducth and Vietnamese.

ISBN 90-5808-103-6

Subject headings: wastewater/anaerobic treatment/rubber latex processing.

To my parents,
my wife,
my children Tran Viet and Ha Viet,
and all friends.

Acknowledgements

I would like to express my thankful acknowledgement to my "promotor" Gazte Lettinga for giving me not only the opportunity to study at his department, but also for supporting the development of anaerobic wastewater treatment for some agro-industries in Vietnam.

The financial aid of WOTRO (Stichting voor "Wetenschappelijk Onderzoek van de Tropen") is greatfully acknowledged. It has been a most significant support for my laboratory in Vietnam.

I thank Dora Lettinga for her enjoyable hospitality: she made me feel at home when I was staying in the Netherlands.

I am also grateful to the members of the analytical staff, Johannes van der Laan and Martin de Wit for their help with the chromatographic determinations, Sjoerd Hobma and Jo Ackerman-Jacobs for the chemical analyses. I acknowledge Liesbeth Kesaulya-Monster and Heleen Vos for their cordiality and assistance at the secretary's office.

It was a pleasure to work together with the anaerobic group of this department, among them Look Hulshoff Pol, Jules van Lier, Marjo Lexmond, Joost van Buuren, Salih Rebac and some master' students.

I have highly appreciated the support of Vietnamese colleagues, among them Bui Thuy Phuong, Nguyen Thi Phuong Loan, Huynh Ngoc Phuong Mai, Hoang Quoc Hung who assisted me in laboratory work and Tran Thi My Dieu and Bui Thi Doan Trang who helped me in formatting this thesis.

The substantial support received from my father, Nguyen Nhu, my mother, Nguyen Phuc Lien Chau, my wife, Tran Thuy Lien, my sons, Nguyen Tran Viet and Nguyen Tran Ha Viet (Holland – Vietnam) was very important for me, especially when I stayed in the Netherlands. For this I am immensely indebted to them.

PROPOSITIONS

1. With his statement, "The Capetown group solved the riddle of dense granule development as well as the mechanism of the UASB", Speece makes clear that he either did not make a thorough literature search on the sludge granulation topic, or did not understand the crucial importance of a factor like 'selection pressure' in anaerobic sludge granulation (R. E. Speece, "Anaerobic Biotechnology for Industrial Wastewater", page 145).

2. The major problem in the first start-up of a full scale UASB-reactor at a rubber latex processing factory in Vietnam is meeting properly the guidelines for sludge granulation.

3. Extensive wastewater (post-) treatment methods like lagoons should not be applied in densily populated regions/countries.

4. Investment in improving transport facilities (e.g. road, vehicles) will lead to significant lower pollution loads in the rubber latex processing industry in Vietnam.

5. Developing countries tentatively need very much applied rather than academically oriented research, both technological and sociological, particularly in the field of environmental protection.

6. An excellent place to stay for Vietnamese PhD-researcher during winter time in Wageningen Agricultural University is 30^0C room in the Biotechnion.

7. A parallel between a wastewater treatment system and the Vietnamese education practice is that the influent is generally of a poor quality while the effluent has to meet high standards.

8. After some adaptation "Hutspot" and "New herring" are really the most delicious typical Dutch foods for some Vietnamese.

9. The first action to be undertaken for accomplishing a robust and sustainable environmental protection is to educate the people, or at least to provide them with adequate and understandable information about pollution prevention and treatment and reuse of waste and wastewater.

Propositions belonging to the thesis "Sustainable Treatment of Rubber Latex Processing Wastewater-The UASB - System Combined with Aerobic Post-Treatment".

Nguyen Trung Viet
Wageningen 25 October 1999

CONTENTS

Chapter 1 Anaerobic wastewater treatment processes 1-1

1.1 Introduction 1-2
1.2 Anaerobic processes 1-3
1.3 Application of anaerobic processes in wastewater treatment 1-9
1.4 UASB processes 1-14
1.5 Scope of the thesis 1-17

Chapter 2 Rubber latex processing and wastewater 2-1

2.1 History of rubber production in Vietnam 2-2
2.2 The rubber tree *(Hevea brasilliensis)* 2-4
2.3 Rubber latex processing in South Vietnam (Mekong Delta) 2-6
2.4 Wastewater from rubber latex processing in South Vietnam 2-11
2.5 Environmental problems 2-16
2.6 Conclusions 2-16

Chapter 3 Feasibility studies of rubber latex processing wastewater based on the UASB process in Vietnam 3-1

3.1 Introduction 3-2
3.2 Materials and methods 3-4
3.3 The specific methanogenic activity (SMA) of sludges available in Vietnam 3-7
3.4 Anaerobic biodegradability of rubber latex processing wastewater 3-18
3.5 Anaerobic biodegradation of the protein contained in rubber latex processing wastewater with granular sludge 3-30
3.6 The effect of pH on anaerobic biodegradation of rubber latex processing wastewater with Vietnamese digested pig manure sludge 3-42
3.7 The effect of presence of O_2 and mixing conditions on the specific methanogenic activity test 3-46
3.8 The effect of storage time on the SMA of granular sludge 3-52
3.9 Conclusions 3-56

Chapter 4 Application of the UASB process to treat rubber latex processing wastewater 4-1

4.1 Introduction 4-2
4.2 Materials and methods 4-3
4.3 Granulation experiments with digested pig manure sludge (DPMS) on rubber latex processing wastewater 4-6
4.4 UASB treatment of RLP wastewater 4-16
4.5 The effect of pH on the performance of UASB system 4-28
4.6 The effect of effluent recirculation on UASB performance 4-38
4.7 Conclusions 4-51

Chapter 5 Post-treatment process, waterhyacinth and algae treatment of rubber latex processing wastewater 5-1

5.1 Introduction 5-2
5.2 Materials and methods 5-4

5.3 Results 5-7
5.4 Discussion 5-16
5.5 Conclusions 5-19

Chapter 6 Full-scale experiment treating rubber latex processing wastewater 6-1

6.1 Introduction 6-2
6.2 Design of full-scale rubber latex processing wastewater treatment plant 6-2
6.3 Results and discussion 6-8
6.4 Conclusions 6-13

Chapter 7 Summary and discussion 7-1

7.1 Introduction 7-2
7.2 Objective of the thesis 7-2
7.3 Characteristics of rubber latex processing wastewater in Vietnam 7-3
7.4 Feasibility studies of the UASB-reactor for treatment of rubber latex processing wastewater in Vietnam 7-3
7.5 Lab-scale UASB treatment of rubber latex processing wastewater in Vietnam 7-4
7.6 Aquatic plant pond system, post-treatment 7-5
7.7 Full-scale wastewater treatment plant 7-5
7.8 Suggestion for future research 7-6

Hoofdstuk 7 Samenvatting en discussie 7-7

7.1 Inleiding 7-8
7.2 Doel van het proefschrift 7-8
7.3 Eigenschappen van het rubber/latex afvalwater in Vietnam 7-9
7.4 Toepasbaarheiasonderzoek van de UASB-reactor voor de behandeling van rubber/latex afvalwater in Vietnam 7-10
7.5 Behandeling van rubber/latex afvalwater met laboratoriumschaal UASB-reactoren 7-10
7.6 Systeem van een vijver met waterplanten nazuivering 7-11
7.7 Behandeling van RLP-afvalwater op praktijkschaal 7-12
7.8 Aanbevelingen voor verder onderzoek 7-12

Chương 7 Tóm tắt và thảo luận 7-13

7.1 Giới thiệu chung 7-14
7.2 Mục đích của luận án 7-14
7.3 Tính chất của nước thải sơ chế mủ cao su tại Việt Nam 7-15
7.4 Nghiên cứu khả thi sử dụng bể UASB xử lý nước thải sơ chế mủ cao su tại Việt Nam 7-16
7.5 Xử lý nước thải sơ chế mủ cao su bằng mô hình phòng thí nghiệm UASB tại Việt Nam 7-16
7.6 Hệ thống hồ sinh vật, xử lý triệt để 7-17
7.7 Trạm xử lý nước thải 7-18
7.8 Kiến nghị các nghiên cứu tiếp theo 7-18

References 8-1

Curriculum Vitae

Chapter 1

Anaerobic Wastewater Treatment Processes

1.1 INTRODUCTION

Since 1990, after the transition from a purely command economy towards more market oriented growth models, Vietnam has developed economically rapidly with a growth rate of 9.0-9.5% a year, which belongs to the highest economical growth rates among South-East Asian countries which has been the most active economical area in the world for a number of decades. This high economic growth was a result of a rapid industrialization and exploitation of natural resources. Indeed, this development has given economic benefit and also increased living standards to majority of the people. But the impulse for rapid economic development is far stronger than the social incentives for scientific investigation or for the advancement of capacities in government resource management. As a consequence of this outright disregard of the impact of these activities to the environment, numerous serious environmental problems have arisen (Lohani, 1984). Especially the untreated wastes discharged to the environment from factories and industrial areas, from import-export zones and from densely populated urban areas result in tremendous environmental problems. A common visible problem is the heavy water pollution, because the wastes (wastewater and solid waste as well) are generally discharged to the receiving waters. One of industries with a high environmental pollution potential concerns the rubber latex processing (RLP) industry.

Annually, more than 29 RLP factories with capacity of 170,000 ton/year (Chapter 2) discharge approximately 4.2-5.1 million cubic meter of wastewater with high pollution strength (Table 1.1) to the environment, apart from the pollution of receiving water bodies, it also causes heavy pollution to the air. This pollution affects the health of residents living in the neighbourhood of the factories quite detrimentally.

At present four wastewater treatment plants have been installed at 4 RLP factories. One of the treatment plants uses the aerobic activated sludge process and the others use the stabilization ponds system with aquatic plants, such as waterhyacinth or algae. The operation experiences of both these types of systems show a number of serious drawbacks, viz.:

Activated Sludge Process

- High investment cost for aeration tanks (concrete work), because of the large volumes required and for equipment;
- Most equipment had to be imported;
- High maintenance cost due to high energy consumption;
- Production of huge amounts of exceed sludge;
- Clogging problems with pumping systems due to accumulation of rubber block;

Stabilization Pond System

- Air pollution with very offensive smell and accumulation of rubber on surface of anaerobic pond;
- Very large area requirements, i.e. a stabilization pond system with surface area of 2 ha does not suffice for treating an amount of 800 m^3 of wastewater a day;
- Ground water pollution;
- High algae concentration (up to 120 mg/L) in effluent.

Table 1.1 Characteristic of effluent wastewater from RLP factory in South Vietnam

Parameters	Unit	Concentration
pH		5.59 - 5.72
Acidity	mg $CaCO_3$/L	160 – 220
Alkalinity	mg $CaCO_3$/L	150 – 210
COD	mg/L	1.811 - 4.589
BOD	mg/L	1.720 - 4.360
SS	mg/L	180 – 250
N-NH_3	mg/L	200 – 296
N-Org	mg/L	800 - 1,500
Glucose	mg/L	200 – 600
VFA	mg CH_3COOH/L	1,200 - 1,800

In view of the mentioned big environmental problems and regarding the requirements of RLP factories, a thorough study of various possible treatment processes looks essential in order to enable the selection of the appropriate technology for RLP wastewater treatment under Vietnamese conditions, both with respect to the economic and technology.

Among available wastewater treatment processes, anaerobic process, especially the so-called UASB-process has been chosen as main direction of the study.

1.2 ANAEROBIC PROCESSES

Natural life on earth has started with anaerobic bacteria. Anaerobic microbes mark the first sign of life on earth, *c*. 3.5 x 10^9 years ago; that of the aerobic organisms evolved later, *c*. 5 x 10^8 years ago. The earliest microbial technologies were developed some 6,000-8,000 years ago; they concerned anaerobic fermentations for the production of methanol, lactic and other fatty acids (Hughes, 1979), and a their application were mainly in food processing.

Anaerobic microorganisms and processes have attracted the interest and attention of scientists and engineers by the end of the last century, mainly for reason that many of these organisms and processes either improved or spoiled food and drinks. In particular the anaerobic processes which were found capable to convert organic waste compounds into methane attracted the attention (Zehnder, 1988).

In the field of waste treatment, the first anaerobic processes developed were those treating settled wastewater solids (sewage sludge), i.e. systems developed by Louis H. Mouras, France in 1860 (Buswell, 1957), and by Donald Cameron for the city of Exeter, U.K in 1895 (Nyns *et al.*, 1979). Increasing attention has been paid to anaerobic treatment processes over the last 2-3 decades, particularly also as one of the consequence of the energy crisis in 1973. At that time the researchers working in this particular field constituted only a very small group, but since then it developed rapidly and the group of scientist dealing with anaerobic processes in the meantime has become a good sized 'community' that is still steadily expanding (Zehnder, 1988; Lettinga, 1995).

Even though they have been applied for waste treatment since beginning of the twentieth century ("Emscher brunner" in Germany), anaerobic systems have long been considered by the 'established sanitary engineering world' as being inherently too inefficient and too slow for practical application in wastewater treatment. This especially was the case in the industrialized world (Zehnder, 1988). However, despite this reluctant attitude and commercial disinterest of the established wastewater engineering world, more recently the anaerobic wastewater treatment (AnWT) concept has developed rapidly and sustainably which the worldwide increased interest can be attributed partially to the principle advantages AnWT offers over the conventional aerobic processes (Zehnder, 1988; Lettinga *et al.*, 1979, 1980, 1983a, 1983b, 1995; de Zeew, 1984; Speece, 1996), viz.:

- Its high process stability when operated properly.
- The high degree of waste stabilization that can be achieved at high organic loading rates, consequently at minor space requirements.
- Low production of excess of stabilized thick sludge, which results in a very significant reduction of waste biomass disposal cost.
- The good dewatering characteristics of excess sludge.
- The low nutrient requirement, consequently the considerable reduction in cost of nitrogen and phosphorus supply.
- Elimination of off-gas air pollution.
- Very low consumption of high grade energy, if any at all.
- Energy recovery in the form of methane.
- Little if any foaming with wastewaters containing surfactants.
- Biodegradation of aerobic non- or poorly biodegradable compounds.
- Reduction of chlorinated organic toxicity levels.
- Enabling seasonal treatment, because adapted anaerobic sludge can remain unfed for a period of one year and more without any appreciable deterioration.

Perhaps the most important advantages of AnWT are that organic matter is converted into methane and that sludge can be preserved unfed for a considerable period of time.

Since last two decades considerable emphasis has been put in the world on programs developing biogas digesters, particularly in various tropical countries, e.g. China, India, Thailand, Vietnam (Nyns *et al.*, 1979).

At present, the number of lab-scale, pilot-scale and full scale investigations made on AnWT and the applications already realized is quite impressing.

Anaerobic biological reactions and microbiology

In anaerobic waste treatment, complex organic compounds are biologically converted to methane, carbon dioxide, hydrogen and hydrogen sulfide (if sulfate present). The conversion proceeds via a sequence of successive bacterial processes and a variety of microbiological reactions. The bacterial processes depend strongly on various genera of obligate and facultative bacteria, on the waste characteristics and environmental conditions as well, e. g. pH, temperature, presence of inhibitory/toxic compounds or products (intermediates), nature and characteristics of organic compounds, presence and availability of nutrients, etc.

The anaerobic microbial processes and factors affecting the processes have been studied by many researchers, and have been well reviewed and described in detail by Hughers (1979), Pfeffer (1979), Zeikus (1979), McInerney and Bryant (1979), Pavlostathis and Giraldo-Gomez (1991).

In general and for practical purposes, the anaerobic digestion process can be sub-divided into four main processes (McCarty, 1964; Pfeffer, 1979) and three trophic anaerobic microorganisms groups can be distinguished (Iza *et al.* 1991):

- Hydrolysis
- Acidogenesis (fermentation)

- Acetogenesis, and
- Methanogenesis.

Many specific substrates, intermediates and anaerobic microbial communities are involve (see Fig. 1.1).

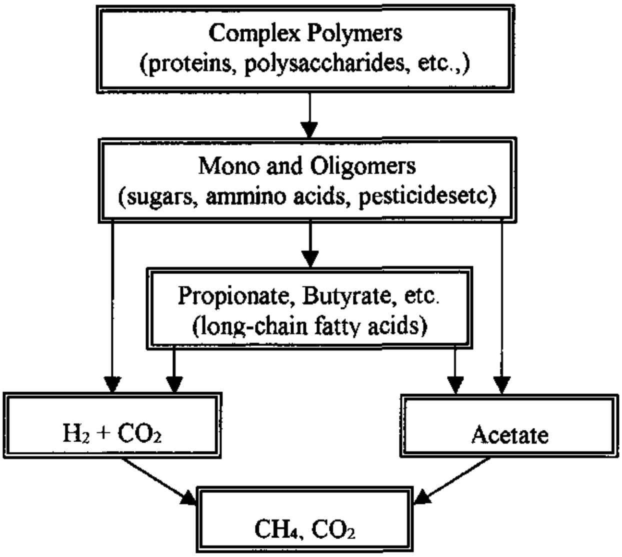


Fig. 1.1 Anaerobic digestion of complex substrates (After Guier and Zehnder, 1983).

Hydrolysis. As bacteria only can take up organic matter in soluble form, the microbial assimilation or heterogeneous, particulate biopolymers requires the breakdown or hydrolysis as the first step (Stronach *et all.*, 1986). In the hydrolysis or liquifraction step, insoluble higher molecular organic compounds, such as lipids, proteins and carbohydrates, are hydrolyzed to soluble simpler compounds, such as pyruvate, amino-acids, sugars, etc. In other words, hydrolysis is the conversion of bio-polymers into individual monomers. These reactions are catalyzed by extracellular enzymes such as cellulases, amylases, proteases and lipases, which are excreted by hydrolytic bacteria. Populations of 10^8-10^9 hydrolytic bacteria per mL of mesophilic sewage sludge was found, consisting of proteolytic (*Eubacterium)* and cellulolytic (*Clostridium)* bacteria (Zeihus, 1979). But detailed studies on generic identification of the predominant hydrolytic bacteria in anaerobic digester have not been well reported.

In many cases, especially for wastes containing a high concentration of suspended solids, hydrolysis is the slowest process. It depends on the generation of the required extracellular enzyme (Koster, 1989) and the process is influenced by factors like pH, temperature and detention time (Pfeffer, 1979; Ghosh and Klass, 1978; Guijer and Zehnder, 1983), the characteristics of organic compounds (Zehnder, 1988; Chan and Pearson, 1970).

Acidogenesis. In acidogenesis, the products of hydrolysis step viz. the long chain fatty acids, amino-acids, sugars and alcohols are metabolized intra-cellularly by hydrolytic and non hydrolytic bacteria. The main products of this process are volatile fatty acids (VFA) like acetate, propionate, butyrate, valerate and H_2/CO_2, while also formate, lactate can be formed, depending significantly on factors like the composition of organic matter, the acidogenic bacteria present, the environmental conditions. The process is conducted by fermentative and acidogenic bacteria, which are rather resistant to low pH value. As a consequence the formation of VFA can still proceed at pH values as low as pH 4.

Acetogenesis. In the acetogenesis step amino-acids, simple sugars are fermented to acetate and the higher VFA such as propionate, butyrate are oxidized microbiologically to acetate, while also H_2/CO_2 can be converted into acetate. These reactions depend mainly on the environmental conditions.

Table 1.2 Acetogenic reaction

Reaction
$CH_2CHOHCOO^- + 2H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 2H_2$
$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$
$CH_3CH_2CH_2CH_2COO^- + 2H_2O \rightarrow CH_3COO^- + CH_3CH_2COO^- + H^+ + 2H_2$
$CH_3CH_2OH + H_2O \rightarrow CHCOO^- + H^+ + 2H_2$
$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$

Methanogenesis. In the methanogenic step, acetate is converted into methane and CO_2, while also from H_2 and CO_2 methane can be generated. According to Jeris and McCarty (1965), McInerney and *et al.* (1979), Amith (1986) and Koster (1989), approximately 70% of methane originated from acetate and 30% from carbon dioxide reduction with hydrogen. Some methanogenic bacteria are capable to convert directly formic acid and methanol to methane.

Table 1.3 Methanogenic reactions

Reaction
$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$
$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$
$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$
$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$
$4HCOO^- + 2H^+ \rightarrow CH_4 + CO_2 + 2HCO_3^-$
$4CH_3NH_2 + 2H_2O + 4H^+ \rightarrow 3CH_4 + CO_2 + 4NH_4^+$

Methanogenic bacteria seem to microbiologically more divers than the other trophic groups associated with anaerobic digestion; populations of 10^8 methanogens per mL have been detected in sewage sludge (Zeikus, 1979). According to Zeikus *Methanobacterium, Methanospirillum, Methanosarcina* and *Methanococcus* are four dominant genera of hydrogen oxidizing methanogens, while an organism like *Methanothrix* metabolizes acetate but not H_2/CO_2. Methanogenic genera utilize a very narrow range of substrate as energy sources, some of them even only one or two compounds (McInerney *et al.*, 1979), and in general their substrates are restricted to one- (i.e. H_2/CO_2, CH_3OH, CO, HCOOH, CH_3NH_2) and two-carbon (i.e. acetate) compounds. This illustrates the big importance of the preceding steps in case of treatment of relatively complex substrates.

In general, the methanogenic bacteria can be considered to be the organisms being most sensitive with respect to pH, temperature and toxic compounds.

Based on the 'main' features of microbial populations in anaerobic digestion can be summarized as follows:

A. Hydrolytic bacteria
B. Hydrogen-producing acetogenic bacteria
C. Homoacetogenic bacteria
D. Methanogenic bacteria

The anaerobic digestion of organic matter to methane represents a quite stable processes when performed under defined (self-) controlled environmental conditions, despite the diversity of organisms that can be involved and the high substrate specificity of methanogenic bacteria. In a balanced system, population stability provides optimal conditions for anaerobic metabolism including the supply of essential nutrients, removal of inhibitory process metabolites and/or increasing specific catabolic rates (Zeikus, 1979; Kato, 1994; Lettinga, 1995).

Factors Affecting the Anaerobic Digestion

pH. Except the acidogenic process, pH affects all anaerobic processes quite strongly. In the past, pH values of 6.6-7.6 were considered suitable for all anaerobic bacteria (McCarty, 1964) with an optimum pH range between 7.0-7.2. A drop of pH below 6.6 was considered to be quite inhibitory for the methanogenic bacteria, and pH<6.2 even acute toxicity was presumed to occurs to these bacteria. But at date, the detrimental effect of lower pH-values to methanogenic bacteria has been found to believe to become significant at pH-values lower than 6.2, and the effect of pH is also related with the presence of compounds, such as ammonia, propionate and acetate, and with inhibition of other anaerobic bacteria. So acidogenic bacteria continue to produce acids down to pH-values of 4.5 (Pfeffer, 1979). A few non-methanogenic anaerobes (e.g. *Sarcina ventriculi*) even can grow at pH values as low as 2 (Zeikus, 1979).

The presumed mechanism of the detrimental pH-effect is that lower pH values favour proton reduction to hydrogen but not hydrogen oxidation to protons. Thus, methanogens may not function at low pH, because they employ oxido-reductase for hydrogen oxidation and establishment of proton gradients during catabolism of one carbon compounds and acetate. The pH also affects indirectly bacterial activities through protein structure of the cell.

Temperature. To date, it is generally accepted that anaerobic bacteria can be grouped in three optimal ranges of temperature:

1.	Psychrophilic:	10-12 °C
2.	Mesophilic:	30-35 °C
3.	Thermophilic:	50-55 °C

Changing temperature from the mesophilic range to the thermophilic range will result in the establishment of a quite different special composition of the sludge, due to the fact that many mesophilic organisms will not survive (Zeikus, 1979; Zinder, 1988; van Lier, 1995). On the other hand when decreasing the temperature from the thermophilic range to mesophilic or psychrophilic conditions, many thermophilic organisms will survive, while mesophilic and/or psychrophilic organisms possibly can grow in. Temperature obviously also influences the disassociation of VFA and ammonia, and this indirectly may affect the anaerobic bacteria.

Oxygen. It is well known that the growth and metabolism of all obligatory anaerobes are inhibited by oxygen. But it is essential to note here that the oxygen toxicity is affected by a number of factors, such as partial pressure, composition of the growth medium, and cell density (Hughes, 1979).

Redox potential (E_h). The effect of redox potential have been discussed by a number of researchers (Hughes, 1979; Pfeffer, 1979; Kato, 1994). E_h-values prevailing in anaerobic digestion generally are in the range -150 mV to -420 mV.

Heavy metals. There exist still relatively very few informations about the effect of heavy metal on anaerobic digestion. Most of relevant researches on the effect of heavy metal deal with assessment of the effect of trace amounts of heavy metals (Lettinga, 1995). The results in Table 1.2 present the heavy metals requirements of *Methanosarcina barkeri* Fusaro (DSM 804). Based on anaerobic bacteria cell structure, it is well recognized that heavy metals play a very important role in the production of enzymes required for the catalysis of biochemical reactions. Of the trace elements tested (Co, Ni, Fe, Zn, Mn, Al, Se, B, Mo, Cu), Co was found the element affecting methanogenesis from methanol quite significantly. The optimal concentration of cobalt for the growth of methanol utilizing methanogens and acetogens was 0.05 mg/L. With the requirements for cobalt are met, the methane production became 3 times higher than under conditions were cobalt was deficient (Florencio *et al.*, 1993, 1994a, 1994b).

Table 1.4 Trace element composition and requirement of *Methanosarcina barkeri* Fusaro (DSM 804) grown on methanol (Florencio, 1994b)

Trace element	*Methanosarcina barkeri* Fusaro (DSM 804)	
	Cell content[a] (mg/g cell)	Exp. nutrient requirement[b] (mg/g cell)
Na	9200	8756
K	2500	16131
S	11000	9245
P	12000	12806
Ca	3800	3616
Mg	1700	1614
Fe	2150	230
Ni	135	71
Co	60	57
Mo	60	nr[c]
Zn	130	nr[c]
Mn	5	nr[c]
Cu	10	nr[c]

[a] *From Scherer et al. (1981, 1983, 1989)*
[b] *From Nishio et al. (1992)*
[c] *not reported*

Ammonia. Several studies have been published dealing with the effect of ammonia-nitrogen on the anaerobic digestion. The results of recent investigations reveal that the effect of ammonia to anaerobic digestion depends significantly on the ammonia concentration and environmental conditions as well, such as pH, temperature, extent of adaptation of the system. In the past it was found that ammonia-nitrogen concentrations in the range of 200-1,500 mg/L don't exert a strong adverse effect on the methanogenesis, while at concentrations in the range of 1,500-3,000 mg/L ammonia is becoming inhibitory at pH values above 7.4 and at concentration exceeding 3,000 mg/L ammonia-nitrogen it is becoming quite toxic at all pH values. Results obtained in some experiments revealed that methanogenesis still proceed well at ammonia-nitrogen concentrations higher than 5,000 mg/L (van Velsen and Lettinga, 1979), although following a long period of adaptation. The experimental results of recent studies confirmed these findings. After adaptation the maximum specific methanogenic activity at an ammonia-nitrogen concentration of 2,315 mg/L was higher than the maximum specific methanogenic activity at an ammonia-nitrogen of 1,900 mg/L before adaptation (Koster, 1989).

Toxic compounds. A variety of compounds, including particularly also xenobiotics, can severely inhibit anaerobic digestion processes, e.g. disinfectants at concentration of 0.2% v/v, phenolic compounds at 0.5% v/v and detergents 0.1% w/v also inhibit anaerobic digestion (Nagarwala, 1985). It falls beyond the scope of this introduction to provide detailed information about this matter.

1.3 APPLICATION OF ANAEROBIC PROCESSES IN WASTEWATER TREATMENT

Since the first description of methane emanating from aquatic mud in 1976 by Volta, anaerobic processes and methanogenic bacteria have received increased scrutiny and promotion of scientific community (Oremland, 1988). Originally, in 1881, anaerobic processes were considered to be suitable for solid waste stabilization, such as cattle dung (cow, horse, pig) and household garbages. For a long time, anaerobic processes were considered to be only feasible for the treatment of solid waste and slurries. However, since 1950 a new generation of advanced reactor has been developed for treatment of wastewater.

During the last two decades the many alternative biological processes that have been developed and investigated, including stabilization ponds systems and high rate aerobic systems and AnWT-processes as well. Later processes have received considerable attention, although not really in the established sanitation world. New groups came up who particularly focussed their activities on the development and implementation of AnWT-reactors for low strength industrial wastewaters. Industries became very interested in AnWT, because of the big advantages of AnWT compared with the aerobic wastewater treatment processes, i.e. (Lettinga, 1995):

- Very low investment cost, because inexpensive reactors are used.
- Very low operation cost, because anaerobic wastewater treatment systems generally can be operated with little if any consumptive use of high grade energy.
- Smaller amount of chemicals required to control pH and because the supply nutrient for low growth of anaerobic bacteria is negligible.
- Instead of consuming energy, useful energy in the form of biogas can be recovered from organic wastewater.
- It can be applied at practically any place and at any scale.
- Very high space loading rates can be applied in modern anaerobic wastewater treatment systems, so that the space requirements of the system are relative small.
- The volume of exceed sludge produced in anaerobic wastewater treatment generally is significantly lower, viz. in terms of absolute quantity (kg organic matter) but also in terms of volume, because of its excellent dewatering capacity.
- The excess sludge generally is well stabilized.
- Anaerobic organisms can be preserved unfed for long periods of time (exceeding one year) without any serious deterioration of their activity, while also other important characteristics of anaerobic sludge general remain almost unaffected, e.g. the settleability of the sludge.
- It can be combined with post-treatment methods which enable the recovery of useful products like ammonia or sulfur.

At the present state of knowledge - little if any serious drawbacks can be anymore brought up against anaerobic treatment, although the following should be mentioned:

- The relatively high susceptibility of methanogens and acetogens to a variety of xenobiotic compounds.
- The presumed low stability of anaerobic treatment according to reports of the sanitary engineering world. However, as a matter of fact many upsets of anaerobic digestion system which manifested in the past can be attributed to a lack of knowledge of the most basic principles of the processes. As a matter of fact, AnWT-processes are highly stable, provided the system is operated in the proper

way, e.g. is not seriously overloaded as was the case in many of the upsets. This means that the process should be sufficiently understood by engineers and operators.

- The slow "first" start-up does not hold anymore as a drawback. A lot more is understood of the growth conditions of anaerobic organisms, and gradually large quantities of highly active anaerobic sludge from existing full scale installations are becoming available, so that the start-up of new full scale installations can be made within a few weeks, sometimes even a few days.
- Anaerobic treatment can be accompanied with mal-odorous nuisance problems, but such problems can be prevented quite easily and definitely, because almost completely tight reactors can be applied, and mal-odorous compounds present in the effluent can be eliminated by using microaerophilic methods.

When AnWT-systems are used for primary and secondary treatment in combination with proper post-treatment systems, it can be stated that AnWT does not suffer anymore from any drawbacks.

Fundamental Aspects of Anaerobic Wastewater Treatment Technology

For the proper design and application of AnWT-systems it is essential to know and understand the important process technological aspects of anaerobic rector systems, and the (bio-) chemistry and microbiology of anaerobic digestion process itself (Lettinga, 1995). This means knowledge about:

- Anaerobic sludge immobilization, i.e. start-up of anaerobic rectors.
- Kinetics of anaerobic conversion reactions by immobilized biomass.
- Effect of process conditions imposed to the system.
- Effect of environmental conditions prevailing on the anaerobic treatment systems.

Bacterial sludge immobilization, granulation

The key for modern biotechnology is the *immobilization of the proper bacterial sludge*. The required high sludge retention in anaerobic treatment systems only can be accomplished on the basis of biomass immobilization. However, it should be understood that in AnWT it is not just a matter of immobilizing bacteria, but to develop and to immobilize well balanced bacterial consortia. This is needed because of the existence of various syntropic conversion reactions in anaerobic digestion, the detrimental effect of higher concentrations of specific intermediates, and the strong effect of environmental factors like pH and redox potential (Kato, 1994). An excellent immobilization process is the formation of granular sludge (granulation). Viable granular sludge has two characteristics:

- High viable biomass density.
- High settling velocity.

Kinetics of anaerobic conversion reaction in immobilized biomass

Mathematical descriptions of the kinetics of anaerobic treatment so far in fact merely exist for dispersed cultures. Useful kinetic models for immobilized biomass have not yet been developed. For the degradation of substrate in immobilized biomass, external and internal mass transfer processes generally play an important role. Both for the substrate(s) and end-product(s) concentration gradients may prevail in immobilized biomass. Mass transport inside biological matrices is attributed merely to diffusion kinetics, i.e. according Fick's law (Lettinga, 1995). Diffusion coefficients for solutes inside biofilms were found to be lower than those in clean water. In general the following kinetic model equations can be used in anaerobic processes:

First order

$$\mu = \frac{kS}{S_o - S} \qquad \frac{-dS}{dt} = kS \qquad S = \frac{S_o}{1 + kO_c}$$

Grau *et al.*

$$\mu = \frac{\mu_{max}S}{S_o} - b \qquad \frac{-dS}{dt} = \frac{\mu XS}{YS_o} \qquad S = \frac{S_o(1 + k_dO_c)}{\mu O_c}$$

Monod

$$\mu = \frac{\mu_{max}S}{K_s + S} \qquad \frac{-dS}{dt} = \frac{\mu_{max}XS}{Y(K_s + S)} \qquad S = \frac{K_s(1 + k_dO_c)}{O_c(\mu_{max} - k_d) - 1}$$

Contois

$$m = \frac{u_{max}S}{BX + S} - b \qquad \frac{-dS}{dt} = \frac{\mu_{max}X S}{Y(BX + S)}$$

$$S = \frac{BYS_o(1 + bO_c)}{BY(1 + k_dO_c) + O_c(u_m - k_d) - 1}$$

Chen & Hashimoto

$$\mu = \frac{\mu_{max}S}{KS_o + (1 - K)S} - b \qquad \frac{-dS}{dt} = \frac{\mu_{max}XS}{KX + YS}$$

$$S = \frac{KS_o(1 + k_dO_c)}{(K - 1)(1 + k_dO_c) + \mu_{max}O_c}$$

where,

X = microorganism concentration, mg/L

S_o *and* S = influent and effluent concentration of the growing-limiting substrate, mg/L

Y = growth yield coefficient, mg/mg

O_c = mean cell residence time, days

k_d = specific microorganism decay rate, h^{-1}

k = the maximum specific substrate utilization rate

K_s = half-velocity constant, substrate concentration at one-half the maximum growth rate, mass/unit volume

Process-conditions imposed to the reactor system

The loading potentials of an anaerobic treatment system for a specific wastewater are determined by the process conditions imposed to the system, i.e. *the substrate loading rate to the viable biomass, the substrate level in the reactor, the mixing conditions, the operational temperature.*

Environmental conditions in anaerobic treatment

The environmental conditions prevailing in an anaerobic reactor partially depend on the imposed process conditions and the wastewater characteristics and indirectly also on the loading rate imposed to the system. Important environmental factors to be considered are toxicity, pH, temperature, availability of nutrients and trace elements, concentration of intermediates.

Anaerobic wastewater treatment technology

Reactor technology. To enable an anaerobic reactor system to accommodate high space loading rates for treating a specific wastewater the following five conditions should be met:

- High retention of viable sludge in the reactor under operational conditions.
- Sufficient contact between viable bacterial biomass and wastewater.
- High reaction rate and absence of serious transport limitations.
- The viable biomass should be sufficiently adapted and/or acclimatized.
- Prevalence of favorable environmental conditions for all required organisms inside the reactor under all imposed operational conditions.

Anaerobic reactors. An essential difference between anaerobic and aerobic wastewater treatment systems is that the loading rates of anaerobic reactors generally are not limited by the supply of any reagent, like oxygen in aerobic systems (Lettinga, 1995). During the last three decades several high rate anaerobic reactors configurations have been developed, as has been reported by Iza *et al.* (1991), Iza (1991), Joung (1991), Kennedy and Droste (1991), Nahle (1991), Wang (1994), Lettinga (1991, 1995). The following reactors have been developed:

1. **Anaerobic contact reactor**. This type of reactor is very similar to the aerobic suspended activated sludge process. In this system a mixing device is considered to be needed in order to achieve effective contact between retained biomass and wastewater. After treatment suspended biomass is separated by either flotation, settling or filtration.

2. **Anaerobic filter reactor (AF)**. The AF can be operated with upflow or dowflow feed mode. There exist quite a lot of modifications of this AF-system, i.e. depending on the type stationary phase used in the systems, and the mode of operation, e.g. Dowflow Stationary Fixed Film Reactor (DSFF). The inert materials used can consist of sheets, rings or spheres as packing in loose-fill or modular configuration. The idea is that biomass becomes attached and/or entrapped to or between the packing material. The main drawback of this AF-system is channelling, resulting in dead-zone formation up to about 35-43% volume of reactor.

3. **Upflow anaerobic sludge blanket (UASB)**. The UASB-process relies on the retention of a flocculent or granular sludge. This retention of sludge is based on an early and efficient gas-solid-liquid separation by using a proper device (GSS) which is installed in the top-part of the reactor. The system relies on the excellent settling properties and high activity of the anaerobic sludge developing in the reactor. The advantages and drawbacks will be reviewed in paragraph 1.4.

4. **Fluidized bed reactor (FB).** In this reactor system fine inert carrier particles (e.g. fine sand, antracith, etc.) are used to allow active biomass attachment to the carrier surface. The particles with attached biofilm are kept fluidized by application of high upflow liquid velocities. The main operational problem with the FB-system is to adjust such a flow rate that 'all' particles are kept dispersed (fluidized), both during start-up but also after the start-up. This in fact inherently is impossible, because the average density, shape and size of the particles differ widely.

5. **Expanded granular sludge bed (EGSB).** In the EGSB-reactor, the wastewater to be treated is pumped upward through a bed of granular sludge. Effluent is recycled to dilute the incoming waste and to provide an dequate flow to maintain the sludge bed in an expanded condition. Because a large biomass can be maintained, the EGSB-reactor can also be used for treating municipal wastewater and low strength wastewater as well at very short hydraulic retention time.

Table 1.5 presents the application of anaerobic processes in wastewater treatment. Among them UASB is widest applied in this field.

Table 1.5 Application of anaerobic processes in full scale wastewater treatment (Iza *et al.*, 1991)

Wastewater	Contact	UASB	FB/EB	AF	DSFF
Alcohol distillery	+	+	+	+	+
Beet sugar		+			
Brewery	+	+	+		
Cellulose condensate	+				
Chemical		+		+	
Citric acid	+	+			
Confectionery		+			
Domestic sewage		+	+	+	
Enzyme manufacture				+	
Fish processing		+			
Guar gum				+	+
Landfill leachate		+		+	
Meat processing	+	+			+
Mill processing/cheese production	+			+	
Organic acids		+		+	
Paper mill		+			
Pharmaceutical	+	+			
Pectin factory	+	+			
Pig manure				+	+
Potato processing		+		+	
Slaughterhouse		+			
Soft drink bottling		+	+	+	
Starch processing	+	+		+	
Surge factory	+	+			
Thermal sludge liquor			+	+	
Vegetable canning	+	+			
Yeast	+	+			

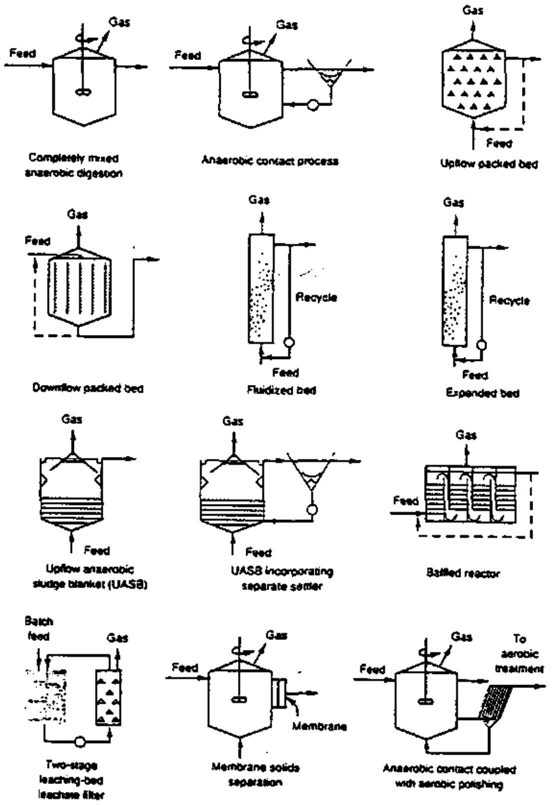


Fig. 1.2 Types of anaerobic reactors

1.4 UASB-PROCESSES

The Upflow Anaerobic Sludge Bed (UASB) process concept is based on the idea that anaerobic sludge inherently exerts satisfactory settling properties, provided the sludge is not exposed to heavy mechanical agitation (Lettinga *et al.*, 1980, 1983; Lettinga and Hulshoff Pol, 1991; Lettinga, 1995). For achieving the required sufficient contact between sludge and wastewater, the conventional UASB-system relies on the agitation brought about by biogas production and on an even feed distribution at the bottom of the reactor. Sometimes the hydraulic upflow velocity is raised by applying effluent recycling.

The most important feature of the UASB-system is the sludge granulation phenomenon. Sludge aggregates will be dispersed under influence of up flowing biogas and wastewater. This mixing brought about by the biogas is very important for achieving the desired contact. The dispersed sludge aggregates generally can be retained sufficiently well in the reactor by separating the biogas in an early stage, which is accomplished by using a gas collector assembly (GSS-device) placed in the upper part of the reactor. The collected biogas is released from the system via pipes connected to the device. In this way an in-built settler is created in the upper part of the reactor. Finer sludge particles can coalesce here and then settle down, and ultimately slide back into the digester compartment. The GSS-device constitutes an essential accessory of an UASB-reactor. This is excellent design of an UASB-reactor.

Table 1.6 Full scale UASB-plants constructed before September 1990 (After Lettinga and Hulshoff Pol, 1991)

Wastewater	Number of UASB	UASB volume (m^3)
Alcohol	20	52,000
Bakers' yeast	5	9,900
Bakery	2	347
Brewery	30	60,600
Candy	2	350
Canneries	3	2,800
Chemical	2	2,600
Chocolate	1	285
Citric acid	2	6,700
Coffee	2	1,300
Dairy and cheese	6	2,300
Distillery	8	24,000
Domestic sewage	3	3,200
Fermentation	1	750
Fruit juice	3	4,600
Fructose production	1	240
Landfill leachate	6	2,495
Paper and pulp	28	67,197
Pharmaceutical	2	400
Potato processing	27	25,610
Rubber	1	650
Sewage sludge liquor	1	1,000
Slaughterhouse	3	950
Soft drinks	4	1,385
Starch (barley, corn, potato and wheat)	16	33,500
Sugar processing	19	23,100
Vegetable and fruit	3	2,800
Yeast	4	8,500
Total	205	339,609

When a high sludge concentration consisting of dense of viable biomass can be retained under operational conditions, extremely high organic space and hydraulic loading rate can be applied in a UASB-reactor. With sugar wastewater organic loading rates (OLR) were reached up to 30-45 kg COD/m^3.d. With a sucrose wastewater even an OLR of 80-100 kg COD/m^3.d and a hydraulic retention time (HRT) down to 2-2,5 h were applied under thermophilic conditions (van Lier *et al.*, 1994; van Lier, 1994). At the same temperature condition the lowest loading rate was 6-10 kg COD/m^3.d when the UASB-system was used for treating coffee wastewater (Lettinga *et al.*, 1989). Under mesophilic conditions the UASB-process has been applied for a variety of wastewater (Table 1.5), i.e. at very high OLR and short HRT.

Until now already quite a lot of UASB-processes have been installed in practice and/or have been investigated at lab-scale and pilot-scale for treatment of industrial and domestic wastewater, e.g. for the purpose to improve the basic knowledge and/or the proper operation procedure.

In the application of UASB-reactor the major difficulty generally is the start-up of the system, especially when a proper seed sludge is not available. It is important to apply an adequate procedure in the start-up, because it may save time needed for start-up with maybe more than a month in case a poor quality seed sludge has to be used, and in case of a high quality seed sludge to a few days

(Lettinga, 1995). The start-up procedure to be applied depends on factors like (Lettinga, 1991, 1995, Hulshoff Pol, 1989; de Zeeuw, 1984):

I. *Seed sludge characteristics*

A variety of seed materials can be used, e.g. digested and raw sewage sludges, different types of manure, aerobic activated sludge and even inert organic and inorganic carrier particles, although in latter case only when anaerobic organisms are present in the raw wastewater. The presence of 'proper' carrier materials (e.g. size, gravity, surface properties) for bacterial attachment in the reactor is essential.

II. *Mode of operation*

It is essential to retain the heavy carrier ingredients present in the seed material, and to accomplish during the initial phase of start-up a complete removal of the lighter fractions of the seed sludge. This can be achieved by applying a sufficient selection pressure (mixing and superficial liquid velocities in the system). In this respect the following recommendations can be made:

1. Finely dispersed sludge washed out from the system should not be returned.

2. Effluent recycling should be applied in case the influent $COD_{biodegradable}$ exceeds 3 g/L to reinforce the selection pressure.

3. The organic loading rate should be increased stepwise, always after at least 80% of the $COD_{biodegradable}$ is eliminated. In this way the sludge loading rate is raised relatively rapidly. The acetate concentration should be maintained at a low level, e.g. below approximately 200 mg/L. In this way growth-in of organisms with a high substrate affinity is enhanced

4. Some mechanical mixing in the reactor can be beneficial because it promotes sludge segregation (the selection pressure).

III. *Wastewater characteristics*

1. The strength of the wastewater.

2. Granulation proceeds faster at lower substrate influent levels, i.e. in the range 1-3 g $COD_{biodegradable}$/L.

3. Composition of the wastewater

4. Granulation proceeds very well on soluble protein and slightly acidified carbohydrates, viz. substantially faster than on substrates merely consisting of VFA.

5. A high concentration of Ca-salts of the VFA will lead to $CaCO_3$-scaling problems with granular sludge.

6. Nature of the pollutants

7. Dispersed organic and inorganic matter retards the granulation process and therefore should not be present at concentrations exceeding approximately 100-200 mg/L (depending on the soluble $COD_{biodegradable}$).

VI. *Environmental factors*

1. Temperature

   Granulation proceeds best at optimal mesophilic and thermophilic conditions.

2. pH

   The pH value should be maintained at higher than 6.2.

3. Nutrient and trace elements

   All *essential growth factors,* N, P, S and trace elements should be present in sufficient amount and in available form.

4. Toxic compounds

   Toxic compounds should be absent at inhibitory concentrations.

1.5 SCOPE OF THE THESIS

The main objective of this thesis is to assess the applicability of UASB-process to treat RLP wastewater and also to assess the efficiency of suitable post-treatment processes to anaerobic treatment process. Laboratory experimental data will be used to design a pilot and full scale wastewater treatment plant in Lai Khe and Long Thanh Rubber Latex Processing Factory, Binh Duong and Dong Nai province. Lab-experiments were carried out in Vietnam from 1991 to 1995 and at Department of Environmental Technology, Wageningen Agricultural University, the Netherlands, during two periods, viz. November 1990 to May 1991 and May 1993 to August 1993. The full scale wastewater treatment plant in Long Thanh has been operated for 4 months since August 1995. The operation results of the full-scale plant will also be evaluated.

Chapter 1 presents a review of anaerobic wastewater treatment processes. Chapter 2 deals with the assessment of important characteristics of RLP wastewater. Results of observations and measurements made at six RLP factories will be presented, while also the various steps in rubber production will roughly described in this chapter.

Chapter 3 deals with investigations on the feasibility of anaerobic process to treat RLP wastewater, i.e. determination of the specific methanogenic activity of four types of available sludges in South Vietnam, the anaerobic biodegradability of RLP wastewater, the anaerobic biodegradation of protein, effect of pH on anaerobic process using batch experiment, the effect of oxygen and mixing condition on the specific methanogenic activity (SMA) test, and the effect of the storage time on the SMA of sludge.

Chapter 4 presents experimental data obtained in the UASB-reactors treating RLP wastewater, including also the effect of pH and of effluent recirculation.

Chapter 5 deals with the treatment efficimcies found in post-treatment processes, i.e. the stabilization ponds system with aquatic plants like waterhyacinth and algae.

Chapter 6 describes the design of the full scale RLP wastewater treatment plant at Long Thanh RLP factory, Dong Nai province and preliminary experimental data obtained during four months operation.

The results are summarized in chapter 7, and also the conclusions will be presented here.

Chapter 2

Rubber Latex Processing and Wastewater

2.1 HISTORY OF RUBBER PRODUCTION IN VIETNAM

Today about 65% of the world rubber production including both synthetic and natural rubber is used in the automotive industry, specially for the production of tires (Wessel, 1990). Although there is a significant degree of substitutability between natural and synthetic rubber, the former is superior for use in tires of airplanes and other heavy equipment, radial tires of cars, latex products and adhesives. In other words, synthetic rubber can not replace completely natural rubber. A general view is that natural rubber is technically suited for roughly up to 70% of the total market.

The world production of natural rubber amounted in 1990 to about 6.4 x 10^6 tons, but the demand is about 8.0 x 10^6 tons (Webster and Paardekooper, 1990). Its gross value exceeds 4.5 billion US$ annually and almost all output is traded. Virtually all natural rubber comes from the rubber tree *Hevea brasiliensis*.

It is estimated that the demand for rubber will grow annually by about 4.8% in the period 1980-2000, from 13 million tons in 1980 to 33.5 million tons by the end of the century (Wessel, 1990). Limitations in the oil production capacity have significantly improved the competitive position of natural rubber against synthetic rubber. Some years ago, due to the effects of world economic growth resulting in a decrease to automotive industry, the production of natural rubber was stable at a low level in both productivity and price. However, from the end of 1993 onwards the natural rubber demand has increased greatly by virtue of the development of automotive and other industries. The price of processed rubber has increased from 700 US$/ton to 2,000 US$/ton. Presently, the General Rubber Company of Vietnam receives a lot of orders from Japan, Germany, England, Korea, and Singapore to supply natural rubber.

The rubber tree was discovered in America by Columbus in the period 1493-1496. Brazil was the first rubber exporting country in the XIX century (Webste and Baulkwill, 1989). In Vietnam the first rubber tree (*Hevea brasiliensis*) was planted in 1887. In the period between 1900 and 1929 the French colonists expanded the rubber tree areas. At the end of 1920 the total rubber tree area in Vietnam was about 7,000 ha with rubber production of 3,000 t/year, mainly rubber sheet.

Along with the development of the rubber industry in the world, during 1920-1945, the French colonial government rapidly increased the rubber tree areas in Vietnam at a rate of 5,000-6,000 ha/year. By the end of 1945 the total area was about 138,000 ha with a total production of 80,000 tons/year. After the independence in 1945 the Vietnamese government continued to develop the rubber industry and the planted area increased to some hundred thousands of hectares.

After the reunification of North and South Vietnam in 1975, the rubber latex processing industry could become the second most important exporting agro-industry in Vietnam (rice export is the first). Favorable climatic and soil conditions and the application of new technology greatly contributed to this success. In 1999 there are 21 rubber companies exploiting 29 rubber latex processing factories with a total rubber tree area of 300,000 ha and a productivity of 169,567 tons/year (growth rate 1996/1998: 12,000 ton/year). It is foreseen that the planted area will rise to 500,000-700,000 ha with a capacity of 240,000 t/year in the year 2005. Table 2.1 presents the capacity of rubber companies in Vietnam.

All rubber companies are situated in the mountainous areas of South Vietnam, benefiting from the suitable climate and soil. Presently, the main products of rubber latex processing factories are block rubber and concentrated latex of which the first forms for 90% of the total production. Most of the products are exported to Asian and European countries.

Table 2.1 Production capacity of rubber companies in Vietnam (1992-1998)

No	Rubber Company	Number of Factory	Production capacity 1992	1996	1998
			Ton/year		
01	Dong Nai	5	31,400	41,000	35,036
02	Dau Tieng	2	8,300	25,500	35,147
03	Binh Long	1	7,500	14,500	14,017
04	Phu Rieng	2	7,400	20,000	16,500
05	Phuoc Hoa	2	1,500	22,000	17,543
06	Loc Ninh	1	3,700	6,500	5,010
07	Tay Ninh	2	3,400	5,500	7,007
08	Ba Ria	1	-	5,000	16,200
09	Dong Phu	1	2,500	4,000	7,743
10	Tan Bien	1	30	4,000	3,935
11	Quang Tri	1	20	400	1,476
12	MangYang	1	50	500	750
13	Chu Se	1	25	500	2,614
14	Chu Pah	1	500	1,500	990
15	Chu Prong	1	400	1,500	2,080
16	Ea H'Leo	1	40	500	1,073
17	Krong Buk	1	25	500	1,000
18	KonTum	1	15	500	630
19	Binh Thuan	1	-	-	440
20	Chu Se II	1	-	-	24
21	VNRRI	1	-	-	352
	Total	29	66,805	153,900	169,567

Source: Annual Report of Vietnam Rubber Research Institute VNRRI (1993)
Annual Report of General Rubber Company of Vietnam (1997)
Annual Report of General Rubber Company of Vietnam (1999)

2.2 THE RUBBER TREE (*Hevea brasiliensis*)

2.2.1 HISTORY

Hevea brasiliensis (Natural Order *Euphorbiaceae*) is a native of the tropical rain forests of South America (Edgar, 1958), where it grows in association with many other species of trees, climbing plants, and undergrowth, under conditions of high humidity.

The genus *Hevea* is a member of the family of the *Euphorbiaceae*. There are nine distinguishable species: *H. brasiliensis*, *H. benthamiana*, *H. camporum*, *H. guianensis*, *H. mycrophylla*, *H. nitida*, *H. pauciflora*, *H. ridigifolia* and *H. spruceana*. Of these, *H. brasiliensis* is the only species extensively planted at a commercial scale. Three other species, *H. nitida*, *H. pauciflora* and *H. spruceana* are used as sources of resistance to South American leaf blight. All nine species occur in Brazil, six in Colombia, five in Peru and Venezuela, two in Bolivia, Guyana and Surinam, and one in French Guyana and Ecuador (Loren, 1962; National Academy of Science, 1977).

Even although the rubber tree was discovered in America, the original home region of the rubber tree is Brasil. In 1876, Henry Wickham collected 70,000 seeds near Boim, between the Tapajo and Madeira rivers and shipped them to England. From there more than 2,000 seedlings were sent to South East Asia, where we find presently the most important rubber producing countries: Malaysia, Indonesia, China, Thailand, Vietnam. At present, Indonesia produces the biggest amount of rubber products, viz. more than 1 mill. ton a year.

2.2.2 COMPOSITION OF LATEX

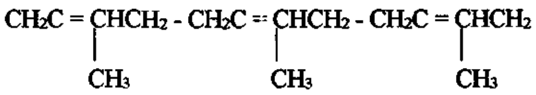
Physiology

Latex of the rubber tree (*Hevea brasiliensis*) is the cytoplasm of specialized cells present in the tree known as laticifers. Latex is formed in the latex vessels which exclusively occur in the phloem region and it is composed of a colloidal suspension of rubber particles in an aqueous serum, cytoplasm (C serum) and of lutoids (Bobilioff, 1923; Polhamus, 1962; Soedjanaatmadja *et al.*, 1995). Upon centrifugation, rubber latex is divided into a floating layer of rubber particles, the C serum and a bottom fraction consisting of lutoid body (Moir, 1959). *Hevea* latex is a hydrosol in which the dispersed particles are strongly protected by a complex film made of protein, neutral lipid and phospholipid. Rubber is the principal water insoluble component of latex and it occurs as discrete particles.

Latex is tapped and collected from the rubber tree as raw material for producing rubber products. The composition of latex collected by tapping is not similar to that of the latex in the vessels. Depending on the physiological variation in flow, the composition of latex collected after tapping and that inside the vessels may vary.

Rubber content

The rubber content of freshly tapped latex may vary from 25-40% (wet weight) but usually ranges between 30 and 35%. The basic molecule of rubber is an isoprene polymer (*cis*-1,4-polyisoprene $[C_5H_8]_n$), having a molecular weight of 10^5-10^7. It is synthesized in the plant via complicated processes from carbohydrates. Its function in the plant in unknown yet. Rubber production takes place at the expense of growth.



$$\begin{array}{l}CH_2C = \underset{|\atop CH_3}{C}HCH_2 - CH_2C = \underset{|\atop CH_3}{C}HCH_2 - CH_2C = \underset{|\atop CH_3}{C}HCH_2\end{array}$$

Fig. 2.1 Chemical structure of natural rubber.
(*cis*-1,4-polyisoprene)

Some important chemical and physical characteristics of rubber latex in Vietnam are summarized in Table 2.2.

Table 2.2 Chemical and physical characteristics of rubber latex in Vietnam

Characteristics		Concentration
Dry Rubber Content (DRC)		28 – 40
Protein		2.0 – 2.7
Sugar		1.0 – 2.0
Mineral salt		0.5
Lipid		0.2 – 0.5
Water		55 – 65
Density	Rubber	0.932 – 0.952
	Serum	1.031 – 1.035

All parameters are expressed in percentage of wet weight. Density is expressed in ton/m^3.

Particulate composition

The dominant particulate phase of freshly collected latex is the rubber hydrocarbon. Rubber particles make up 30-40% of the whole volume of latex and occur in sizes ranging from 0.02-3.00 μm with the majority having a diameter of approximately 0.10 μm. Rubber particles are usually spherical but sometimes oval or pear shaped. They are strongly stabilized in suspension by a film of adsorbed protein and phospholipid.

Next in abundance are the lutoid particles amounting to 10-20% of the volume. The lutoids are sub-cellular membrane-bound bodies ranging in size from 2-5 μm. The membrane encloses a fluid serum referred to as lutoid serum or B-serum. The lutoid serum is a destabiliser of rubber hydrocarbon. Another type of particle in latex is called the Frey-Wysling particle which is spherical, usually larger in size than rubber and of yellow color (Wessel, 1990; Webster and Paardekooper, 1990).

Chemical composition

Excluding rubber and water, the other substances present in fresh latex are mainly carbohydrate, proteins, lipids and inorganic salts. Besides a variety of other constituents are present in minor concentrations.

Carbohydrate. Quebrachitol (methyl inositol) is the most concentrated single component in the serum phase, constituting about one per cent of the whole latex. The concentration of sucrose, glucose and fructose in latex is influenced by various factors such as plant material, tapping system and chemicals used for rubber tree stimulation.

Protein. The total protein content of fresh latex is approximately 5-20 g/L latex (Edga, 1958; Tata, 1980; Kush, 1994) of which about 20% is adsorbed on rubber particles, an equal quantity found in the bottom fraction and the remainder (60%) in the liquid phase. The adsorbed proteins and phospholipid impart colloidal stability to the latex. The presence of 15 protein bands was demonstrated in the serum of fresh latex. The pH at the isoelectric point of rubber particles in fresh latex varies from pH 4.0-4.6. The variation of pH has been ascribed to the presence of more than one protein on the rubber particle. The proteins that have been studied in detail are alphaglobulin, hevein, fibrillar proteins and basic proteins. Among these, alphaglobulin has the highest concentration in fresh latex serum. It is one of the types of protein adsorbed to the surface of the rubber particles and it is responsible for the colloidal stability of latex. Lutoid particles in young latex vessels contain a protein deposited in the form of bundle of microfibrils. This microfibrillar protein, which has a lower isoelectric point than hevein, comprises about 40% of the total protein of lutoid particle in young latex vessels but it is absent in older vessels. Hevein is a major component of the bottom fraction of latex. More than one half of lutoid-body fraction is hevein which is a very stable protein (Soedjanaatmadja *et al.*, 1995).

Lipid. The lipids of fresh latex consist of fats, waxes, sterols, sterol esters and phospholipids. These compounds are all water insoluble and concentrated in the rubber phase. The amount of lipid in the latex amounts to 0.2-0.5% (weight of latex).

Other constituents. Up to nineteen amino acids have been identified in latex. Nucleotides contained in latex are important as co-factor and are intermediates in biosynthetic processes. The total concentration of inorganic ions in fresh latex is 0.5% and the main ions are potassium, magnesium, copper, iron, sodium, calcium and phosphate. Low molecular weight thiols, which are of importance for the redox potential of the system, and enzymes (normally present in cytoplasm) are also present in latex.

The composition of latex varies significantly with the season. During the dry season the rubber content is higher than in the wet season.

2.3 RUBBER LATEX PROCESSING IN SOUTH VIETNAM (MEKONG DELTA)

Generally, for the production of natural rubber, latex is collected in the forest and treated with ammonia in *Hevea* forest. After separation of the rubber particles at RLP factory, the water layer, called serum, usually is discharged into the environment in South Vietnam. The rubber latex processing procedure depends mainly on the products to be manufactured and the raw materials, i.e. in Vietnam, the main products are block rubber and concentrated rubber. The main materials used are latex and cuplum. Cuplum is latex coagulated in the field (in the *Hevea* forest) due to uncontrolled conditions, i.e. when the latex was not collected in time, e.g. within 2-3 days, because the latex will coagulated naturally in the cups used to collect latex flowing from the rubber tree, and/or when a bowl is broken and the latex dropped on the ground, etc. Obviously latex has a significantly higher commercial value and use than cuplum, which in fact generally is of a low quality.

The RLPs described below are based on the survey and observations of several RLP factories in South Vietnam from 1991-1998. These are also used in all Asian rubber producing countries, i.e. Malaysia, Thailand, Indonesia, India, etc.

2.3.1 PREVENTION OF FIELD RUBBER COAGULATION

Latex immediately issued from the tapping cut may become contaminated with particles from the bark and vegetable tissue through which various micro-organisms are introduced in the latex. The free surface of the latex is exposed to the air which also contains spores of micro-organisms. The longer the latex stands at a warm place, and especially when in contact with dirt, the greater is the risk of decomposition (Edgar, 1958). Immediately after the latex exudes after tapping, the mechanism of natural clotting begins by the activation of enzymes already present in the latex. In addition, bacteria entrapped from the atmosphere or already present in the containers etc., will act in a manner similar to that, which gives risk to milk fermentation. They react mainly on the dissolved sugar and proteins present in the serum, and form acids and putrid substances. These acidic materials will eventually induce coagulation of the latex by the fact that they reduce the pH and neutralize the electric charge on the particles. If the trees are wet, water soluble bark substances (tannins and specific cations such as calcium and magnesium) may be washed into the latex. Tannins react with proteins and they destabilise the rubber particles. The cations probably activate the native latex enzymes and accelerate the spontaneous clotting process. They also react with proteins. The occurrence of pre-coagulation during the wet season is probably also connected with an alteration of the tree metabolism and hence of the relative amounts of non-rubber substances in the latex, leading to a decreased stability of the colloidal suspension. The contamination of latex leads to premature uncontrolled coagulation.

The usual method applied in Vietnam to prevent premature coagulation is to add anti-coagulant to the latex in the tapping cups and collecting buckets in order to increase pH of latex. The anticoagulant must be added as soon as possible after the tree is tapped.

Anti-coagulants are particularly necessary under wet weather condition and with lattices which show a strong tendency to pre-coagulation (Edgar, 1958). That is a reason why the amount of anti-coagulant used during the wet season is higher than in the dry season. Anti-coagulants used in Vietnam are ammonia, sodium sulphite, formalin. Furthermore blending processes and the choice of chemicals are important factors to ensure the production of uniform and consistent grades. Ammonia is recommended and used commonly in Vietnam because of its advantages:

- It is cheap
- It can be locally produced
- It is less harmful to labors
- It gives less severe environmental pollution
- It can be reused in agriculture.

As mentioned above, the amount of ammonia to be added to latex for prevention of natural coagulation depends on the season:

- Wet season: 1.0-2.0 kg/tons dry rubber (0.1-0.2% wet weight)
- Dry season: 0.5-1.5 kg/tons dry rubber (0.05-0.15% wet weight)

It also depends on the distance from collection site to processing factory; longer transportation distances demand for a higher amount of ammonia. It is obvious that a higher added amount of ammonia will need a higher amount of formic or acetic acid for neutralization of the latex in the factory. Moreover, a lower quality of rubber products will result when it has been exposed to higher concentration of ammonia, etc..

2.3.2 RUBBER LATEX PROCESSING

The production of block rubber

Block rubber can be made from latex or field cuplum..

The production of block rubber from latex. As mentioned above, the raw material collected from the rubber forest (2-40 km from factory) is prevented from natural coagulation by careful blending of chemicals such as ammonia, and it is transported to the factory by trucks or tractors from 10 a.m. to 2-3 p.m. At the RLP factory latex is first filtered through a crude 20# mesh screen and a fine 60-80# mesh screen to remove clotted rubber, particles, leaves and vegetable tissues. Then it is transferred to a dilution tank which is equipped with blade stirrer. After having determined the dry rubber content (DRC), the latex is diluted with water to reduce DRC from 27-40% to 20-22% because a high DRC latex is difficult to mix uniformly with chemicals, and it coagulates too rapidly and the coagulum breaks too easily during crushing.

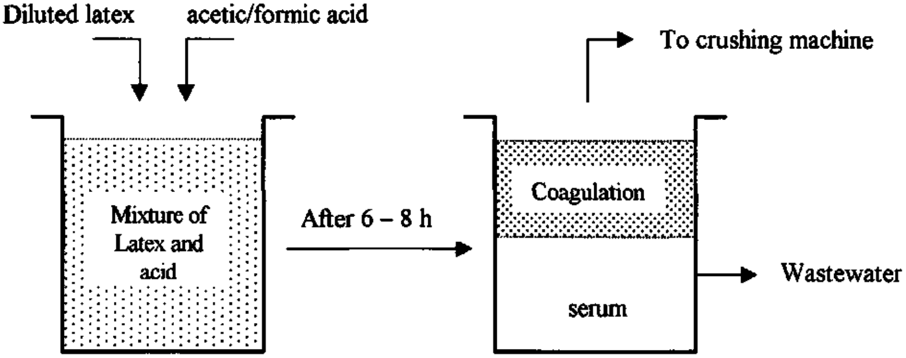


Fig. 2.2 Schematic diagram of latex coagulation

There are three main steps in producing block rubber from latex. The first step is coagulation. Diluted latex from the dilution tank is transferred to coagulation troughs and an organic acid is added on the way to the troughs. A 2% acetic acid solution is normally used to neutralize ammonia added in the field and to reduce the pH to 5.0-5.2, i.e. close to the pH 4.3 at the isoelectric point. The use of formic acid gives a higher quality and more beautiful color of the block rubber, but it is more expensive and harmful (due to evaporation) than acetic acid. The coagulation troughs are filled up with a mixture of latex and acid one by one. A sodium sulfite solution is sprayed on the surface of troughs to prevent surface oxidation. The floor, the dilution and chemicals preparation tanks are washed immediately after this step. The coagulation process takes about 6-8h.

The second step concerns crushing and milling. After completion of the coagulation, the coagulum is transferred to the crushing machines. Water is added to the coagulation troughs in order to float up the coagulum, because floating on water the coagulum is easy to move to the crushing machine. The purpose of the crushing step is to wash out uncoagulated rubber particles, and to remove excess acid, salts, uncoagulatex rubber, etc. After crushing, milling is done by passing slabs of the coagulum through successive pairs of adjustable rollers of which the final one is grooved such to imprint on each sheet the "ribs" to increase the surface area for drying. Each roller is equipped with water sprayers to wash away non-rubber particles. The coagulum is pressed, cut in small pieces and granulated. The coagulation troughs are washed after second step and ready for next shift.

In the third step granulated rubber is dried by hot air (using fuel) and pressed in blocks. The diagram of block rubber latex processing process applied in South Vietnam is shown in Fig. 2.3.

The production of block rubber from field cuplum. It especially is of interest for areas where big amounts of the field cuplum are available. As in field coagulation dirt is entrapped during collection, transport and storage it needs special cleaning and blending procedures, such as submerging in water in tanks for few days. The subsequent operations of milling, size reduction, drying and balling are similar to those of latex processing (see Fig. 2.3).

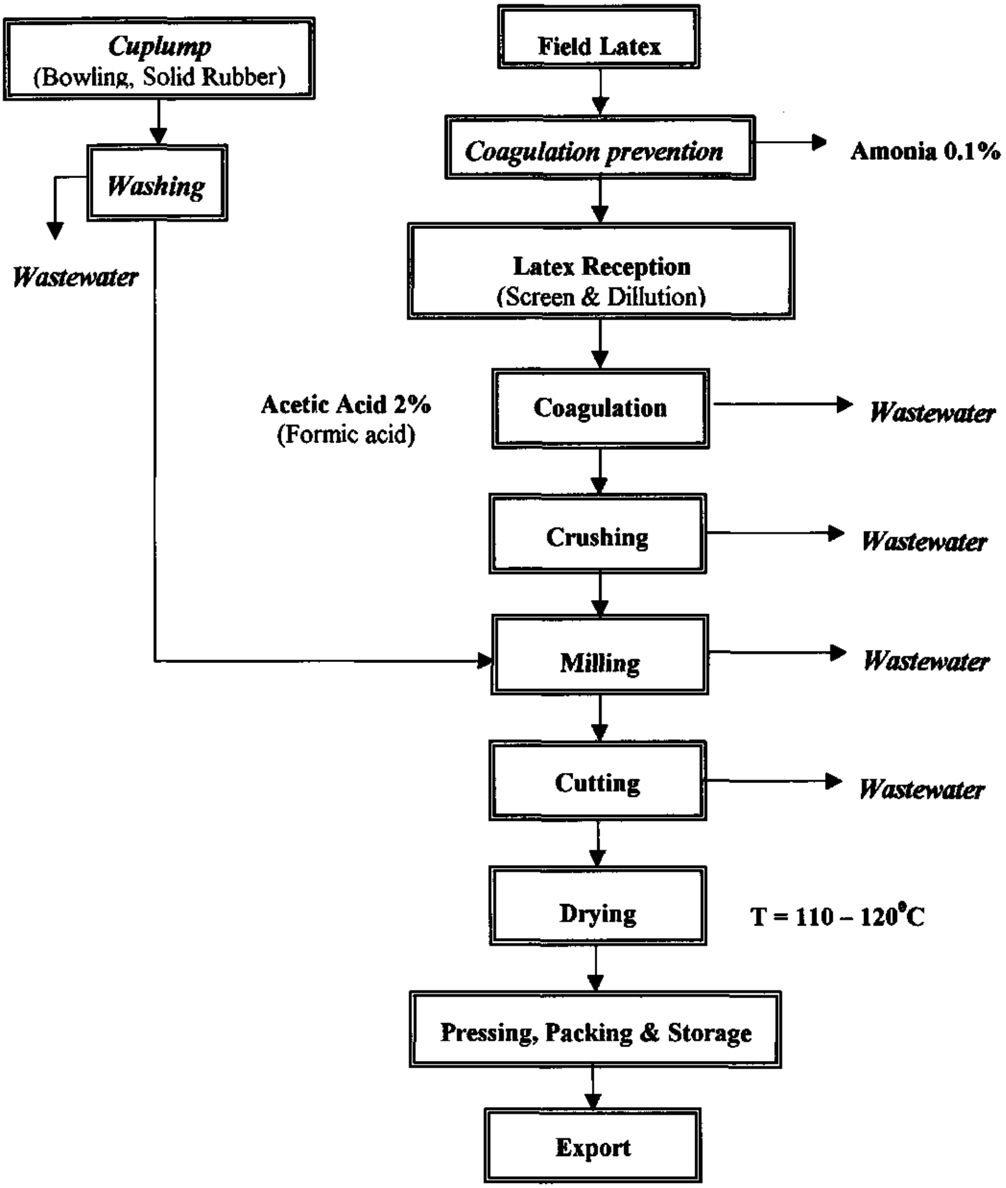


Fig. 2.3 Diagram of block rubber processing.

The production of concentrated rubber from latex

Rubber latex collected in the field is pre-treated by screening, washing and ammonia addition before it is processed. After centrifugation the latex contains 60-70% rubber, but the water layer (serum) still contains up to 8% (by wet weight) dry rubber, the water phase is discharged to a skimming tank for natural coagulation or acidified coagulation. The concentrated latex produced contains very high amounts of ammonia. Various methods are used to concentrate the latex, e.g. centrifugation, evaporation and creaming. Thereafter the concentrated rubber is put in the stainless steel containers for export. After centrifugation, the centrifugal machines are washed and the wastewater is discharged into the sewerage.

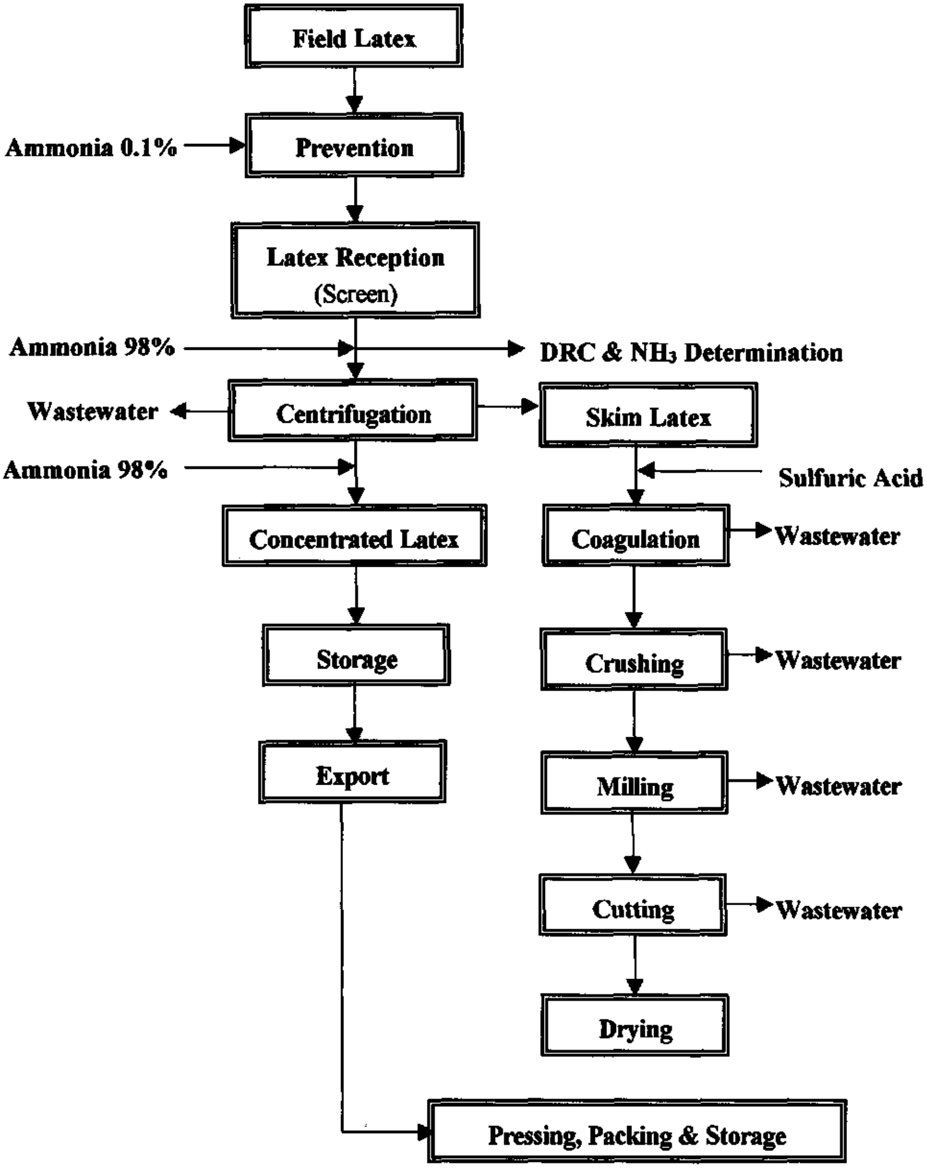


Fig. 2.4 Diagram of concentrated rubber processing

This product is widely used in Vietnam and various other countries in the world to manufacture gloves, condoms, mousse, shoes, etc. The diagram of the processing is presented in Fig. 2.4.

2.4 WASTEWATER FROM RUBBER LATEX PROCESSING IN SOUTH VIETNAM

2.4.1 INTRODUCTION

Like other industries, a rubber factory demands water for the processing. The standard quantity of water needed for rubber latex processing amounts to 30-35 m^3/ton (dw). In Vietnam, surface water and ground water is used.

A large quantity of water is used in rubber latex processing for washing, dilution of the latex and in further processing steps. Consequently a quite big amount of wastewater, including also that obtained for washing of floor, machines and cleaning tanks and serum generally will be discharged to receiving waters. This effluent contains a certain quantity of uncoagulated rubber particles and a quite high content of soluble pollutants, e.g. acetic/formic acid, sugars, proteins, lipids, carotenoids, inorganic and organic salts. These pollutants obviously affect quite adversely the ecology and the health of people living in the surrounding environment. The main pollution problems caused by rubber latex processing wastewater concern the discharge of substantial amounts of biodegradable organic compounds and the offensive smell of the wastewater. Table 2.3 presents the characteristics of natural rubber latex processing wastewater in India and Malaysia.

Table 2.3 Characteristics of natural rubber latex processing wastewater in Malaysia[a] and India[b]

Parameter		Concentration	
		Malaysia	India
pH		4.8 – 6.3	5.8
COD	mg/L	2450 – 4300	5350
BOD	mg/L	2100 – 3600	3200
DS	mg/L	nd	23100
SS	mg/L	240 – 650	920
SO_4^{2-}	mg/L	nd	4080
N_{tc}	mg/L	560 – 650	680
$N\text{-}NH_3$	mg/L	120 – 240	410

[a] *Edga, 1958.*
[b] *Mastrigt and Jordans, 1995.*
nd - not determined.

It is well known that quantity and quality of wastewater including their regime and fluctuation are the most important parameters for selecting the proper technology and to design facilities of wastewater treatment plant. This part of chapter 2 presents the assessed data concerning wastewater characteristics and also the regime of wastewater flow as prevailing in some RLP factories, but especially in the Long Thanh factory, South Vietnam. In latter factory a full-scale RLP wastewater treatment plant was designed and constructed, during the period 1993-1995.

2.4.2 MATERIAL AND METHODS

Rubber latex processing factories studied

The general survey of the assessed characteristics and the flowrate concern the data collected in six rubber latex processing wastewaters:

1. Lai Khe, Binh Duong province, 352 ton/year.
2. Binh Long, Binh Duong province, 14,000 ton/year.
3. Hang Gon, Dong Nai province, 8,500 ton/year.
4. Cam My, Dong Nai province, 10,000 ton/year.
5. An Loc, Dong Nai province, 10,000 ton/year.
6. Long Thanh, Dong Nai province, 10,000 ton/year.

A more detailed survey was carried out at Long Thanh RLP factory.

The main measurement were carried out from June, 1992 to August, 1995 in the dry season and wet season. And up to now (January 1999) the measurement has been continued at Cua Paris rubber latex processing factory in Binh Duong province with capacity of 10,000 ton/year.

Flowrate measurement

As described above, rubber latex processing wastewater is discharged from three sources:

- Washing coagulation troughs including serum
- Crushing, milling and cutting machines
- Washing and cleaning dilution and chemical tanks and floor.

At all rubber latex processing factories in South Vietnam the wastewater is conveyed to the environment via open rectangular channels from which rubber particles and garbage are easy to remove, so that clogging problems as caused by recoagulation of rubber particles can be avoided.

Three methods were used to measure the flowrate of wastewater from:

(1) **Coagulation wastewater (serum):** the volume of the coagulation trough, the number of troughs discharging the wastewater at the same time and the discharge time measured by stopwatch, were used to calculate a flowrate of coagulation wastewater;
(2) **Milling and cutting wastewater:** it was assessed by measuring the filling time of a bucket with a known volume;
(3) **Overall factory wastewater:** a V notch weir system was used to measure the flow of whole factory.

The total wastewater quantity of the factory can also be estimated from the wastewater pump flowrate.

Sampling

Both grab and composite samples were taken to determine wastewater composition.

Grab samples were taken at each processing steps to assess the fluctuation in the wastewater concentration and composite samples were used to calculate a total amount of pollutants discharged to the wastewater treatment plant or to the environment. Composite samples were obtained by mixing grab samples together based on the flow proportion.

Grab wastewater samples were taken at six RLP factories and 24 hours sampling was applied in Lai Khe and Long Thanh factory.

Normally, the working time at most factories is 16 hours for 2 shifts (8 hours each). From 12 a.m. to 9 p.m. there is no milling and cutting wastewater. But during the rubber harvest season (2-3 months) the working time of most factories is full continuous for 3 shifts of 8 hours each daily. Based on these working period the sampling schedule was established.

Analyses

All parameters pH, acidity, alkalinity, COD, BOD, suspended solid (SS), ammonia ($N\text{-}NH_3$), organic nitrogen (N-org), glucose, phosphate ($P\text{-}PO_4^{-2}$), volatile fatty acid (VFA) were analyzed according to "Standard Methods for the Examination of Water and Wastewater"" (APHA, 1985, 1992, 1995).

2.4.3 RESULTS AND DISCUSSIONS

Except at the Long Thanh and the Lai Khe factory, the survey and sampling were carried out at least 4 times. During the period 1991-1993 Lai Khe factory was surveyed in more detail and the Long Thanh factory has been surveyed in detail since 1992. The flowrate and wastewater characteristics presented in this chapter summarize the experimental data of Long Thanh factory in comparison with other factories. The data are presented in Table 2.4.

Wastewater of coagulation process (Serum & Washing)

After about 8-12 hours coagulation, water is added continuously to the coagulation troughs in order to float up coagulum, which then is conveyed to the crushing machine one by one. The crushing takes about 20-30 min for each trough depending on the strength of coagulum, the harder is the coagulum the longer is the crushing time required. And then serum is discharged into the sewage channel before the trough is washed. During low and high season, crushing is carried out from 9-10 p.m. to 10 a.m. or to 2 p.m. next day.

Because of standardized design, the coagulation trough of all factories are the same with dimension W x L x H = 0.43 x 28.5 x 0.65 m and a volume of 6.4 m^3, approximately. The number of troughs vary from factory to factory depending on the production capacity, for instance, Long Binh, Long Thanh and Lai Khe factories have 29, 35 and 12 troughs, respectively. Under normal conditions, the minimum and maximum number of troughs discharging wastewater at the same time is two and six, respectively.

Discharging time is approximately 10 minutes resulting in a minimum wastewater flowrate of 0.64 m^3/min. x 2 troughs = 1.28 m^3/min. or maximum flowrate of 0.64 m^3/min. x 6 troughs = 3.84 m^3/min.. The observations made at factory showed that due to the limited number of labors, the troughs were washed discontinuously, and consequently the flow pattern of the serum drained from the coagulation tanks is intermittent and during tank washing the flowrate and pollution of the wastewater fluctuate widely. However the washing period varies from about 6-12 hours depending on the number of labors and the season and the total volume of wastewater from coagulation troughs of Long Thanh factory is about 224-300 m^3 corresponding to 35 troughs.

Before water addition the volume of serum in a trough is about 1.5-2.0 m^3 while the coagulum contains about 50% water.

Serum generally still contains a very high content of uncoagulated rubber particles (colloidal), acetic (or formic) acid, sugar (glucose, fructose,...), lipids, proteins depend significantly on:

1. **The season:** latex harvested in dry season is more concentrated and higher in DRC than in the wet season. And consequently the amount of ammonia then need for preventing coagulation in the field is less resulting in a smaller amount of acetic/formic acid for coagulation. The amount of water used for dilution is higher.

2. **Transportation distance:** the longer is transportation distance the higher is the amount of ammonia required.

3. **Skill of staff:** the skill of operators responsible for adjusting the dose of acetic/formic acid for coagulation is the most important factor affecting the concentration of rubber particles in the serum. The less skilled are the staff, the higher will be the amount of uncoagulated latex in the serum. The results of serum sample analyses of different troughs during the same coagulation batch show that COD concentration ranged from 5,000-22,000 mg/L, sometimes COD coming up to 149,000 mg/L due to supply of an insufficient amount of acid to drop pH to 5.0-5.2. A substantial fraction of the latex then could not coagulate and consequently will be discharged to the wastewater. Obviously this also means a serious drop in the efficiency of the rubber production process.

4. **Mixing condition:** poor mixing conditions lead to an increase in the amount of acid to be used because a substantial amount of acid will be entrapped in the rubber block.

5. **Amount of water used for floating, washing:** the higher amount of water used the lower will be the COD concentration.

During discharging period of serum from the coagulation trough to sewerage, the effluent color is white milkish and the COD increased. Serum is the most polluted wastewater. During coagulation trough washing, the concentration of COD, VFA, sugar of the washing wastewater drop rapidly, i.e. the COD from 5,000-9,000 mg/L to 1,800-2,400 mg/L. The composition of the wastewater is shown in Table 2.4.

Wastewater of crushing, milling and cutting process

The wastewater discharged from the crushing machine contains a very high concentration of pollutants because in this step coagulum is crushed and all excess acid, sugars, proteins, lipids, non coagulated rubber particles, inorganic salts, etc., are washed out. The results show that the wastewater extracted from coagulum contains a high COD concentration of 13,775-14,206 mg/L, pH of 5.18-5.35, glucose concentration of 161-333 mg/L and a very low N-NH_3 concentration of 38-59 mg/L. In this step a small amount of wastewater is discharged, in the range of 6.98-12.54 m^3/h. The Long Thanh factory has 3 crushing machines, but the quantity of wastewater does not depend on the number of crushing machines.

The wastewater produced from the milling and cutting machines amounts to 25-29 m^3/ton dried rubber and the discharges are stable during working time. The variation in the wastewater quantity depends on the number of milling machines used and the production capacity. In each factory 2-3 sets of successive milling machines are applied. When one set of the successive milling machine is working, the flowrate is 8.64 m^3/h. The maximum quantity of wastewater from the milling machines is 25.92 m^3/h. In the cutting step, water is recirculated, therefore a small amount of wastewater is discharged to the sewage.

Compared to serum, the wastewater of the milling and cutting process is very stable in both quantity and quality. COD and BOD concentration amounted 1,800-2,400 mg/L and 1,700-2,100 mg/L, respectively, glucose was 120-140 mg/L, but VFA 860-1,800 mg/L was high, pH 6.12-6.43 was higher than pH of serum and crushing wastewater. Comparing the results obtained from other factories and in different season reveals that the concentration of milling and cutting wastewater is stable and that it depends merely on the amount of water used for washing.

The flowrate also depends on the raw materials, for instance, cuplum uses more water than coagulated rubber, and final product (sheet rubber, block rubber, etc.,)

Table 2.4 Characteristics of RLP wastewater

Characteristic		Processes		
		Coagulation	Milling & Cutting	Sewer
pH		4.98 – 5.24	6.12 – 6.43	5.72 – 5.59
Acid.	$mgCaCO_3/L$	1,150 – 1,870	120 – 150	160 – 220
Alk.	$mgCaCO_3/L$	1,250 – 1,280	15 – 35	150 – 210
COD	mg/L	5,015 – 9,962	1,800 – 2,400	1,811 – 4,589
BOD	mg/L	4,859 – 8,780	1,700 – 2,100	1,720 – 4,360
SS	mg/L	273 – 777	1,000 – 1,200	180 – 250
$N-NH_3$	mg/L	450 – 890	130 – 152	200 – 296
N- Organic	mg/L	810 – 1,565	45 – 120	800 – 1,500
Glucose	mg/L	1,200 – 2,500	120 – 140	200 – 600
$P-PO_4$	mg/L	420 – 450	56 – 74	-
VFA	mg/L	4,200 – 5,600	860 – 1,800	1,200 – 1,800

The biggest quantity of wastewater is discharged from milling and cutting processes, but the flowrate is very stable during the working time. Despite the fact that the quantity of coagulation wastewater is rather low its flowrate is very high and therefore temporarily affects significantly the overall flowrate of the factory, although for a very short period of time.

Generally, there are two open channels of wastewater constructed in most factories: one for the serum wastewater, one for the milling and cutting wastewater. With respect to the treatment processes, an equalization tank combined with certain pre-treatment method plays very important role in reducing the loading rate and establishment of good condition for biological processes.

Besides the main product, block rubber, most big rubber factories produce a concentrated rubber from latex. Skim drained from centrifuges to coagulation troughs for coagulation contains extremely high concentration of ammonia 1,925-4,576 mg $N-NH_3/L$, resulting in high pH 8.75-9.60, COD and glucose range 89,430-146,542 mg/L and 5,872-6,788 mg/L, respectively, because skim contains up to 8% DRC. Due to the high pH sulfuric acid is often used for coagulation. A wastewater treatment process consumes a significant amount of alkali for neutralization. But fortunately, concentrated rubber has been produced in small quantity only few months yearly.

2.5 ENVIRONMENTAL PROBLEMS

RLP wastewater contains a quantity of uncoagulated rubber particles and a very high amount of dissolved pollutants, such as acetic acid, sugars, proteins, lipids, carotenoids, inorganic and organic salts. These compounds are readily biodegradable by bacteria and this will result in a high oxygen consumption upon discharge of the wastewater in receiving surface water. With a productivity of 170,000 ton/year 29 rubber latex processing factories discharge annually 4.2-5.1 mill. m^3 wastewater and 20,000-25,000 ton organic matter (BOD) to the environment. When anaerobic condition occurs in receiving waters, hydrogen sulfide and mercaptan are formed, which cause a very heavy nuisance. Sometimes the bad smell will diffuse with air up to a distance of 4-6 km from the factory. Actually, wastewater can be reused for irrigation but it must be diluted before use because of high nutrient concentration which will affect the crops. All rubber latex processing factories are discharging wastewater to receiving water, e.g. streams, river, lakes, etc. For instance, the Binh Long factory discharges wastewater to a lake, and after 2 years, due to protein degradation rubber particles coagulated and floated up to the surface forming here a very thick layer. Grass and trees have grown very well on the surface layer, but fish, zoo-plankton, etc., could not survive in water because anaerobic condition. Ground water can also become contaminated by rubber latex processing wastewater. So several shallow wells surrounding the Long Thanh factory could not be used any longer. It also appeared that ammonia evaporating from the process corroded a zinc steel roof of factory and domestic houses.

It is quite clear that wastewater should be treated in order to protect the environment and that methods should be applied which are sustainable.

2.6 CONCLUSIONS

At present, the rubber latex processing industry produces a big amount of rubber products 170,000 ton/year for export and it became the second most important exporting agro-industry in Vietnam. However, apart from the economic benefits, the RLP industry also discharges huge amounts of waste to the environment. Especially wastewaters with high concentration of pollutants cause heavy pollution to surrounding environment.

The survey and examined data obtained in six RLP factories, mainly in Long Thanh factory, reveal that RLP wastewater is produced from two main processing steps: the coagulation (serum) and the milling, cutting step.

The coagulated wastewater contains a high COD concentration, viz. up to 5,015-9,962 mg/L, and is low pH 4.98-5.24. The total quantity of coagulated wastewater amounts to 224-300 m^3/d with high fluctuation at the Long Thanh factory.

The quantity of crushing and milling wastewater amounts to 1,500-1,800 m^3/d at the Long Thanh factory which is up to 80-90% of the total wastewater amount. However this wastewater contains lower COD concentration, viz. of 1,800-2,400 mg/L, and is higher in pH viz. 6.12-6.43. The flowrate of 8.64-25.92 m^3/h is stable during the working time and depends on only the working number of successive milling machines.

At present, there are only four wastewater treatment plants for rubber latex processing in Vietnam based on the aerobic activated sludge process and stabilization ponds system. According to Vietnamese environmental legislation, all factories must construct wastewater treatment facilities. A variety of treatment processes are being applied to treat this wastewater in the neighboring countries of Vietnam, e.g. Thailand, Malaysia, Indonesia. All the biological processes implemented consist of stabilization ponds with aquatic plants or of the aerobic activated sludge process. These processes either require high land use or are high in energy consumption. Up to now, rubber latex processing wastewater treatment comprises a big problem.

Based on experiences, abroad the discussions with factories and especially regarding the advantages of anaerobic wastewater treatment processes reviewed in Chapter 1, the best options to reduce environmental pollution problems are:

1. Improvement of labor skill to save raw materials (latex) and to reduce the amount of organic

matter discharged to environment.

2. Use of pH meters for proper control of the coagulation process.
3. Improvement of transportation roads to increase the speed of trucks so that the amounts of ammonia and acetic acid needed in the process can be reduced substantially.
4. Application of high rate modern anaerobic processes for primary treatment of the wastewater.

Chapter 3

Feasibility Studies of Rubber Latex Processing Wastewater Treatment Based on the UASB Process in Vietnam

3.1 INTRODUCTION

In recent years, the interest in anaerobic wastewater treatment processes has increased rapidly, because anaerobic treatment method offers important advantages over aerobic wastewater treatment processes as mentioned in Chapter 1. Several high rate anaerobic wastewater treatment reactor configurations have been developed such as the Upflow Anaerobic Sludge Blanket (UASB) (Lettinga et al., 1979, 1980, 1983a, 1983b), the Expanded Granular Sludge Bed (EGSB) (Lettinga, 1995), the Anaerobic Filter (AF) (Tilche and Vieira, 1991), the Downflow Stationary Fixed Film Reactor (DSFF) (Bories *et al*, 1988; Thirrumurthi, 1988; Kennedy and Droste, 1991; Berardino, 1994), the Anaerobic Fluidized Bed (AFB) (Timmermans and Van Haute, 1984; Gommers *et al.*, 1988; Athanasopoulos, 1990; Iza, 1991), the Anaerobic Baffled Reactors (ABR) (Nachaiyasit and Stuckey, 1994) and the Anaerobic Membrane Bioreactor (AMR) (Cadi *et al.*, 1994; Beaubien *et al.*, 1994). These reactors have been successfully used to treat many types of wastewater, for instance, alcohol, yeast, bakery, canneries, chocolate, chemicals, landfill leachate wastewater (Lettinga and Hulshoff Pol, 1991), slaughterhouse wastewater (Sayed et al., 1987), pulping wastewater (Sierra et al., 1990), debarking wastewater (Field et al., 1989), tapioca processing wastewater (Oanh et al., 1998), etc. All the sludge bed reactors are based on a high retention of active sludge which has excellent settling characteristics such as granular sludge or well settling flocculent sludge. From the experience obtained in anaerobic reactor operation it is well known that the start-up of the reactor plays a crucial role and many factors such as the seed sludge used and wastewater characteristics, reactor design, proper operation, imposed loading rates, presence of nutrients and trace elements, etc., are known to play a role.

Anaerobic digestion converts biologically degradable carbonaceous materials into methane and carbon dioxide. Consequently, the organic matter biodegradability is one of the most important parameters. The organic matter content can be determined by COD with paper and membrane filtration for the different organic fractions present. Besides the organic matter content, the assessment of the actual biodegradability of the wastewater pollutants is an important first step prior to the application of a biological treatment process. Biodegradability determination is of particular importance in the context of the treatment of industrial wastewater that contain biologically recalcitrant constituents. Several biodegradability assays have been described in the literature (Shelton and Tiedje, 1984; Battersby and Wilson, 1988; Standing Committee of Analysts, UK. Dept. of the Environment, 1988; Birch *et al.*, 1989). The analytical methods used to assess the biodegradability vary with the different procedures and may be summarized as follows (Iza *et al*, 1991):

(a) Percentage removal of total/soluble COD and/or BOD.
(b) Percentage removal of total volatile suspended solids (VSS).
(c) Amount of methane produced per unit COD removed (total or soluble) or per unit VSS introduced.
(d) Identification and quantification of intermediates, e.g. VFA, in case of incomplete methanogenesis during the test.

Characterization of sludge, such as sludge activity, SVI, settling velocity, TSS, VSS, ash, etc., are important parameters. The present methods used to determine sludge activity can be classified as follows:

Metabolic activity assay using batch test

(1) Specific biogas production rate based on defined substrate and the amount of VSS.
(2) Specific methane production rate or specific COD removal rate based on defined substrates and the quantity of volatile suspended solids.
(3) Specific substrate conversion rate (acetate, H_2-CO_2, formate, propionate, butyrate, glucose, etc.).

Microbial population assay

(4) Most probable number (MPN) enumeration.
(5) Immunological assay
(6) Light and electronic microscopic observations.

Intercellular material assay

(7) Coenzyme F_{420} content.
(8) Ether-linked membrane content.
(9) Hydrogenate content.

In the case of Vietnamese situation, for the assessment of the wastewater biodegradability the analytical method (a) and for the metabolic activity the batch experiment using method (2) are the most suitable due to a lack of equipment, laboratory facilities and its "low cost".

Objectives of present research

In practice, the use of a proper seed sludge is of very big importance to save time for reactor start-up. Therefore, this study was conducted to assess the availability of proper seed sludge in South Vietnam with respect to the start-up of a UASB-reactor to treat RLP wastewater. In addition, similar assays also are used to determine some parameters related to the anaerobic treatment process.

In this chapter, the following studies will be presented and discussed:

(1) Assessment of the specific methanogenic activity (SMA) test of some available sludge in South Vietnam.
(2) Anaerobic biodegradability of rubber latex processing wastewater.
(3) Anaerobic biodegradation of protein-containing samples.
(4) The effect of pH on anaerobic biodegradation of RLP wastewater using batch experiments.
(5) The effect of oxygen and mixing on SMA test.
(6) The effect of the storage time on the specific methanogenic activity of granular sludge.

3.2 MATERIALS AND METHODS

Experimental conditions

Most of the experiments presented in this chapter were carried out at the laboratory of the Department of Environmental Engineering, Ho Chi Minh City University of Technology, from June 1991 to June 1995, while some additional experiments were conducted at the laboratory of the Department of Environmental Technology, Wageningen Agricultural University, The Netherlands during November 1990 - May 1991 and May - October 1993.

In Vietnam, all experiments were conducted under ambient conditions (uncontrolled temperature) and in The Netherlands, the experimental reactors were incubated in 30±2°C room.

Experimental reactors

Batch experiments were carried out in two types of reactor configuration (see Fig. 3.2.1):

1. Intermittently stirred flasks (15 sec at 140 rpm every 10 minutes) with working volumes of either 2.5 L or 5 L. Methane production was monitored with modified 10 L Mariotte flasks containing a 5% NaOH solution to remove CO_2 and H_2S from the biogas.

2. Serum bottles with a working volume of 250 mL, 500 mL and 1000 mL closed by aluminum screw caps and butyl rubber septums. Methane production was monitored with 1000 mL serum bottle containing a 5% NaOH solution to remove CO_2 and H_2S from the biogas.

Substrates

Different substrates were used depending on the purpose of the experiments.

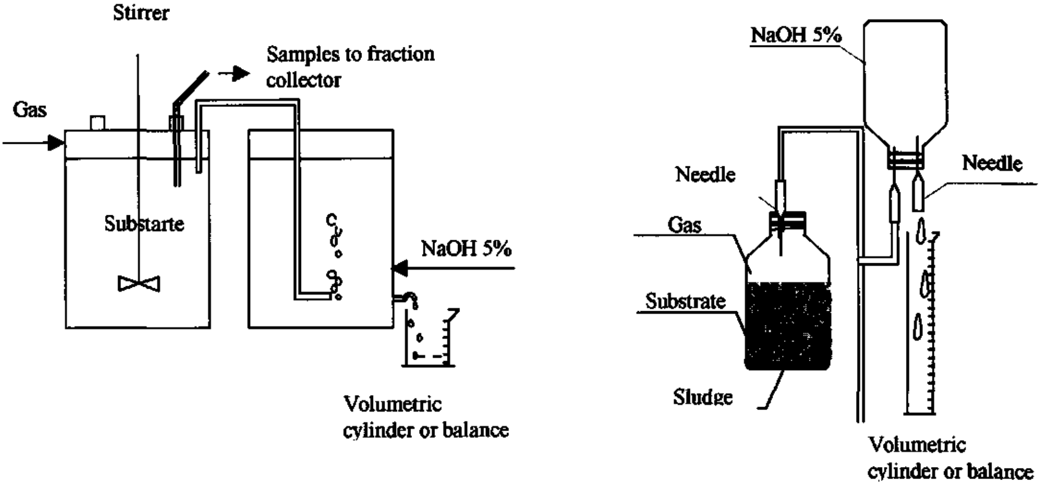
Nutrients and trace elements

In order to ensure that no nutrient or trace elements would be deficient during the experimental period, always a nutrient and trace element solution was added and the basal medium contained the following nutrients (per liter): NH_4Cl, 0.28g, K_2HPO_4, 0.25g; $MgSO_4.7H_2O$, 0,1g; $CaCl_2.2H_2O$, 0.01g; $NaHCO_3$, 0.4g; yeast extract, 0.1g; and trace elements (per liter): $FeCl_2.4H_2O$, 2mg; H_3BO_3, 0.05mg; $ZnCl_2$, 0.05mg; $CuCl_2.2H_2O$, 0.038mg; $MnCl_2.4H_2O$, 0.5mg; $(NH_4)_6Mo_7O_{24}.4H_2O$, 0.05mg; $AlCl_3.6H_2O$, 0.09mg; $CoCl_2.6H_2O$, 2mg; $NiCl_2.6H_2O$, 0.092mg; $Na_2SeO_3.5H_2O$, 0.166mg; EDTA, 1mg; resazurine, 0.2mg; 36% HCl, 0.001mL. The nutrients and trace elements were prepared as a concentrated stock solution and diluted when supplied.

Analyses

Volatile fatty acid (VFA). In The Netherlands, samples were taken and analyzed for acetate, propionate and butyrate with an HP 5890 gas chromatograph (Palo Alto, CA) equipped with a computing integrator (Spectra Physics 4100). The 2 m x 2 mm glass column was packed with Supelcoport (100- to 200-mesh) coated with 10% Fluorad FC 431. The temperature of the column is 130°C. The temperatures of the inject port and flame ionization detector were 220°C and 240°C, respectively. Nitrogen saturated with formic acid was used as carrier gas at a flow of 40 mL/min. Before use, the gas chromatograph was calibrated with standard VFA solution and peak areas were measured and compared with a standard VFA mixture (precision, +3%), and samples were centrifuged for 5 min. at 10,000 rpm in centrifuge model IEC Micromax.

In Vietnam, the titrimetric method described in the *Standard Methods* was used to determine total VFA. Samples were also centrifuged for 5 min. at 5,000 rpm in a centrifuge model HERAEUS labofuge A (Germany) or filtered using Whatman filter paper GF/A No 54 with pore size of 45 μm.



a) *Intermittently stirred flask*

b) Serum bottle

Fig. 3.2.1 Schema of batch experimental reactors.

Biogas composition. Gas samples (CH_4, O_2, CO_2, H_2) were taken daily and analyzed.

Methane, oxygen and carbon dioxide were determined with a Fisons - GS 8000 series - MFC 800 gas chromatograph equipped with two columns connected in parallel; split ca. 1:1; column 1: 1.5 m x 2 mm teflon, packed with Chromosorb 108, 60-80 mesh and column 2: 1.2 m x 2 mm steel, packed with molecular sieve 5A (60-80 mesh). The carrier gas was helium at a flowrate of 45 mL/min.. The temperatures of the oven, detector and injector are 40°C, 100°C, and 110°C, respectively. The detector used as a thermal conductivity detector (TCD). Sample size is 100 μL using Dynatech A-2 pressure-locked syringe (Baton, Rouge, LA). All gas sample analyses were conducted after calibration with a standard gas mixture.

Hydrogen was determined in a HP 5890 chromatograph equipped with a steel column (1.5 m x 2 mm), packed with molecular sieve 5A (60-80 mesh). Argon is used as the carrier gas at a flowrate of 20 mL/min.. The temperature of the oven, detector and injector are 40°C, 110°C, and 125°C, respectively. The detector is thermal conductivity detector (TCD). The sample injection volume is 100 μL. Sample analyses were conducted after calibration with standard hydrogen gas.

COD, pH, alkalinity, N-Org, N-NH_3, TSS, VSS, ash, glucose. COD, pH, alkalinity, ammonia, organic nitrogen, TSS, VSS and ash were examined according to the *Standard Methods* (APHA, 1985, 1992), except glucose.

Chemical oxygen demand (COD) was analyzed using the closed reflux, titrimetric method as described in the *Standard Methods* (1985). The sample was oxidized with potassium dichromate 0.0167 M in sulfuric acid (18 M) under pressure at 150°C in closed borosilicate 25 mL vessel for 2 h. The oxidized sample was titrated with standard ferrous ammonium sulfate (FAS) titrant 0.1 M.
Samples for soluble COD were centrifuged for 5 min. at 5,000 rpm (in Vietnam)-10,000 rpm (in The

Netherlands) or filtered using Whatman glass microfibre filter paper GF/A with pore size 45 um. The open reflux method was used to examine the samples with COD concentration higher than 50 mg/L.

pH was measured immediately after sampling with a pH meter model WTW 537 microprocessor and combined gel electrode. Titrimetric method with a 0.2 N sulfuric acid solution was used to determine alkalinity and the pH meter was used to indicate the pH break points.

Ammonia was analyzed using titrimetric method. The sample was distilled in distillation apparatus Galenkamp. Evaporated NH_3 was absorbed by boric acid and titrated by a 0.2N hydrochloric acid solution.

Organic nitrogen was examined using Macro-Kjeldahl method. The sample was firstly distilled to remove ammonia and then digested to convert organic nitrogen to ammonia before distillation.

TSS and Ash of sludge were determined at 103-105°C and 550±50°C, respectively. VSS was calculated by subtraction of ash from TSS.

Glucose was determined according to phenol-sulfuric acid method (Lindner and Shomer, 1984). To a sample containing up to 90 μg and 0-400 μg sodium azide in a volume of 2 mL, 1 mL of 5% phenol in distilled water is added. Thereafter 5 mL of conc. H_2SO_4 was vigorously injected into the center of the test tube. The mixture was then stirred for a few seconds on a Vortex, allowed to cool to room temperature for about 20 min. and the absorbance is measured at 485 nm.

Experimental procedure

The procedure for individual assays is described in detail in each experiment. Substrate (COD) depletion was used in all assays.

All experiments were carried out in duplicate or triplicate (flask or serum bottle) with two to four successive feeds and the data were compared.

Substrate and nutrient were fed to reactors intermittently after batch termination and the reported parameters were analyzed daily or once two days.

3.3 THE SPECIFIC METHANOGENIC ACTIVITY (SMA) OF SLUDGES AVAILABLE IN VIETNAM

3.3.1 INTRODUCTION

After more than three decades research and efforts of implementation, anaerobic treatment method presently indeed enjoys an increasing popularity (Lettinga, 1995) and several anaerobic processes have been applied widely in the world to treat wastewater, specially for agro-industrial wastewaters (Lettinga *et al.*, 1985, 1988, 1991). But the evolution occurred only relatively rapidly after high rate anaerobic reactors such as UASB, EGSB, AF, AFB, etc. had been developed. Up to now, more than 800 high rate anaerobic wastewater treatment plants with different capacities have been constructed in the world, most of them installed in Europe, Africa and Asia. where UASB-process occupies more than 250 units (Lettinga and Hulshoff Pol, 1991). The most important reasons for the popularity of the UASB-process are its relatively simple design, its good performance for a wide range of wastewater and the formation of excellent types of anaerobic sludge, e.g granular sludge or well settling flocculent sludge. A granular type of sludge, which provides a high biomass density with a high settling velocity, often (if not all) develops in a UASB-reactor. However, one drawback of the UASB-process is its difficult first start-up using a flocculent unadapted sludge. A rather long period of time is needed to reach the design organic loading rate. This might represent a real - although temporary - problem for the application of UASB in countries like Vietnam where so far very few wastewater treatment plants have been installed and digested sewage sludges are hardly available.

From several previous experiments and applications, it is well known that - in order to overcome this problem - the UASB-process has to be operated under the proper start up procedure and by following the (seed) important sludge characteristic by assessing the SMA of sludge, sludge volume index (SVI), settling velocity, etc. The SMA is one of the most important characteristics to be determined. Based on the SMA of sludge, the viable anaerobic biomass and the initial organic loading rate can be selected.

Several experimental methods have been developed to assess the SMA of anaerobic sludge such as a batch assay using a liquid displacement method for gas measurement, a headspace method using serum bottle of 100 mL, F_{420} determination (de Zeeuw 1984). James (1990) developed a new method for assessment of the specific methanogenic activity using a respirometer. At the department of Environmental Technology, Wageningen Agricultural University, The Netherlands, the batch methods are commonly used because of its simplicity and "low cost".

The investigations described in this paragraph deal with characterizing the available seed sludges in Vietnam for the start-up of UASB-reactors by using the SMA-assay. From the experimental results obtained, types of proper sludge were selected to inoculate laboratory UASB-reactor for treating RLP wastewater.

3.3.2 MATERIALS AND METHODS

Experimental conditions

All experiments were conducted in Vietnam from June 1991- May 1995 under ambient temperature conditions, i.e. in the range of 27-34°C. The method (de Zeew, 1984) used at the Department of Environmental Technology, Wageningen Agricultural University, was modified for these investigations, viz. N_2/CO_2 flushing was not carried out and instead of intermittent mechanical mixing, manual mixing three times a day was applied.

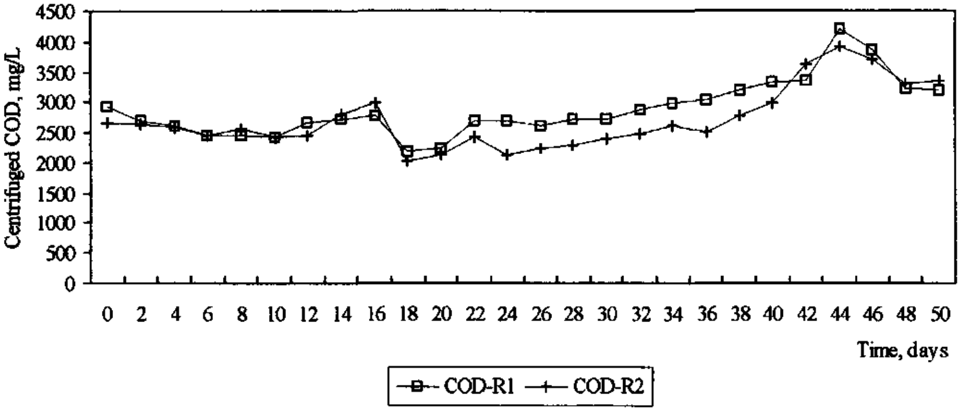


Fig. 3.3.1 The results of SMA test for fresh pig manure sludge in South Vietnam.
R1, R2: duplicate experimental bottles.

Digested pig manure sludge. The TSS content of DPMS was low (i.e. 4.1%) due to the poor dewatering characteristics. The VSS content is 72.63% and the SMA of DPMS amounted to 0.13-0.26 g COD/g VSS.d which is the highest of the investigated locally available sludges (STS, CS). The results of the SMA tests conducted with different types of DPMS revealed that DPMS needed about 16-18 days for the first feed and 8-12 days for both second and third feed to degrade completely the VFA. The course of the COD reduction found in the second and third feed were very similar (see Fig. 3.3.2). With a fresh DPMS taken from a well operating biogas digester no differences between the first, second and third feed was found.

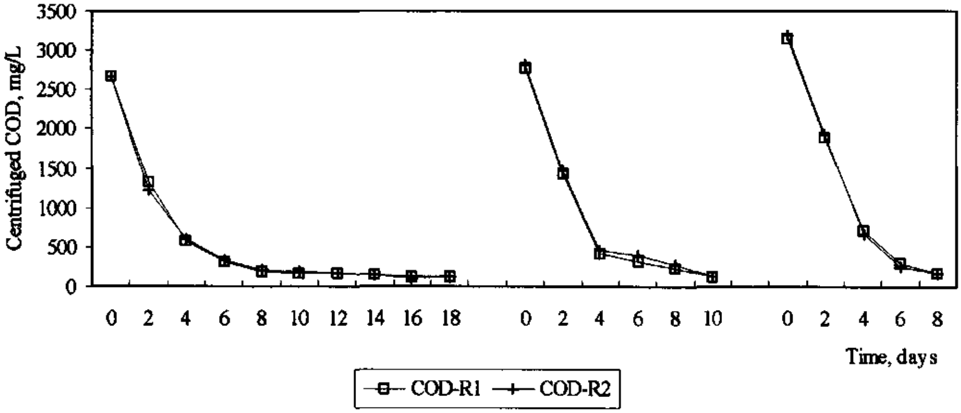


Fig. 3.3.2 The results of SMA test for digested pig manure sludge in South Vietnam.
R1, R2: duplicate experimental bottles

City canal sludge. The moisture content of CS is low (TSS of 16.53 %) while the ash content is high (69.66%). The inorganic fraction mainly consisted of sand. The SMA of CS is rather low (0.12-0.15 g COD/g VSS.d) and it needed about 18-20 days for the first feed and 8-10 days for the second and third feed to complete the VFA degradation (see Fig. 3.3.3). The period of time required for determining the SMA of CS depended strongly on the site where sludge was taken.

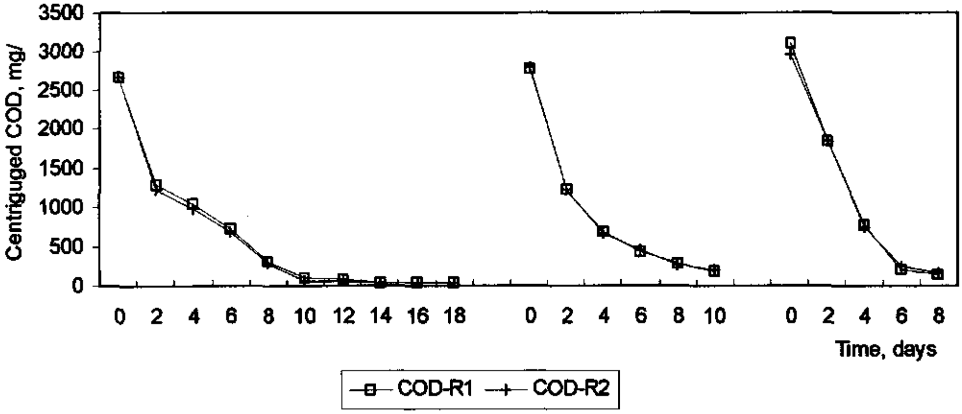


Fig. 3.3.3 The results of SMA test for city canal sludge in South Vietnam.
R1, R2: duplicate experimental bottles

Septic Tank Sludge. The TSS, VSS and ash content of STS are 7.69%, 72.87% and 28.7%, respectively, which are very similar values found for DPMS (see Table 3.3.1). But the SMA of STS (0.11-0.12 g COD/g VSS.d) is slightly lower than that of DPMS, presumably, because not all organic compounds were already digested and a smaller part of the VSS consists of viable biomass. STS needed about 38-50 days for the first feed and 18-20 days for the second and third feed (see Fig. 3.3.4).

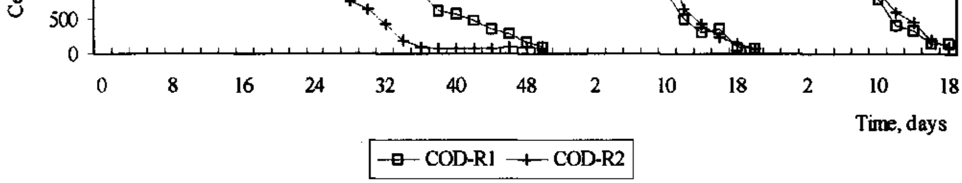


Fig. 3.3.4 The results of SMA test for septic tank sludge in South Vietnam.
R1, R2: duplicate experimental bottles

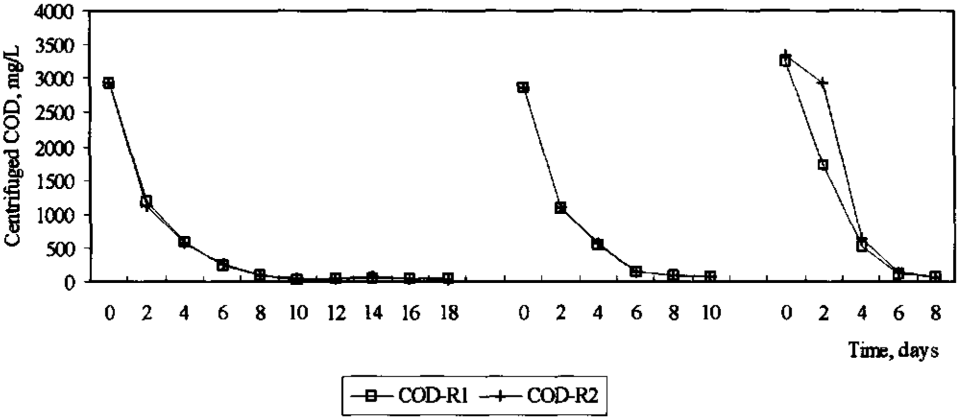


Fig. 3.3.5 The results of SMA test for Dutch Granular Sludge
R1, R2: duplicate experimental bottles

Compared to Dutch DPMS which contained a very high amount of ammonia (10,068 mg NH_4^+-N/L), DPMS in Vietnam is lower in NH_4^+-N content (viz. 1,691 mg NH_4^+/L). The reason for this difference is that urine is collected separately at pigsty in Vietnam for use as fertilizer.

From the experimental data obtained in the SMA test with Dutch DPMS, i.e. at a high ammonia content, shown in Fig. 3.3.6, it can be seen that ammonia is quite inhibitory for methanogens. During the first 8-9 days any VFA (COD) was not degraded and the concentration of COD-VFA remained at 2,715 mg/L, and from then onwards the COD-VFA concentration started to drop slowly to 2,258-2,282 mg/L at day 20 and 1,820-1,852 mg/L at day 25. The COD_t (COD determined by titrimetric method) increased from 3,200 mg/L at the beginning to a value of 4,514-4,560 mg/L at day 9 as a result of hydrolysis of part of solid organic fraction of pig manure. During the next period of time the COD_t decreased to 4,056-4,089 mg/L at day 20 and 2,900-3,100 mg/L at day 25.

According to the results obtained it looks that ammonia does not strongly inhibit the acetogens which convert butyrate into acetate. During the first 8 days butyrate was converted slowly, i.e. its concentration dropped from 628 mg/L to 519 mg/L and then rapidly from day 9-10 to day 16-17 (see Fig. 3.3.6). Beyond day 22-24 the concentration of butyrate was 5-10 mg/L.

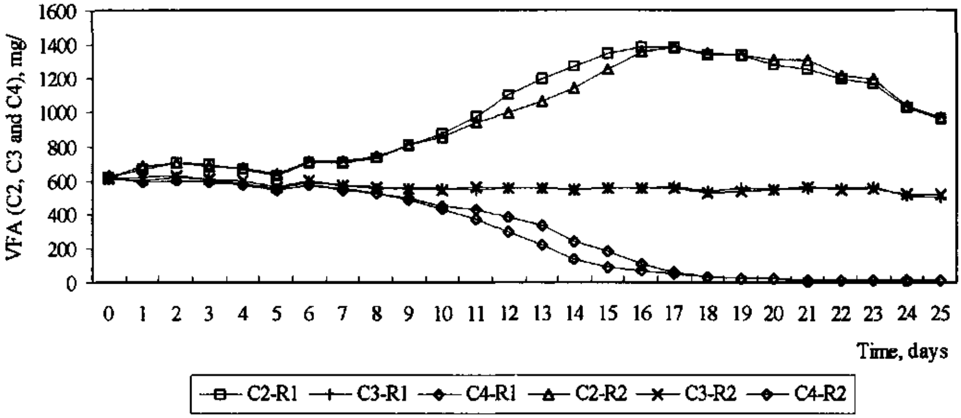


Fig. 3.3.6 The degradation of VFA in the SMA test with a high ammonia containing Dutch DPMS. *R1, R2: duplicate experimental bottles*

From these results it is clear that methanogenesis on acetate is strongly inhibited while also little if any propionate is degraded within a period of 25 days. The results obtained with the low ammonia concentration DPMS from Vietnam (see Fig. 3.3.2) show that any inhibition did not occur in that case.

The data of previous investigations (Koster, 1989) revealed that after adaptation, anaerobic bacteria can tolerate ammonia concentrations up to 6,000 mg/L and even up to 7,800 mg/L. The results obtained in the present study reveal that methanogens even can tolerate and recover from an ammonia concentration of 10,680 mg/L.

In a batch experiment conducted at high NH_4^+ concentration a long period of time is needed for adaptation. The situation is different compared to a continuous flow reactor where the liquid with the high NH_4^+ concentration can be replaced by a liquid with a lower N-NH_3 concentration. Observation made in a lab-scale UASB-reactor (Chapter 4, paragraph 4.3) showed that after 2-3 days when ammonia was washed out, the activity of the sludge could be recovered and then the gas production resumed after a period of 7-10 days.

3.3.4 DISCUSSIONS

The SMA of anaerobic sludge is an important selection criterium for seed sludge of a UASB-reactor (Zeew, 1984; Hulhoff Pol, 1989; James *et al.*,1990; Iza *et al.*, 1991) because it:

- Classifies the potentials of sludge in converting a soluble VFA substrate into methane and carbon dioxide.
- Determines the permissible initial organic space loading together with the amount of sludge present in the reactor at the beginning of the start-up.

Moreover results of a SMA-test also provide information about:

- The evolution of sludge activity during start-up by applying the tests to periodically sludge samples taken from the reactor.
- Presence of toxic compounds.

The specific methanogenic activity of sludge is defined as the methane production rate of the sludge (g CH_4-COD/g VSS.d). In this study, the SMA of the sludges (g COD/g VSS.d) was calculated from the substrate (COD) depletion rate and the amount of sludge present in the assay (2-3 g VSS/L). It is necessary to mention that the amount of new biomass produced during the experimental period generally is small compared to the initial amount of active biomass. At a COD of the standard VFA solution of about 2,600 mg/L and a yield (Y) of methanogens of 0.024 g VSS/g COD.d (de Zeeuw, 1984), the total amount of newly produced active biomass after the third feed amounts to 0.187 g VSS. Although this amount is small compared to the initial total VSS of seed sludge (2-3 g/L), it still can be substantial in case the starting activity of the seed sludge was very small. On the other hand, it is possible to calculate the amount of COD that is degraded by 0.187 g VSS (new active biomass) based on the theoretical SMA of methanogens, consequently the rest amount of COD is converted by the old biomass. However, from a practical point of view, the results still can be applied for selecting the proper seed sludge, the amount of sludge to be supplied to reactor and the initial loading rate to be imposed to the system, because according to the start-up procedure proposed by Hulshoff Pol (1989); Lettinga and Hulshoff Pol (1991) and Lettinga (1995) the initial COD concentration and organic loading rate should be 2-3 g/L and 1.5-3 kg COD/m^3.d, respectively, at the beginning of start-up period, depending on the quality and amount of seed sludge.

One of the basic conditions to be met for a high rate anaerobic wastewater treatment system like the UASB-process is that the retained sludge will obtain a high specific activity (Hulshoff Pol, 1988; Lettinga *et all*, 1985, 1991; Lettinga, 1995; Iza *et al.*, 1991). During the first start-up period of a UASB-reactor, the initially specific activity of sludge frequently is very low, but a highly active sludge gradually will develop in the reactor under proper start-up operational condition (Hulshoff Pol, 1989). In fact, any type of sludges can be theoretically used as seed sludge, but obviously the start-up will be completed earlier when using a higher quality seed sludge. For that reason the SMA tests were carried out in order to find the more proper seed sludge.

The experimental data of the various SMA assays (see Fig. 3.3.2. 3.3.3 and 3.3.4) reveal that the reduction rate of COD-VFA concentration found in duplicate tests after three successive feeds in all cases was almost the same. The deviations found in the first feed between the duplicate test generally were very small, while exactly the same pattern was found in the third and/or fourth feed. The specific activity of the sludge therefore was calculated from the results of the third feed.

The results in Fig. 3.3.2, 3.3.3 and 3.3.4 show that during the first feed the reduction rates (or activity of sludge) generally were very low, because anaerobic bacteria need a certain period of time for adaptation to the new substrate, particularly to high VFA concentrations. The DPMS and CS sludges needed about 10-18 days in the first feed to reduce the substrate (COD) concentration to approximately 100 mg/L. In the second and third feed they both need about 8-12 days for completing the degradation. The GS needed only 8 day during the first feed to reduce the COD concentration from 2938 mg/L to 87 mg/L and the SMA calculated from the slope of the curves in the first and third feed were almost the same. The SMA of the DPMS and CS ranged from 0.15-0.26 g COD/g VSS.d and 0.12-0.15 g COD/g VSS.d., respectively.

The results in Fig. 3.3.2, 3.3.3 and 3.3.4 also show that the substrate depletion rate is high at a COD concentration exceeding 250-300 mg/L depending on the type of sludge and once the COD-VFA concentration had become in the range of 250-300 mg/L, indeed the reduction rate dropped down very rapidly, which partially can be explained by mass transport limitation. Low substrate concentrations affect the rate of mass transfer negatively in methanogenic biofilm of in granular sludge (Dolfing 1985), but the substrate reduction rate is also affected by K_s value (Kato, 1994). So the maximum specific activity of sludge should be calculated at COD concentrations exceeding 250-300 mg/L. Comparing the results obtained with the DPMS, CS and GS (see Fig. 3.3.7) indicates that at high COD concentrations only a small difference of the COD reduction rate was found for the DPMS, CS and GS, but at a low COD concentration, i.e. below 250-300 mg/L, the difference can be seen clearly for the DPMS, CS and GS.

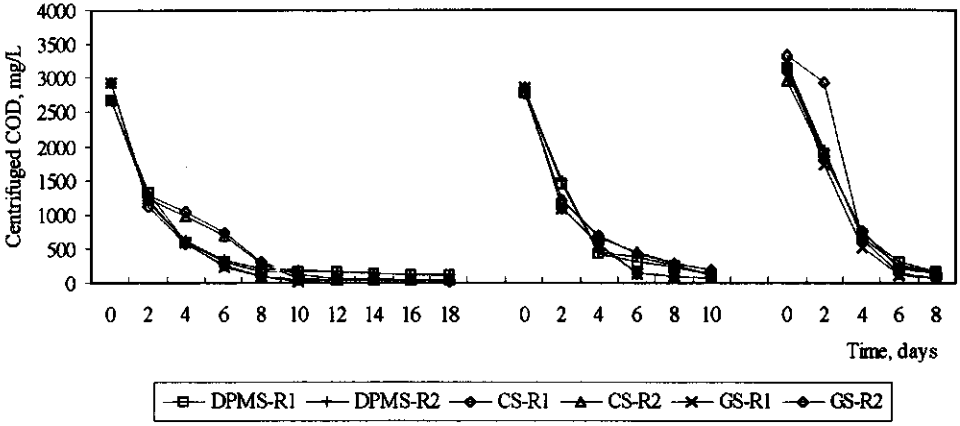


Fig. 3.3.7 The comparison of COD reduction rate between DPMS, CS and GS.
R1, R2: duplicate experimental bottles

It could be expected that the initial COD reduction rate for a sludge like FPM, only can be negligible and consequently also that of the gas production. Apparently the content of viable methanogenic organisms in the FPM is very low. Therefore using the FPM sludge for start-up of the UASB-reactor a long period of time would be needed.

The SMA of the CS as seed material is sufficiently high (0.12-0.15 g COD/g VSS.d), but this sludge contains a very high amount of sand and inorganic matter which might cause clogging problems in the distribution system of a UASB-reactor.

A huge amount of the STS is available in Ho Chi Minh City and since the SMA test indicates that the specific activity is sufficiently high, this sludge could be an attractive seed, although the content of human pathogens could represent a big - although temporary - problem for use. A certain amount of fresh human dung still remains in the sludge.

Based on results of the SMA tests of the sludges and other factors such as available amount in practice, transport conditions, inorganic content, the DPMS is strongly recommended as seed sludge for lab-scale experiments.

In order to apply a procedure of the SMA test in Vietnam, where gas chromatography for the COD-VFA determination is not yet easily possible, a titrimetric COD analysis was conducted concomitantly in order to compare the results. The GS results gave a deviation of 300-500 mg/L with the titrimetric-COD analyses, due to an amount of colloidal present in the centrifuged or filtered samples, and once the COD-VFA concentrations were completely degraded the titrimetric COD concentration still gave a value of 120-160 mg/L (see Fig. 3.3.8a). In case DPMS was used as seed sludge, the deviation between the GS COD-VFA and titrimetric COD concentration was extremely high (see Fig. 3.3.8b).

3.4 ANAEROBIC BIODEGRADABILITY OF RUBBER LATEX PROCESSING WASTEWATER

3.4.1 INTRODUCTION

A number of characteristics of a wastewater are important for designing a wastewater treatment facility. One of these characteristics is the COD concentration which represents a measure for the organic pollution of the wastewater. However, this parameter does not indicate whether the organic matter is biodegradable.

For biological treatment processes, the aerobic or anaerobic biodegradability of organic pollutants in the wastewater is therefore a very important parameter for characterizing the wastewater (Iza *et al.*, 1991). Since the high rate anaerobic biological treatment process often is not sufficient for discharge of the effluent to receiving waters, the COD parameter frequently is also used to assess the remaining organic pollution of the wastewater. In order to find the appropriate post-treatment processes to complete the treatment of the wastewater once again the biodegradable fraction of the COD generally is the relevant parameter.

In practice, the result from the anaerobic biodegradability assay gives a useful indication as to whether biological processes can be applied to treat the wastewater in question.

For assessment of the anaerobic biodegradability of wastewaters several methods have been developed (Iza *et al.*, 1991). In most of these methods the amount of methane produced from a known amount of substrate COD is measured. For this purpose the composition of biogas should be determined. This easily and quickly can be done by gas chromatography, but this method is not available in developing countries like Vietnam, while also the cost of analyses are high.

In the experiments described here a similar procedure as used in the SMA tests was applied (measurement of the depletion rate of the substrate) to assess the anaerobic biodegradability of the RLP wastewater and the effect of the RLP wastewater concentration on the anaerobic biodegradation rate.

3.4.2 MATERIALS AND METHODS

Experimental conditions

The assays were conducted at the laboratory of the Department of Environmental Technology, Wageningen University, The Netherlands and at the Environmental Engineering laboratory, Ho Chi Minh City University of Technology, Vietnam during 1992-1993.

In The Netherlands, all experimental reactors were incubated at 30±2°C. In Vietnam, the reactors were exposed to ambient temperature condition and mixing was achieved manually three times a day. Both assays were conducted with real RLP serum.

Experimental reactors

Serum bottles with total volume of 1200 mL and 600 mL, and an active working volume of 1000 mL and 500 mL, respectively, were used to simulate the experimental reactors. The scheme of the experiments conducted is shown in Fig. 3.4.1. Biogas accumulated in the head space was released daily by using needle. In Vietnam, the bottles were covered by black paper to prevent exposure to sunlight because of algae growth, in The Netherlands the bottles were placed in a dark room.

Inoculum

Three types of sludge were used as seed sludge in this experiment:

- DPMS from a biogas digester in The Netherlands;
- GS from the Latenstein starch factory in The Netherlands;
- DPMS from a pig manure biogas digester in Vietnam.

In The Netherlands, the DPMS and GS had been stored in 5°C room for more than one year prior to use. The GS was brought to Vietnam and was restored here again in a refrigerator since May 1991, i.e. for an additional of 52 months prior to use. Stored sludges were exposed to 30°C or tropical temperature for one day before inoculation of the bottles.

In the experiment in Vietnam the DPMS used had been taken freshly from the biogas digester and screened prior to inoculation to remove big particles.

Before inoculation, the content of TSS, VSS, ash and ammonia of the sludges were determined. The amounts of DPMS and GS inoculated to the bottles were 3 g VSS/L and 2 g VSS/L, respectively, calculated on the basic of the wet weight of the sludge.

Substrate

The serum obtained after the coagulation of rubber latex was used in all experiments.

In The Netherlands, latex was coagulated using formic acid and in Vietnam using acetic acid. Serum was first diluted with tap water in order to obtain the desired concentration. Nutrients and trace elements were added to ensure no depletion of any necessary elements during the experiment.

Analyses

The VFA composition and calculated COD-VFA (in The Netherlands) and the titrimetric filtred/centrifuged COD_t (in The Netherlands and in Vietnam) were measured daily in order to assess the anaerobic biodegradation of RLP waste water. Samples were taken by syringe and needle.

Experimental procedure

All experiments were carried out in duplicate or triplicate. After setting up the experiment the above parameters were analyzed daily and the experiments were carried out with three successive feeds until steady state was obtained. In Vietnam after termination of the first and second feed, the supernatant liquid was removed by siphon and replaced by a fresh full feed. In The Netherlands the procedure was similar as in the VFA experiment, i.e. concentrated wastewater was injected into the bottles after each termination without removing the supernatant. The biodegradability assessment was calculated based on the results of the third feed.

3.4.3 RESULTS

The anaerobic biodegradability of the RLP wastewater.

DPMS and GS were used as inoculum in the investigations. The TSS, VSS, ash and ammonia content of the sludges are shown in Table 3.4.1. The anaerobic biodegradability of the RLP wastewater experiments were carried out several times both in The Netherlands and in Vietnam. The experimental results obtained in The Netherlands are summarized in Table 3.4.2 and shown in Fig. 3.4.1, 3.4.2, 3.4.3.

Table 3.4.1 TSS, VS, ash, ammonia content of the seed sludges

Type of sludge	TDS %	VSS %	Ash %	Ammonia mg/L
DPMS[a]	7.64	6198	38.02	10,068
GS[a]	10.19	78.01	21.09	nd
DPMS[b]	17.76	84.32	15.68	1,691

DPMS[a]	*DPMS from biogas digester in The Netherlands;*
DPMS [b]	*DPMS from biogas digester in Vietnam;*
nd	*not determined*
VSS & ash	*based on TSS*

Experiments with granular sludge conducted in The Netherlands

According to the experimental data obtained in the laboratory at the Department of Environmental Technology, Wageningen Agricultural University, the organic matter present in RLP wastewater is converted via acetate, propionate and butyrate into methane. In the first feed the COD concentration dropped from 1,600 mg/L to 120-160 mg/L in a period of 6-8 days using a granular sludge concentration of 2 g/L. Any VFA then was not present anymore in the medium. Beyond day 8 up to 90% of organic matter was broken down (see Fig. 3.4.1). During this period the acetate, propionate and butyrate raise up at day 2 to maximum concentration of 180, 69 and 68 mg/L, respectively, and the pH increased from 6.5 to 8.0 in all bottles. The peak of the VFA-COD concentration at day 2 approaches the COD_t.

The second feed only needed 6 days to reduce the COD_t concentration from 1663 mg/L to 176 mg/L corresponding to a COD removal efficiency of 89.4%, and the amount of VFA remained was then very small. But the highest VFA concentration already appears at day 1, viz. acetate 453 mg/L, propionate 122 mg/L and butyrate 53 mg/L.

In the third feed, at day 4 only 21 mg/L acetate was left in the medium and the COD concentration dropped from 1,803 mg/L to 186 mg/L at day 5 resulting in 89.7% COD degradation. The results shown in Fig. 3.4.1 allow a good comparison between the COD-VFA concentration and the titrimetric COD_t concentration. It is obvious that more than 80% organic matter in RLP wastewater was converted into VFA. The maximum acetate concentration found was 287 mg/L. The fourth feed gives similar results as the third feed.

The results show that after the COD-VFA was eliminated from the solution, only relatively very small amount (appr. 10% of the original COD concentration) of COD concentration remained in the solution, and the pH in all cases increased from 6.5 to 7.5-8.0. The specific activity of the GS calculated from the third feed amounted to 0.73 g COD/g VSS.d. In this assay the conversion of formiate was not assessed because the formiate analyses was not made.

Table 3.4.2 The anaerobic biodegradability of RLP waste water
(carried out in The Netherlands with GS)

Number of feed		Granular sludge
First feed		
COD_b	mg/L	1600
COD_e	mg/L	160
COD_r	mg/L	1440
E	%	90.0
T	days	9
Second feed		
COD_b	mg/L	1663
COD_e	mg/L	176
COD_r	mg/L	1487
E	%	89.4
T	days	6
Third feed		
COD_b	mg/L	1803
COD_e	mg/L	186
COD_r	mg/L	1617
E	%	89.7
T	days	5

COD_b	*the COD concentration at the beginning.*
COD_e	*the COD concentration at the end.*
COD_r	*the COD removed.*
E	*the COD removal efficiency.*
T	*experimental duration.*

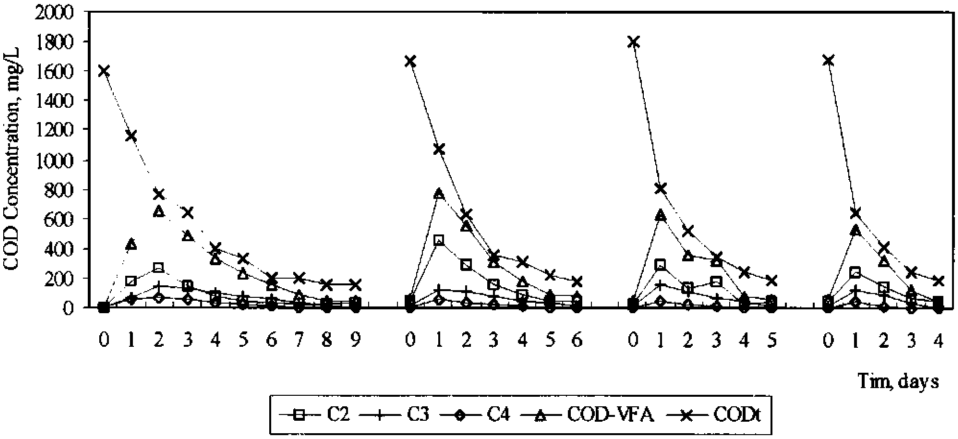


Fig. 3.4.1 Anaerobic biodegradation of RLP wastewater.
(carried out in The Netherlands with GS)

Experiments with Dutch digested pig manure sludge conducted in The Netherlands.

In the experiment carried out with Dutch DPMS, which contained a very high amount of ammonia (10,068 mg/L), the conversion of VFA to methane was seriously inhibited. The $\mathrm{COD_t}$ concentration of the solution increased from 1600 mg/L to 3,200 mg/L after addition of the RLP wastewater (see Fig. 3.4.2), and then to a maximum concentration of 3,485 mg/L. The COD concentration remained unchanged until 15-20th day, but from then onwards it gradually dropped down. Although anaerobic biodegradation of RLP wastewater could not be assessed in this experiment, the products of acidogenic and acetogenic phases manifested clearly in the results (see Fig. 3.4.3). VFA accumulated in the medium, i.e. the COD-VFA increased from 0 mg/L at the beginning up to a maximum concentration of 1343 mg/L at day 12. The VFA mainly consisted of acetate, propionate and a very small amount of butyrate, viz. 869 mg/L, 206 mg/L, and 77 mg/L, respectively. Starting from day 14 the VFA were slowly converted, resulting in a reduction of both COD-VFA and $\mathrm{COD_t}$. The same phenomena were already found in the experiment presented in paragraph 3.3.

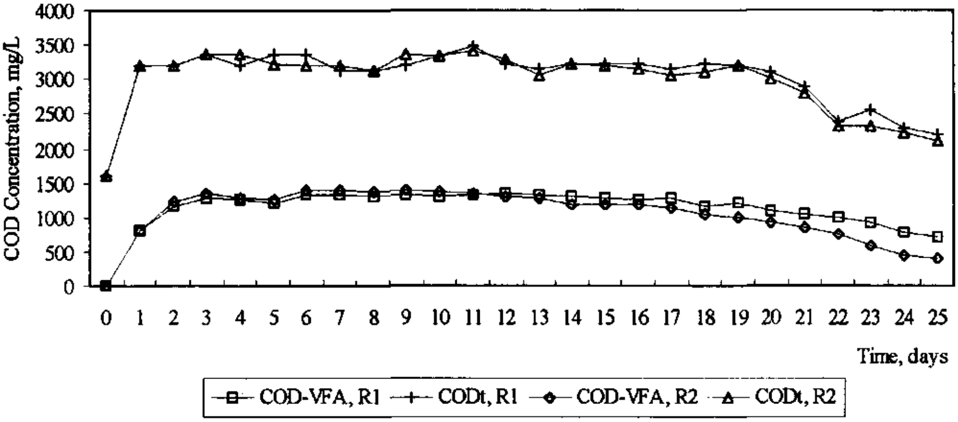


Fig. 3.4.2 The course of the COD-VFA and $\mathrm{COD_t}$ concentration in the experiment conducted with Dutch DPMS as seed sludge and RLP wastewater.
R1, R2: duplicate experimental bottles.

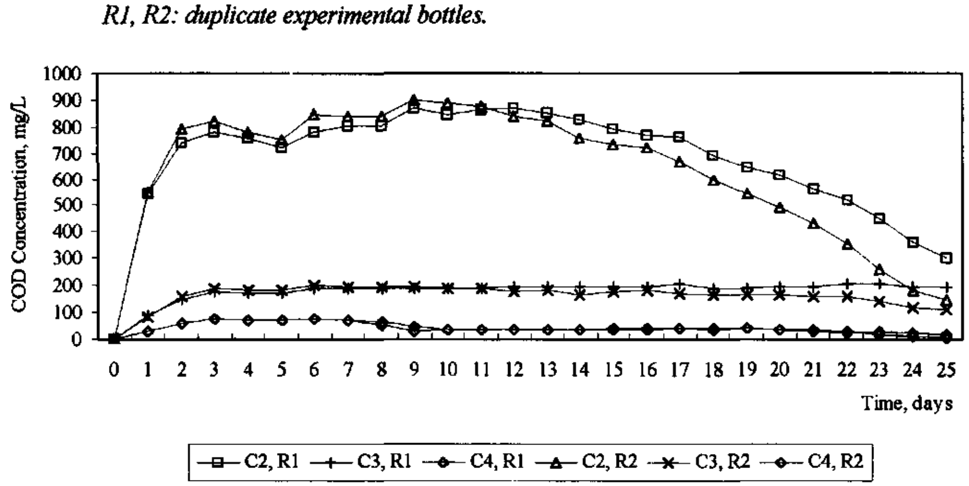


Fig. 3.4.3 The accumulation of VFA in the reactor fed with RLP wastewater and with Dutch DPMS as seed sludge. *R1, R2: duplicate experimental bottles.*

The same experiments to assess the anaerobic biodegradability of RLP wastewater were perpormanced in Vietnam in the period 1992-1993, using five serum bottles with GS and with Vietnamese DPMS. The results are summarized in Table 3.4.3.

Experiments with granular sludge conducted in Vietnam.

In the first feed, the 2 years stored GS needed 18 days to reduce the COD_t concentration from 2,773-3392 mg/L to 73-80 mg/L corresponding to a COD_t removal efficiency of 97.4-97.7%. The COD_t reduction rate was high during the first six days, but at the COD_t concentration below 763 mg/L it dropped. In the second and third feed the GS needed 12 and 8 days to reduce COD_t from 2,192-2,512 mg/L and 2,025-2,045 mg/L to 75-169 mg/L and 124-136 mg/L (see Fig. 3.4.4) corresponding once again to a very high COD_t removal efficiency, viz. 93.3-96.6% and 93.3-93.9%, respectively. It seems that in the sucessive feeds, the COD_t removal efficiency slightly decreased. From the results in Fig. 3.4.4 it furthermore is obvious that in the second and third feed the COD_t concentration at the break point where COD reduction rate declines is somewhat higher than in first feed.

Table 3.4.3 The anaerobic biodegradation of RLP waste water (carried out in Vietnam with DPMS and GS)

Number of feed		GS	DPMS
First feed			
COD_b	mg/L	2773 - 3392	2649 - 2773
COD_e	mg/L	73 - 80	127 - 131
COD_r	mg/L	2700 - 3312	2518 - 2646
E	%	97.4 - 97.7	95.1 - 95.4
T	days	18	18
Second feed			
COD_b	mg/L	2192 - 2512	2160 - 2330
COD_e	mg/L	75 - 169	123 - 187
COD_r	mg/L	2117 - 2343	1973 - 2157
E	%	93.3 - 96.6	91.3 - 94.6
T	days	12	12
Third feed			
COD_b	mg/L	2025 - 2045	1875 - 2145
COD_e	mg/L	124 - 136	169 - 187
COD_r	mg/L	1893 - 1901	1688 - 1969
E	%	93.3 - 93.9	90.0 - 91.8
T	days	8	8

COD_b - the COD concentration at the beginning.
COD_e - the COD concentration at the end.
COD_r - the COD removed.

Table 3.4.4 The experiment with various COD_t concentration

Number of feed		GS					DPMS				
		R_1	R_2	R_3	R_4	R_5	R_1	R_2	R_3	R_4	R_5
First feed											
COD_b	mg/L	2784	5280	7733	10000	2400	2736	5173	7786	9960	2432
COD_e	mg/L	133	214	215	802	38	95	140	215	305	44
E	%	95.2	95.9	97.2	92.0	98.4	96.5	97.3	97.2	96.9	98.2
T_c	days	28	28	28	28	24	28	28	28	28	36
Second feed											
COD_b	mg/L	2783	4573	6527	7817	2590	2751	4123	6254	7973	2779
COD_e	mg/L	237	242	369	855	38	136	209	273	394	34
E	%	91.5	94.7	94.3	89.1	98.5	95.1	94.9	95.6	95.1	98.8
T_c	days	18	18	18	18	16	18	18	18	18	18
Third feed											
COD_b	mg/L	1968	3060	4600	5880	2512	1888	3540	4120	5720	2400
COD_e	mg/L	165	160	300	478	37	105	156	266	330	44
E	%	91.6	94.8	93.5	91.9	98.5	94.4	95.6	93.5	94.2	98.2
T_c	days	16	16	16	16	14	16	16	16	16	16
Fourth feed											
COD_b	mg/L	2712	3809	6019	7428	2585	2585	3980	6019	7428	2585
COD_e	mg/L	208	211	358	493	161	153	201	282	348	62
E	%	92.3	94.5	94.1	93.4	93.8	94.1	94.9	95.3	95.3	97.6
T_c	days	12	12	12	12	12	12	12	12	12	12

COD_b	*COD_t concentration at the beginning.*
COD_e	*COD_t concentration at the end.*
COD_r	*COD_t removed*
R1, R2, R3, R4	*serum bottle number 1, 2, 3, 4 with RLP wastewater, respectively.*
R5	*serum bottle with VFA for comparison.*

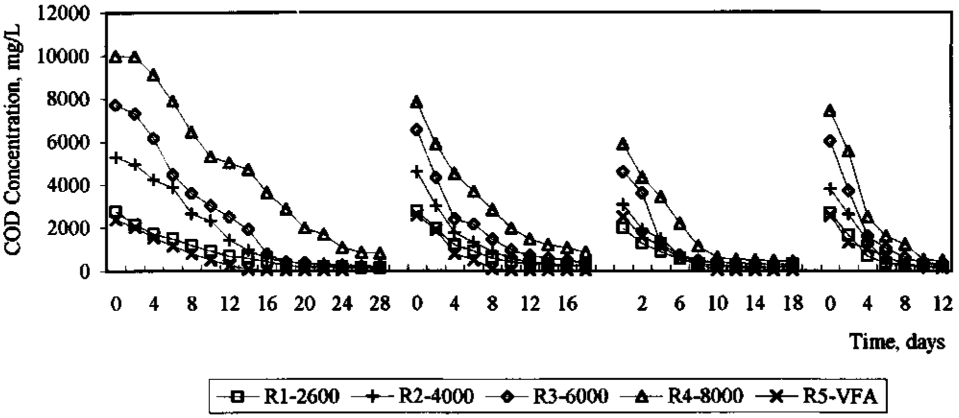


Fig. 3.4.6 The COD reduction obtained at the various COD concentrations in the experiment with GS. *R1, R2, R3, R4, R5: experimental bottles.*

Experiment with DPMS. Contrary to the results presented in Table 3.4.3 in this experiment DPMS gave a slightly better degradation. In the first feed the COD_t concentration was reduced from 2,736-9,960 mg/L to 95-305 mg/L corresponding to a COD removal efficiency of 97.2-98.2% which needed 28 days. In the second feed the anaerobic bacteria already were well adapted to the new environmental conditions and the substrate and they only needed 18 days to give the same results. The fourth feed gives the same COD removal efficiency (94.1-95.3%) as the second feed but at shorter time, i.e. 18 days instead of 12 days (see Fig. 3.4.7).

With both sludge (GS and DPMS), the COD_t removal efficiency generally was higher at the higher COD concentration, but the reduction rate was higher at the higher initial concentration.

Once again the results of this experiment also prove the very high anaerobic biodegradability of RLP wastewater.

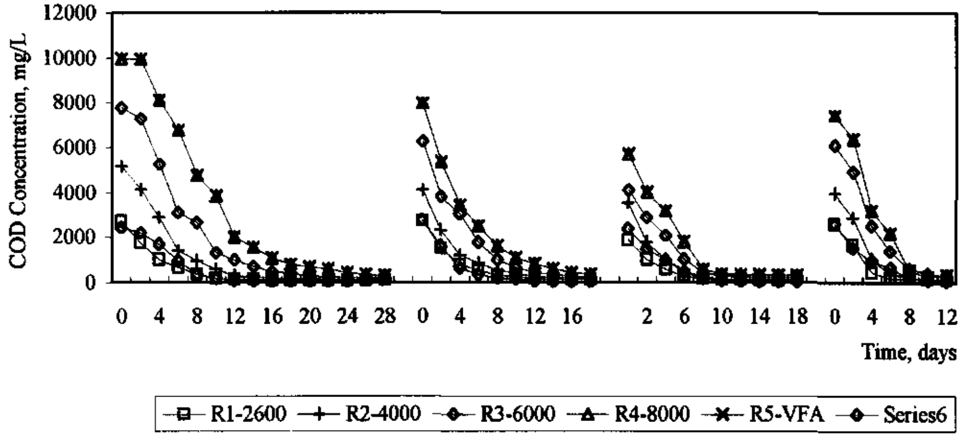


Fig. 3.4.7 The COD reduction in various COD concentration experiment with DPMS. *R1, R2, R3, R4, R5: experimental bottles.*

3.4.4 DISCUSSION

From the characteristics of RLP wastewater presented in Chapter 2 and the results of biodegradability assays of RLP wastewater it is clear that the anaerobic biodegradability of RLP waste water is high, i.e. exceeding 90-95% (if not higher).

Consequently, all the organic components of RLP wastewater, i.e. including proteins (2-2,7%), sugar (glucose 1.5-2%), lipid (1-1.5%) (see Chapter 2), are well biodegradable. The fermentation products formed are mainly acetate and propionate. The amounts of formate and butyrate produced are very small. Any iso-butyrate and valerate could not be detected. Similar results were found with gelatine in previous studies on hydrolysis and acidogenic fermentation of gelatin under anaerobic conditions (Breure *et al.*, 1985) and studies dealing with the granulation in UASB-system (Moosbrugger *et al.*, 1990).

Except in the experiment dealing with the effect of the COD concentration on the anaerobic biodegradability of the RLP wastewater, the degradation of RLP wastewater found with GS was slightly more complete than with DPMS.

In the experiments carried out in The Netherlands with the serum obtained from the formic acid coagulation process, the pH increased during the digestion process up to values of 8 or even higher. This might be the reason for the slightly lower COD removal efficiency found with this type of serum compared to the values found with serum originating from acetic acid coagulation. The experiments with formic acid coagulation carried out in Vietnam gave very similar results as in the experiments conducted in Wageningen, i.e. sometimes the pH increased to 8.9 or 9. The color of sludge then changed to very dark and the gas production and the methanogenesis ceased completely.

It should be mentioned here that the calculated activity of sludge found on RLP wastewater is lower than the true sludge activity because the COD removal rate was determined based on filtered or centrifuged sample. During the anaerobic digestion process also biodegradable suspended organic solids present in RLP wastewater, e.g. protein colloidal matter, lipids, etc., are hydrolysed resulting in an increase of soluble COD which was not included in the initial COD concentration. In addition, since fresh concentrated wastewater was supplied in the successive feeds to the reactor, an increase of final COD should have taken place in case that wastewater would contain non-biodegradable soluble matters. Unless these compounds precipitate or being sorbed to the sludge, they should accumulate in the solution and consequently the COD concentration would increase. However the results of the experiments show that even after the third feed the remaining COD concentration still was the same as in the first feed. Apparently, the organic matter of RLP wastewater is almost completely biodegradable.

For practical application, attention should be paid to the risk of a pH drop in case the load applied is too high, because pH inhibition then might occur in the lower part of reactor. To prevent problems some alkali should be added in that case in order to provide sufficient buffer capacity to the system.

3.4.5 CONCLUSIONS

1. The biodegradability of RLP wastewater exceeds 95%
2. Sugars, proteins and lipids, contained in the RPL wastewater are converted into methane mainly via acetate and propionate.

3. For unadapted sludges the buffer capacity of the system may be insufficient.

4. In case formic acid is used for latex coagulation, the pH will increase to too high values due to degradation of formate.

5. The anaerobic biodegradability of RLP wastewater is almost independent on its COD concentration.

6. Regarding the high anaerobic biodegradability of the RLP wastewater, high rate anaerobic treatment processes represent the ideal solution to combat environmental pollution problems with this type of wastewater in South Vietnam.

3.5 ANAEROBIC BIODEGRADATION OF THE PROTEIN CONTAINED IN RUBBER LATEX PROCESSING WASTEWATER WITH GRANULAR SLUDGE

3.5.1 INTRODUCTION

The anaerobic degradation of proteins is important for the recycling N and S as well as C presented in this category of components in nature. As mentioned in Chapter 2, RLP serum contains 810-1,565 mg N-Org/L as proteins which consists of 14 amino acid, e.g. glycine, alanine, leucine, glutamic, a.o.. This amount of the organic nitrogen compounds is equivalent to about 5,000-9,800 mg/L protein. Under anaerobic conditions, the proteins are first hydrolyzed to peptides and amino acids and subsequently the amino acids are fermented to short-chain or branched-chain fatty acids, ammonia, and CO_2 (McInerney, 1988). The anaerobic biodegradation of some amino acids proceeds according to the reactions shown below:

Alanine & Glycine

$$\begin{array}{l} \mathrm{CH_3CHNH_2COOH + 2H_2O \rightarrow CH_3COOH + NH_3 + CO_2 + 4H} \\ \quad \mathrm{2CH_2NH_2COOH \ + 4H \ \ \rightarrow 2CH_3COOH + 2NH_3} \\ \hline \end{array}$$

$$\mathrm{CH_3CHNH_2COOH + 2CH_2NH_2COOH + 2H_2O \rightarrow 3CH_3COOH + 3NH_3 + CO_2}$$

In this reaction, the amino acid-fermenting clostridia oxidizes alanine while glycine serves as the electron acceptor.

Threonine

Barker (1961) postulated that the formation of only acetate from threonine could involve the direct cleavage of threonine into acetaldehyde and glycine by threonine aldolase according to reaction:

$$\mathrm{CH_3CHOHCHNH_2COOH \rightarrow CH_3COOH + CH_2NH_2COOH}$$

followed by the oxidation of acetaldehyde to acetate and the conversion of glycine to acetate:

$$\mathrm{CH_3CHO + CH_2NH_2COOH + H_2O \rightarrow 2CH_3COOH + NH_3}$$

According to Cardon and Barker (1947) threonine can also be degraded to propionate and butyrate by *C. propionicum*:

$$\mathrm{CH_3CHOHCHNH_2COOH + H_2O \rightarrow CH_3CH_2CH_2COOH + 2CH_3CH_2COOH + 2CO_2 + 3NH_3}$$

Glycine

Glycine firstly is also first converted to acetic acid and ammonia according to reaction:

$$\mathrm{4CH_2NH_2COOH + 2H_2O \rightarrow 3CH_3COOH + 4NH_3 + 2CO_2}$$

Many amino acids are oxidatively deaminated and decarboxylated to the corresponding carboxylic acid:

$$\mathrm{RCH_2NH_2COOH + 2H_2O \rightarrow RCOOH + CO_2 + NH_3 + 4H}$$

The above reactions reveal that one of the final products of protein anaerobic degradation is ammonia. One mol of amino acid produces one to more than three mol of ammonia depending on the type of amino acid. Both a high COD-VFA concentration and a high concentration of the ammonia formed may affect the anaerobic biodegradation process (Koster, 1988).

Besides ammonia, VFA such as acetate, propionate, butyrate are formed in the anaerobic biodegradation and these may lower the pH of treatment system, depending on the other factors, e.g. the amount of ammonia produced, the methanogenic activity, etc.. It is clear that the NH_4^+-N produced in the process can neutralize an equivalent amount of VFA that accumulate in the system.

Results of several studies have been published dealing with how VFA, ammonia affect the anaerobic biodegradation process (Braun *et al.*, 1984; Koster, 1989; Zeeman, 1991) and with protein biodegradation (Breune, 1984). Most of these studies were performed with synthetic media. In the present investigation real RLP wastewater was used in order to assess the anaerobic biodegradation of protein in a medium in presence of other organic compounds such as sugars, lipids and natural inorganic salts.

3.5.2 MATERIALS AND METHODS

Experimental condition

The assay was carried out in Vietnam at ambient conditions during 1993-1994.

Experimental reactor

Serum bottles with a working volume of 1,000 mL and flasks with working volume of 5 L were used as experimental reactors.

Inoculum

The experimental reactors were inoculated with 2 g VSS/L stored granular sludge which is the same granular sludge as used in the RLP wastewater biodegradability assay with a SMA of 0.2 g COD/g VSS.d. The granular sludge originated from Latenstein starch factory, the Netherlands.

Substrate

Substrate was a serum obtained from field latex coagulation, consequently a latex not treated by ammonia.

Analyses

The concentration of ammonia was examined daily as indicator for degradation process. At the end of the experimental period, both ammonia and Kjeldahl organic nitrogen were examined in order to evaluate the process efficiency. Due to the high pH (higher than 7.5), some of the ammonia might leave the system with biogas accumulating in the head space of serum bottle, and so no completely correct results may be obtained.

Experimental procedure

In order to assess the anaerobic biodegradation of proteins, the same procedure, i.e. two successive feeds were applied, as employed as for the SMA test was used. At the end of first feed with RLP

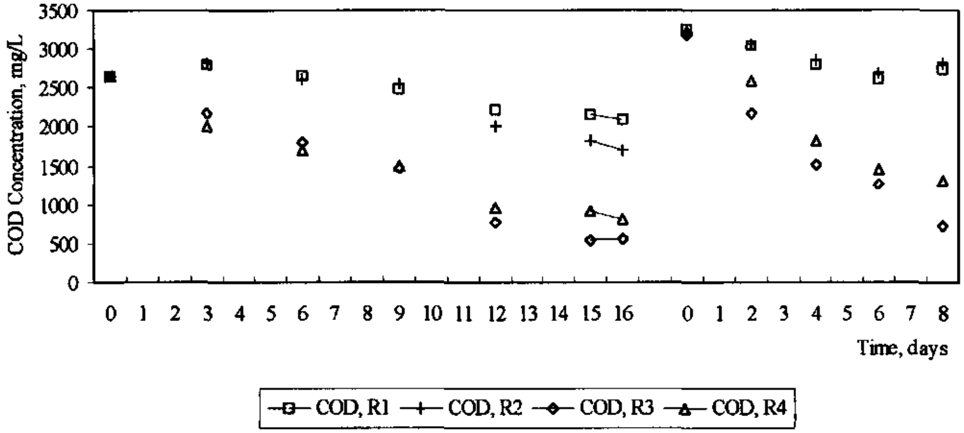


Fig. 3.5.3 The course of the COD reduction during degradation of the protein contained in the RLP wastewater.
R1, R2, R3, R4: experimental bottles.

Apparently first a rapid formation of VFA proceeds, i.e. acetate and propionate, at least more rapid than ammonia formation, so that not all VFA are neutralized. Later the rate of N-NH_4^+ formation exceeds that of VFA and the pH can come up.

Apparently in the beginning the rate of N-NH_4^+ formation proceeds slight faster than of VFA formation but soon the reverse become true.

The Second Experiment Conducted at Lower N-Org Concentration

The second experiment was conducted at a lower N-org concentration, viz. of 78-87 mg/L, which is equivalent to appr. 488-544 mg protein/L.

In the first feed, at pH 4.8, the ammonia concentration had increased from 75 mg/L to 125-131 mg/L after 10 days (see Fig. 3.5.4) and the pH raised from 4.8 to 5.4-5.9 (see Fig. 3.5.5) within first three days, but in batch R_1 it then dropped again slowly to pH 4.7 while in the duplicate experiment it only temporarily dropped to a pH of 5.4 and then raised again. The first raise of the pH coincides with the degradation of protein from 78 mg/L to 26-27 mg/L. However between day 4-8 for some obscure reasons the N-NH_4^+ slightly decreased. In the high pH experiment, the ammonia concentration increased from 75 mg/L to 144-149 mg/L within 5 days and in this period the N-Org concentration dropped from 78 mg/L to 10-12 mg/L. The pH first dropped to 6.3 and then raised to 6.5 at the termination of experiment. The COD concentration in the experiment at pH_b 4.8 and 7.1 dropped from 2100 mg/L to 1643-1800 mg/L and 500-743 mg/L at day 10 (see Fig. 3.5.6), respectively.

Table 3.5.1 The degaradation of protein at diferent N-org concentration and pH values

Feed		R_1	R_2	R_3	R_4
The First Experiment Conducted at High N-org Concentration					
First feed					
pH_b		5.0	5.0	7.0	7.0
pH_e		4.8	4.8	6.8	6.8
$Ammonia_b$	mg/L	31	31	31	31
$Ammonia_e$	mg/L	112	115	150	142
$N\text{-}org_b$	mg/L	157	157	157	157
$N\text{-}org_e$	mg/L	67	71	20	25
E	%	57.3	54.8	87.3	84.1
T	days	16	16	16	16
Second feed					
pH_b		4.9	4.9	7.4	7.4
pH_e		4.9	4.9	7.4	6.8
$Ammonia_b$	mg/L	75	75	85	85
$Ammonia_e$	mg/L	85	86	214	220
$N\text{-}org_b$	mg/L	189	189	189	189
$N\text{-}org_e$	mg/L	129	132	46	48
E	%	31.7	30.2	75.7	74.6
T	days	9	9	9	9
The Second Experiment Conducted at Low N-org Concentration					
First feed					
pH_b		4.8	4.8	7.2	7.2
pH_e		4.7	5.9	6.5	6.5
$Ammonia_b$	mg/L	75	75	75	75
$Ammonia_e$	mg/L	125	131	144	149
$N\text{-}org_b$	mg/L	78	78	78	78
$N\text{-}org_e$	mg/L	26	27	12	10
E	%	66.7	65.4	84.6	87.2
T	days	10	10	10	10
Second feed					
pH_b		4.8	4.8	7.1	7.1
pH_e		4.9	5.0	6.8	6.7
$Ammonia_b$	mg/L	88	88	91	90
$Ammonia_e$	mg/L	138	141	150	150
$N\text{-}org_b$	mg/L	87	87	87	87
$N\text{-}org_e$	mg/L	31	32	14	16
E	%	64.4	63.2	83.9	81.6
T	days	6	6	6	6

$pH_{b,e}$	*pH at the begining and the end of each feed*
$Ammonia_{b,e}$	*ammonia concentration at the begining and the end of each feed*
$N\text{-}org_{b,e}$	*N-org concentration at the begining and the end of each feed*
E	*N-org removal efficiency*
T	*experimental time*
$COD_{b,e}$.	*COD concentration at the begining and the end of each feed*
R_1, R_2	*in duplicate at* pH_b *4.8-5.0*
R_3, R_4	*in duplicate at* pH_b *7.0-7.4*

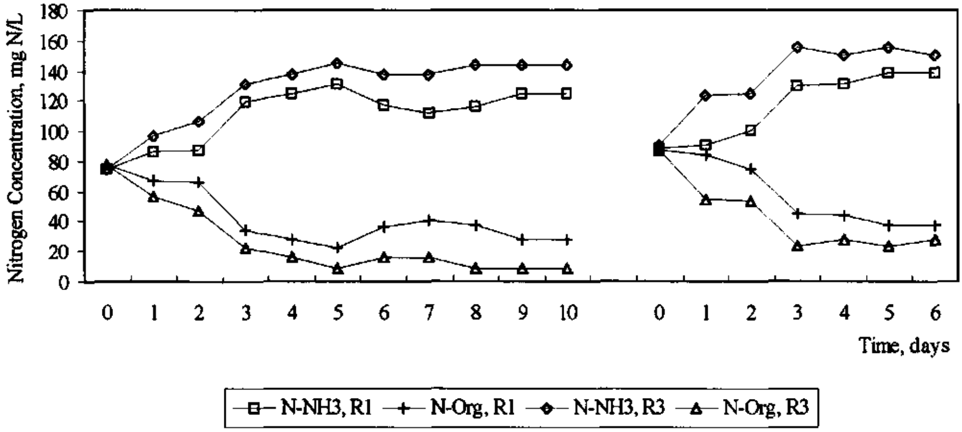


Fig. 3.5.4 The course of the protein degradation at N-Org concentration of 78-87 mg/L (or appr. 488-584 mg protein/L).
R1, R3: experimental bottles.

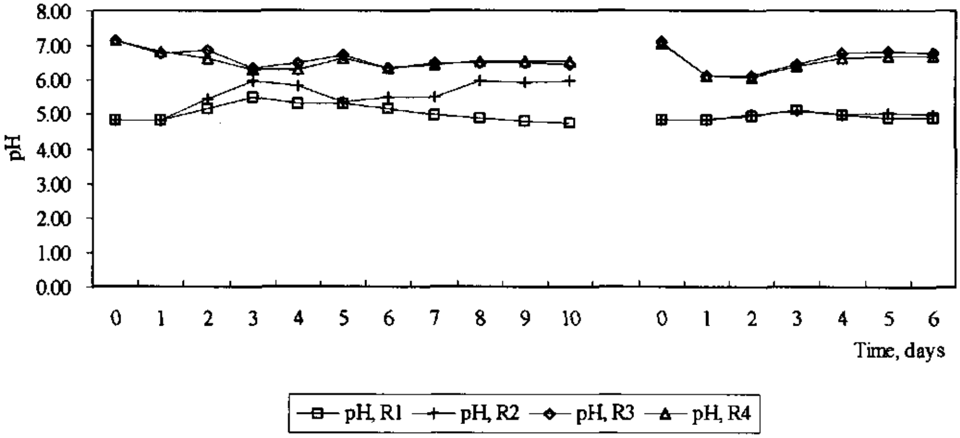


Fig. 3.5.5 The course of the pH during the degradation of protein contained in the RLP wastewater.
R1, R2, R3, R4: experimental bottles.

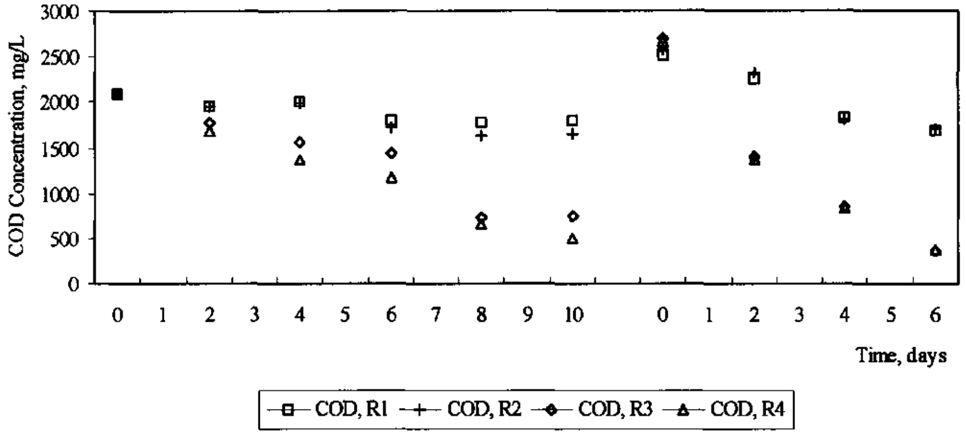


Fig. 3.5.6 COD reduction during degradation of protein contained in the RLP wastewater.
R1, R2, R3, R4: experimental bottles.

In the second feed, the initial ammonia and N-Org concentration were 88-91 mg/L and 87 mg/L, respectively. In this experiment the difference in the amount of degraded protein found between the experiment at pH_b 4.8 and at pH_b 7.1 is small, i.e. at day 6 in experiment R_1 and R_2 (pH_b 4.8), 50-53 mg/L N-Org was degraded, bringing up the ammonia concentration to 138-141 mg/L, while in the experiment R_3 and R_4 (pH_b 7.1), 59-60 mg/L N-Org was degraded and the ammonia concentration came up to 150 mg/L. In the second feed, the degradation process was completed within 3 days and the calculated activity of the sludge amounted to 0.02 g Protein-N-NH_3/g VSS.d.

The third experiment conducted at Low N-Org concentration and with and without nutrients addition

The third experiment conducted was with and without the addition of a nutrient solution. The experiment in which nutrients were added further was divided into series, with and without ammonium chloride addition. All experimental series were carried out in duplicate. The substrate solution was neutralized by NaOH solution to pH 7.1.

The experiment without nutrient addition. In the first feed the pH dropped from 7.1 to 5.5 at day 2 and then raised up to 6.8 at day 6 (see Fig. 3.5.8) The ammonia concentration increased from 20 mg/L to 63 mg/L within first 3 days, and then it dropped to 55-57 mg/L at day 8-9. The N-org concentration decreased from the initial concentration of 79 mg/L to 13 mg/L. The degradation process was completed at day 3.

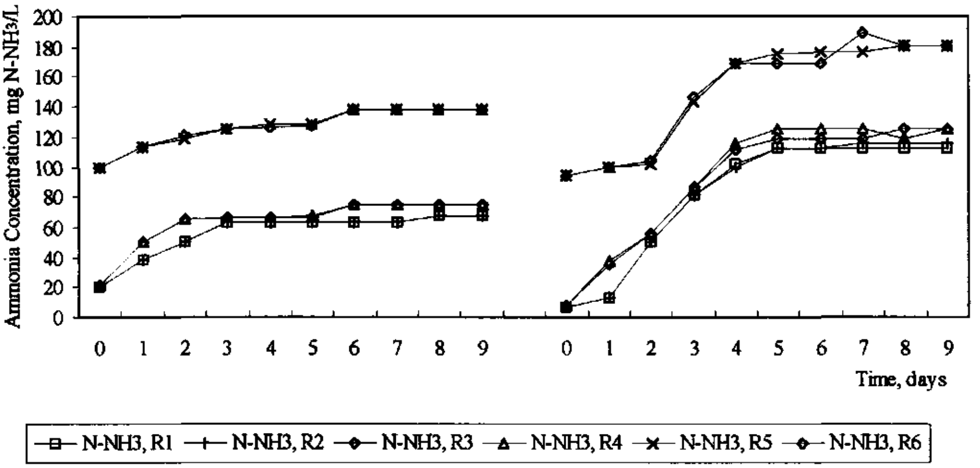


Fig. 3.5.7 The course of the ammonia concentration in experiment with and without nutrient addition. *R1, R2, R3, R4, R5: experimental bottles.*

In the second feed, the pH dropped from 7.1 to 4.9-5.0 during first day, but then it raised slowly to 6.3 at day 7-8. The ammonia concentration increased from 6 mg/L at the beginning to 112 mg/L at day 5 and the protein was completely degraded in this experiment, because the N-org concentration of 0 mg/L at the termination of experiment. Duplicate bottles showed the same results (see Fig. 3.5.7). No explanation is found for this case.

The experiments with nutrient addition, except ammonia. The results of this experiment are very similar as that where nutrients were not supplied, except for the pH, which now remained in the optimal range. In the second feed, the proteins were also completely degraded from 98 mg N-org/L to 0.

The experiment with nutrient addition, including also N-NH_4^+. In this experiment, the pH remains slightly better than in the above two experiments, i.e. in the first and second feed the pH is always higher than 6.5-6.6 and 5.8 (see Fig. 3.5.8). But at the termination of the first and second feed the N-org concentration still was relatively high, viz. of 20 and 24 mg/L, respectively, so it looks that in absence of nutrient the degradation of the proteins proceeds less easily.

The protein degradation reached a steady value after 3-5 days. Surprisingly the COD was degraded in both the low and the high pH reactors. It will discuss in more detail in paragraph 3.6 dealing with the effect of pH.

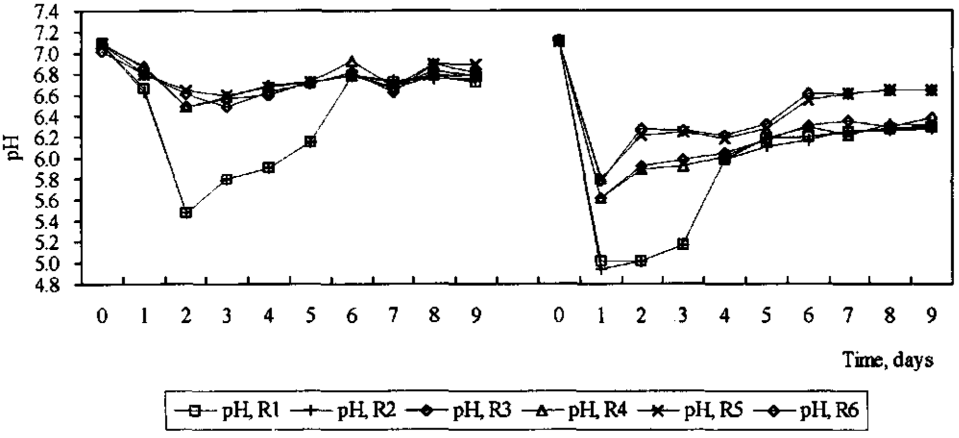


Fig. 3.5.8 The course of the pH in experiment with and without nutrient addition.
R1, R2, R3, R4, R5: experimental bottles.

In most of the experiments, no complete protein degradation occurred within the experimental period, except in the case where NH_4Cl was not supplied. The reason for the poor degradation can be due to the fact that some types of protein is very stable, such as hevein, a small, cystine-rich protein with a polypeptide chain length of 43 residues (Soedjanaatmadja and Subroto, 1995). Comparison of the data obtained learns that at high pH values proteins degrade more completely than at low pH. The calculated activity of the sludge for protein degradation ranged 0.01-0.02 g N-org/g VSS.d. at 26-32°C

During the initial phases of the experiment the pH dropped down from 7.2 to 5.5-6.2 due to the accumulation of VFA. Along with the conversion of the VFA to methane and formation of N-$NH_4^+$the pH gradually increases.

3.5.4 DISSCUSSION

Proteins are found in all living organisms and play an crucial role in living cells. Amino acids are the monomers of proteins. Approximately 20 amino acids are the more common constituents of proteins.

Since in the processing of the rubber latex, almost all the proteins contained in it are washed out to the serum and wastewater, these compounds will be subject to the anaerobic treatment. The anaerobic degradation of proteins proceeds via the well known steps, i.e. successively hydrolysis, acidogenesis, acetogenesis and methanogenesis. The acetogenic and methanogenic degradation reactions are independed on the type and nature of the protein or amino acid, but the acidogenic pathways can differ greatly between the various types amino acids. The RLP serum contains quite a significant amount of proteins, which are composed of 14 amino acids (see Table 3.5.2), which are greatly different in chemical structure. Acidogenes of amino acids takes place in two steps (White *et al.*, 1973), viz.:

1. Deamination step, in which amonia is released and various organic products are formed

2. Oxidation step, where volatile fatty acids (VFA) are formed principally acetic, propionic and butyric acid.

3.6 THE EFFECT OF pH ON ANAEROBIC BIODEGRADATION OF RUBBER LATEX PROCESSING WASTEWATER WITH VIETNAMESE DIGESTED PIG MANURE SLUDGE

3.6.1 INTRODUCTION

On the basis of the results of several previous studies, it is clear that many factors such as the ammonia concentration, pH, toxic organic compounds, heavy metals, nutrients, temperature, etc., affect the anaerobic processes. Their effect now is understood much better than in the past, despite the fact that in various cases experimental results obtained vary greatly from study to study depending on the experimental conditions applied and substrates used. And it is also well known that among the different steps of the anaerobic degradation processes of complex organic compounds, acetogenesis and methanogenesis are the most sensitive steps, specially also to pH.

Since components present in RLP wastewater (see Chapter 2) are readily and rapidly converted in an anaerobic digester into to acetate and other VFA, a rapid drop of pH in anaerobic system may occur when the buffer capacity is too low, and the methanogenic capacity is insufficient, as shown in the previous paragraph. And then consequently the production of N-NH_4^+ from proteins proceeds too slowly.

The investigations described in this paragraph aim at assessing the effect of pH on the anaerobic biodegradation rate of RLP wastewater components and the adaptability of methanogenic sludge to low pH values. Furthermore it is attempted to clear the reason for observed different behavior between batch and continuous system. These insight also may contribute to improve the assays for assessing important sludge characteristics.

3.6.2 MATERIALS AND METHODS

Experimental conditions

The experiments were performed in Vietnam 1992 at ambient temperature (27-34°C), using serum bottles with a working volume of 250 mL and 500 mL as batch reactors.

Inoculum

The inoculum used was digested pig manure sludge (DPMS) obtained from a biogas digester in subdistrict 15, Ho Chi Minh City, Vietnam. In the assays 3 g VSS/L DPMS was applied.

Substrate

In all experiments, diluted RLP serum was used as substrate, together with nutrients and trace elements.

Analyses

To assess the course of the degradation process, each two days the COD concentration was determined (titrimetrically) and the pH was measured.

Experimental procedure

Substrate at the specified pH was added to the bottles containing the DPMS, and after closing they were exposed to the ambient conditions. Two successive feeds were applied and also an experiment with standard VFA substrate was also carried out for comparison.

3.6.3 RESULTS

The experiments were performed at initial pH_b values of 5.0; 5.5; 6.0 and 7.0 and in a COD range of 2,445-2,520 mg/L in the first feed and 2,400-2,688 mg/L in the second, i.e. very similar as in the experiment presented in the previous paragraph. The experimental results are presented in Fig. 3.6.1 and 3.6.2.

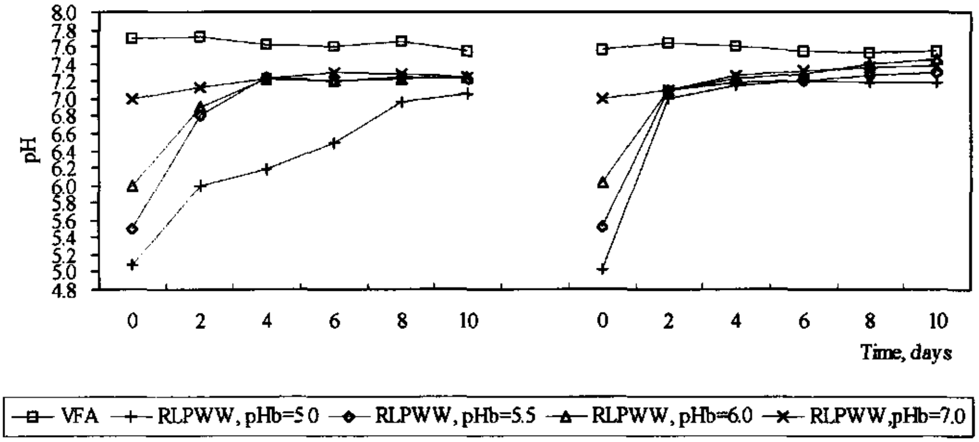


Fig. 3.6.1 The course of the COD reduction obtained with DPMS at various pH_b values with RLP wastewater feeds and the VFA feed.

In the first feed a very similar COD reduction rate was found at the pH_b 6.0 and 7.0, and the COD reduction rate found in both these reactors even was higher than that found in the VFA feed, especially during the first four days when the COD concentration was still high. The degradation of propionate needs more time. However, the difference is not very significant. The feeds at pH_b 6 and 7 needed 5 days to complete the degradation, i.e the COD concentration dropped from 2,490 mg/L and 2,520 mg/L to 265 mg/L and 260 mg/L at day 4, and lower to 76 mg/L and 75 mg/L at day 5, and the end pH was 7.2 and 7.3, respectively. For the feed at pH_b 5.5, a slightly lower COD conversion rate was found. These results with DPMS are much better than those found with GS at about the same conditions in Fig 3.5.6, presumably due to the fact that GS had been stored 2-3 years at ambient temperature, i.e. 27-32°C.

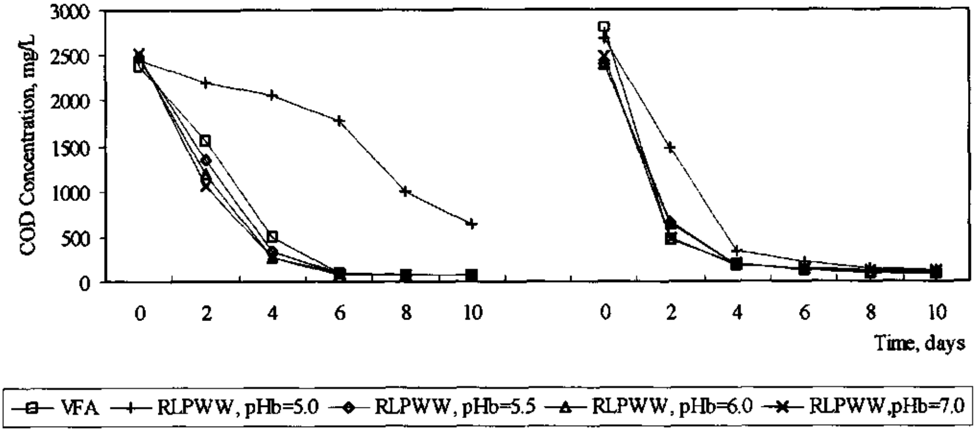


Fig. 3.6.2 The course of the pH in batch experiment conducted at different pH_b values with 3 g VSS/L DPMS and RLP wastewater.

In the experiment at the lowest pH_b, the pH first increased rapidly from 5.1 to 6.00 within two days and then slowly till after 10 days it became 7.1. Due to the low pH the COD concentration dropped much slower, i.e. from 2,445 mg/L to 2,060 mg/L after 4 days, but from then onwards, consequently when the pH was in the more optimal range, the COD concentration to 643 mg/L after 10 days. However it is clear that ultimately the same low value would be attained as in the other feeds.

In the first feed, the calculated SMA of DPMS for RLP wastewater at pH_b 5.0, 5.5, 6.0, 7.0 and with VFA amounted to 0.06, 0.18, 0.19, 0.19 and 0.16 g COD/g VSS.d, respectively. Once again it is clear that Vietnamese DPMS represents an excellent seed material for the first start up of a UASB-reactor.

The results of the second feed were better for all experimental conditions, i.e. at pH_b 6.0 and 7.0 the COD concentration dropped from 2,400-2,480 mg/L to 478-635 mg/L within two days compared to 1,072-1,192 mg/l in the first feed. However the remaining COD concentration after 8 days in both batches (109 and 123 mg/L) was slightly higher which might be caused by non-biodegradable matter in RLP serum. Compared to the first feed, particularly in the feed at pH_b 5.0, the process proceeded quite well, i.e. already the first day pH increased from 5.0 to 6.7 and to 7.0 at the second day, and the COD concentration dropped from 2,688 mg/L to 1,466 mg/L at the second day and to 334 mg/L at the fourth day. Despite the degradation rate was much higher than in the first feed it still was lower than in the other feeds. The SMA of DPMS determined on the RLP serum in the second feed at pH_b 5.0, 5.5, 6.0, 7.0 and with VFA amounted to 0.19, 0.24, 0.24; 0.26 and 0.29 g COD/g VSS.d, respectively.

3.6.4 DISCUSSION

From the previous studies and experiments, it is clear that the risk of the occurence of lower pH values in anaerobic treatment of RLP wastewater due to VFA-production is small, provided the system is operated in the proper way, i.e. no overloading while some effluent recycling should be applied or some alkali supplied to the wastewater.

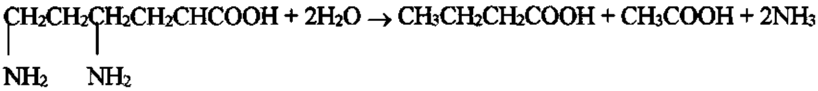
Part of the organic matter present in the RLP wastewater such as sugars and proteins are anaerobically readily and rapidly converted into VFA, mainly into acetate. In overloaded system this can result in a drop of pH, while also coagulation of field rubber latex may occur. According to biochemical reactions shown below, per mole sugar and amino acid at least 2 moles acetate, propionate or butyrate are formed during acidogenesis and when these acids are not sufficiently rapidly converted, this can reduce the pH of a poorly buffered solution to 4.8-5.2, depending on the concentration of polluting components, the methanogenic activity of the system and the amount of $N\text{-}NH_4^+$ formed.

Glucose

$$\begin{array}{l} C_6H_{12}O_6 + H_2O \rightarrow CH_3COCOOH + CH_3COOH + CO_2 + 6H \\ \quad CH_3COCOOH + CO_2 + 6H \rightarrow 2CH_3COOH + H_2O \\ \hline \end{array}$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH$$

Lysine



$$\underset{NH_2}{CH_2}CH_2\underset{NH_2}{CH_2}CH_2CHCOOH + 2H_2O \rightarrow CH_3CH_2CH_2COOH + CH_3COOH + 2NH_3$$

It is very clear that when using an anaerobic process treating high strength RLP wastewater, the pH can drop down rapidly to values below 5, unless sufficient alkali is present. On the other hand it also should be taken in mind that the pH will not rise to values higher than 8.3, except in case of high concentration of formiate present in the RLP wastewater (see paragraph 4.5.6).

The results of the batch experiments reveal that methanogens present in the sludge can take care for pH-recovery even in case the pH dropped to values as low as 4.8. This pH-recovery particularly can explain on the basic of the prevalence of niches with micro-ecosystem where the pH is still suitable for methanogenesis. The more optimal pH regions gradually will expand from the surroundings of niches to the rest of the sludge particles and consequently the overall pH of whole system slowly will increases. In thoroughly completely mixed system and/or at very low pH, such a recovery hardly can occur.

Apart of the existence of micro niches, it should not be excluded that methanogens - particularly those degrading acetate - and possibly to some extent also acetogenes are capable to adapt to lower pH conditions, provided the pH not too low.

Nevertheless, since it is always better to prevent than to cure, it is highly recommended to take measures to avoid drops of pH and/or to buffer anaerobic systems. This will be discussed in chapter 4.

3.6.5 CONCLUSIONS

From experimental results, the following conclusions can be drawn:

- It is very clear that the pH values below 6.0 affect the anaerobic degradation rate of RLP wastewater.
- However, in batch experiment, at pH = 5.0 the methanogens can still gradually improve this system and restore good conditions by conversion of acetate to methane and bicarbonate which increase the buffer capacity of an anaerobic system.

3.7 THE EFFECT OF PRESENCE OF O_2 AND MIXING CONDITIONS ON THE SPECIFIC METHANOGENIC ACTIVITY TEST

3.7.1 INTRODUCTION

The availability of a proper assay for assessment of the SMA of anaerobic sludges is important for the optimal operation of an anaerobic process (de Zeeuw, 1984; Hulhoff Pol, 1989; Iza *et al.*, 1991). Several methods have been developed and applied in various laboratories. The general procedure for carrying out the SMA test is as follows:

- Filling the experimental reactor with a standard substrate, nutrients and trace elements (solution);
- Flushing of the solution with gas mixture of N_2/CO_2 for 15-30 min in order to remove O_2 and closing the reactor airtight.
- Incubation of the reactor in a controlled temperature room.
- Determination of the course of COD concentration or gas production (including its composition).

Sometimes this procedure can hardly be applied in the laboratories in developing countries due to a lack of equipment and chemicals, e.g. pure hydrogen, nitrogen gas and VFA. On the other hand the experience also learns that frequently too little attention is paid to available information concerning the effect of mixing, oxygen concentration (nitrogen gas is used to remove oxygen in solution), concentration and composition of substrates, etc.

For these reasons experiments were conducted at the laboratory of the Department of Environmental Technology, Wageningen Agricultural University, The Netherlands to clusidate the effect of oxygen and mixing condition in order to develop a reliable simple SMAT assay for Vietnamese conditions. An additional objective of the experiments was to demonstrate the feature of anaerobic sludge to retain its activity under unfed conditions. This matters will be discussed in more detail in the next paragraph where results of storage experiments will presented.

3.7.2 MATERIALS AND METHODS

Experimental condition

The investigations were performed in 30±2°C room during November 1990-January 1991.

Experimental reactor

The study on the effect of oxygen and mixing conditions were carried out in serum bottles of 250 mL and 500 mL. Methane production was monitored with 1 L serum bottle containing 5% NaOH (to remove CO_2 from the biogas).

Substrate and nutrients

The substrate used consisted of a mixture of acetate, propionate and butyrate at an initial concentration of each of the individual volatile fatty acid of 600 mg/L. This is equivalent to a total COD of 2.64 g/L. Nutrient and trace elements were added.

Sludge

Stored Latenstein granular sludge was used in the experiments. This sludge had been stored unfed at 5°C room for a period of 30 months. The original SMA of sludge was 0.5-0.6 g COD/g VSS.d.

Analysis

Liquid samples for VFA analysis were taken daily or even more frequently. The composition of biogas was also analyzed daily.

Experimental procedure

New substrate (i.e. a concentrated stock VFA solution) and nutrients were fed to digesters once its substrate concentrations had dropped to value as low as 2 mg/L. The assay was terminated once a constant value for the SMA was obtained. Generally, three to four successive feeds had to be applied.

The assays were carried out under two conditions:

- Without and with N_2/CO_2 flushing.
- With and without mixing with N_2 flushing.

3.7.3 RESULTS & DISCUSSION

The experiments conducted to assess the effect of N_2/CO_2 flush were carried out in duplicate using four successive batch feeds. The experimental data, depicted in Fig 3.7.1 show that the reduction rate of C_2, C_3 and C_4 found in duplicate bottles during four feeds are very similar. Only some slight difference was observed in the first and second feed, but the results of the third and fourth feed were almost identical, so consequently a representative value for the specific methanogenic activity of sludge can be calculated from the results of either of these feeds.

As to be expected regarding the long unfed storage the SMA of sludge found in the first feed is very low. It is clear that anaerobic bacteria need some time for adaptation after one year storage at 4°C room). Although from the VFA also new bacterial sludge will grow in, the reactivation of the sludge during the first feed mainly showed be attributed to adaptation, because the amount of newly formed bacterial matter. Approximately 14 days are needed to reduce the substrate concentration from 2,991 mg COD-VFA/L to less than 20 mg COD-VFA/L (see Fig. 3.7.2).

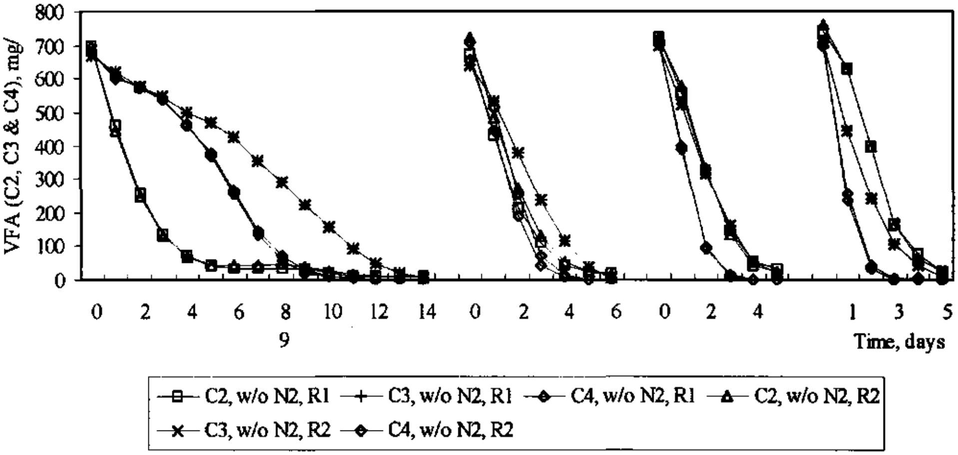


Fig. 3.7.1 The total VFA reduction in duplicate bottles without flushing nitrogen.
R1, R2: duplicate experimental bottles

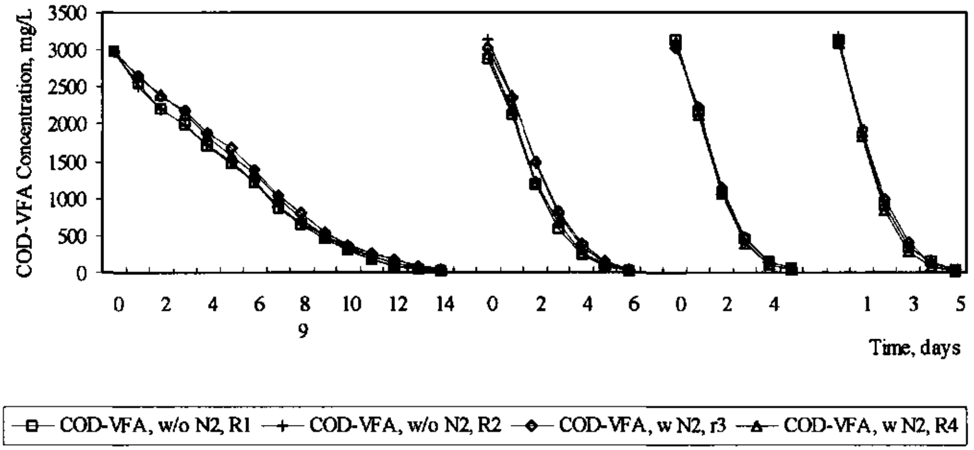


Fig. 3.7.2 The total COD-VFA reduction in duplicate bottles with and without nitrogen flushing conducted with stored GS.
R1, R2, R3, R4: experimental bottles

In the third feed the COD-VFA concentration dropped rapidly from 3,129 mg/L to 905 mg/L within 2 days. Starting at a COD-VFA concentration below appr. 300 mg/L, the reduction rate starts decline due to the fact that at this low substrate concentration the mass transfer limitation in methanogenic biolayer of granular sludge as well as the effect of the substrate affinity increasingly the rate determining factor. Therefore it is clear that in the SMA assay the specific activity of sludge should be calculated from the data obtained at COD concentrations exceeding appr. 300 mg/L. In case of VFA-mixture as substrate the conversion of propionate always needs more time compared to acetate and butyrate (Zeeuw, 1984).

Two experiments, with N_2 flush to remove oxygen and without N_2 flush, were used to investigate the effect of oxygen. The results were illustrated in Fig. 3.7.2 and 3.7.3.

It is clear from these results that little if any difference in the experimental results was found in the experiments with and without N_2 flushing. By visual observation (using resazarine - as oxygen indicator in pink color) and daily measurement of the oxygen concentration in the headspace of the experimental bottles we found that oxygen disappeared completely from the solution after 5-6 hours and dropped to less than 2% in the headspace after 2 days (see Fig. 3.7.4). As at 30°C the dissolved oxygen concentration in wastewater is appr. 7 mg/L, it is clearly that only a very small amount of substrate can be consumed by facultative bacteria and therefore the effect of dissolved oxygen is negligible. Similar observation were made by Kiener et al. (1983) who found that exposure to air up to 10h hardly affected the methanogenic bacteria. Also Kato (1994), and de Zeeuw (1989) found that the effect of dissolved oxygen is small and only temporary.

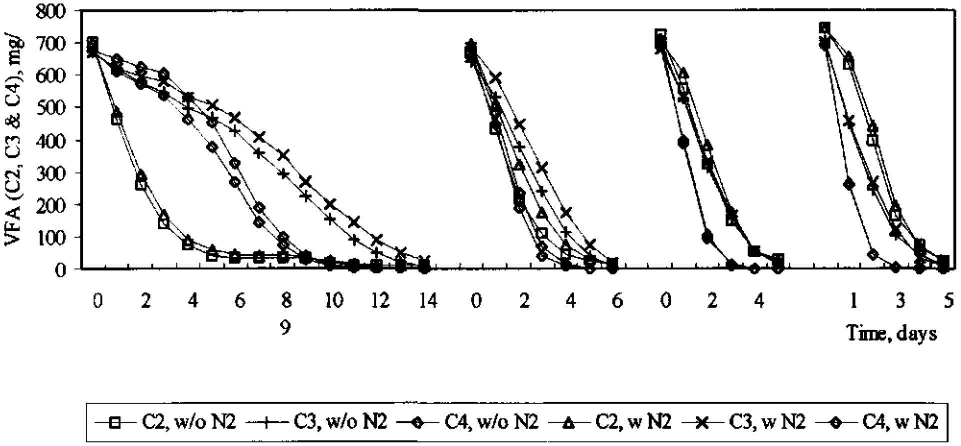


Fig. 3.7.3 The course of C_2, C_3, C_4 concentration in bottles with N_2 flushing and without N_2 flushing.

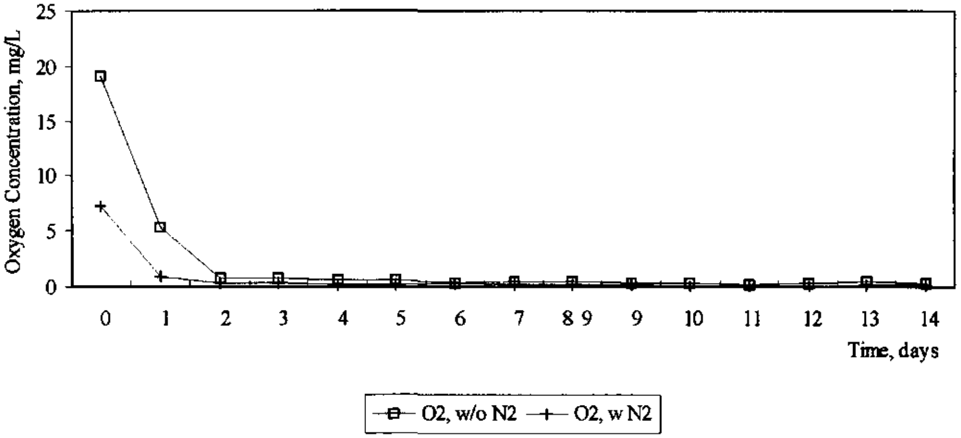


Fig. 3.7.4 The course of the oxygen concentration in the headspace in case the system flushed and not flushed with N_2.

With respect to the effect of mixing a slight difference was obtained in the experiment where mixing was applied compared to the experiment under no mixing conditions. However the experimental data also reveal that mixing affects the substrate (COD-VFA) reduction rate more strongly once the concentration of substrate (COD-VFA) has dropped to below 250-300 mg/L (Fig 3.7.5). Moreover it looks that mixing affects the rate of acetate reduction more positively than that of propionate and butyrate, because for these acids mixing looks even detrimental (see Fig. 3.7.6).

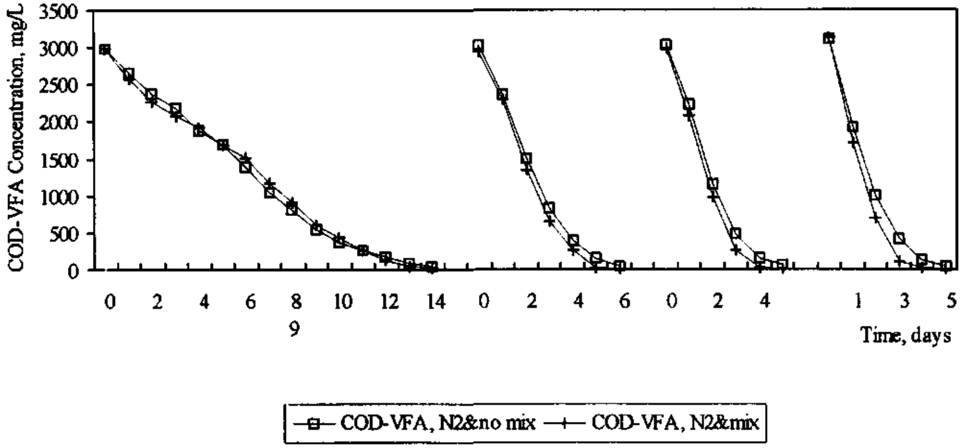


Fig. 3.7.5 The course of the COD-VFA reduction in cases mixing is applied and omitted using stored GS.

For the COD-VFA concentration range 3,129 mg/L to 1,700 mg/L the reduction rates apparently are almost the same, although the reduction rate in case of mixing is applied is slightly higher than in case of mixing is omitted. This phenomenon could be explained by the effect of mixing condition on the concentration gradient in a biolayers which can be estimated from Fick's law (Dolfing 1985):

$$F = - \mu D . dC/dx$$

where, F - the substrate flux,
μ - the porosity of the biolayers,
D - the diffusion coefficient, and
dC/dx - the gradient of the substrate concentration over the biolayers.

or from expression by Monod

$$\mu = \mu_{max} \frac{S}{K_s + S}$$

where, μ - specific growth rate, $time^{-1}$
μ_{max} - maximum specific growth rate, $time^{-1}$
S - concentration of growth-limiting substrate in solution, mass/unit volume
K_s - half-velocity constant, substrate concentration at one-half the maximum growth rate, mass/unit volume

and the rate of substrate utilization:

$$r_{su} = - \frac{\mu_{max} X S}{Y(K_s + S)}$$

where, r_{su} - substrate utilization rate, mass/unit volume.time
Y - maximum yield coefficient, mg/mg (defined as the ratio of the mass of cells formed to the mass of substrate consumed, measured during any finite period of logarithmic growth)
X - concentration of microorganism, mass/unit volume

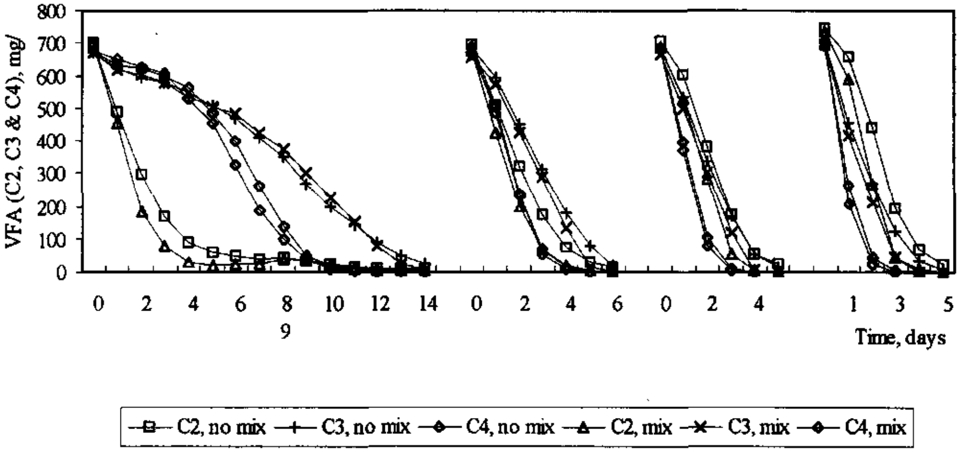


Fig. 3.7.6 The course of the different VFA in case of mixing is applied and omitted.

On the basic of laboratory studies it has been concluded that yield depends on (1) the oxidation state of the carbon source and nutrient elements, (2) the degree of polymerization of the substrate, (3) pathways of metabolism, (4) growth rate and (5) various physical parameter of cultivation (Metcalf & Eddy, 1992). In the defined conditions, i.e. type of wastewater, seed sludge, environmental conditions, etc., Y, μ_{max}, X can be assumed constant during the period of time of experiment, and then r_{su} depends on K_s and S. When S is much higher than K_s, the reduction rate depends mainly on the substrate concentration. When S approaches K_s or becomes lower than apparent K_s, the reduction rate becomes slightly affect. According to Kato (1994) and Lettinga (1995) the mixing reduces the apparent K_s, and therefore the reduction rate will become higher. However, as the SMA of sludge is always calculated from the highest slope of substrate reduction curve, a decrease of the reduction rate at low substrate concentration does not interfere the SMA test.

3.7.4 RECOMMENDATIONS

Based on the results obtained the following recommendations can be made for a standardized SMA-assay under Vietnamese conditions for determining reliable of the max specific activity of a sludge:

- Substrate concentration should exceed 300 mg/L.
- The SMA of sludge should be calculated from the results of the third feed, preferably the fourth feed.
- N_2 flushing and mixing can be omitted in case of granular sludge, and intermittent mixing can be applied in case of non-granular sludge.

This investigation was conducted with granular sludge and it is necessary to investigate on the other sludge in order to withdraw the general standard for SMAT.

3.8 THE EFFECT OF STORAGE TIME ON THE SMA OF GRANULAR SLUDGE

3.8.1 INTRODUCTION

One of advantages of anaerobic wastewater treatment processes compared to conventional aerobic process is that anaerobic organisms can be preserved unfed for a long period of time (exceeding one year) without any serious deterioration, e.g. in their activity and the settleability of the sludge (Lettinga, 1995).

In case of RLP wastewater treatment in South Vietnam this is a very important feature because all RLP factories in Vietnam are out of operation from December to January, because of the *Hevea* tree physiological season. Therefore sludge will remain unfed in an anaerobic reactor for more than one month and during this period it will be exposed to tropical temperature (28-32°C), which certainly will result in quite serious drop of the specific activity (contrary to unfed storage at temperature below 15°C).

However so far there is very few reliable data available concerning the effect of unfed storage at such high temperature on the sludge quality.

For that reason a number of experiments were conducted in order to assess the deterioration in the activity of sludge due to unfed condition under tropical conditions.

In addition to this main objective, the results also may contribute to the establishment of the proper procedure of operation of a RLP wastewater treatment plant in South Vietnam.

3.8.2 MATERIALS AND METHODS

Experimental condition

The assay was conducted in The Netherlands and Vietnam in period 1991 to 1993.

Experimental reactor

Serum bottles with working volumes of 500 mL and 1000 ml were used as the experimental reactors.

Sludge

Granular sludge from the Latenstein starch factory in November 1989, stored in 5°C room, was used in the experiments. This sludge was also brought to Vietnam (in May 1991) and (re)stored under unfed conditions there in a refrigerator and later it was exposed to high ambient temperature under unfed conditions.

Substrate

Standard VFA together with nutrients and trace elements was used as substrate.

Analysis

In samples taken from the assay bottles, after filtration (conducted immediately after sampling), the COD concentration was analyzed and the data obtained were used to assess the SMA of the sludge.

Experimental procedure

In the experiments three successive feeds were applied, i.e. consisting of a concentrated the stock VFA solution. Each time after after exhaustion of the previous feed, an exactly known amount of the stock solution was injected into the bottles. At regular time intervals samples were taken for COD-analysis. From the COD sepletion curves the SMA can be calculated according to the methods described before.

From the values of the calculated SMA of sludge conclusions can be drawn with respect to the effect of storage time on the activity of the granular sludge.

3.8.3 RESULTS AND DISCUSSION

It is clear that the longer the period the sludge remained unfed the lower will be the SMA. The experimental data obtained are shown Table 3.8.1 and Fig. 3.8.1.

Table 3.8.1 The SMA (assessed in the third feed) of granular sludge after different periods of unfed storage at 5 °C)

Specific Methanogenic Activity (g COD/g VSS.d)				
Nov., 1989	Jan., 1991	Jul., 1991	Jan., 1992	Dec., 1993
0.5-0.6	0.48	0.30	0.30	0.21

The initial SMA of the Latenstein sludge in November 1989 amounted to 0.5-0.6 g COD/g VSS.d. After it has been stored for more than one year at 5°C room (from November 1989 to January 1991) the SMA had decreased slightly, i.e. 0.48 g COD/g VSS.d. The sludge was brought to Vietnam in May 1991 and the, as mentioned before, restored in a refrigerator. After two months storage the SMA still amounted to 0.3 g COD/g VSS.d. The reduction rate of SMA was faster than in 5°C room in The Netherlands due to the fact that electricity was only available during 2-3 days a week in Ho Chi Minh city in that period. In January 1992 the SMA still amounted to 3.0 g COD/g VSS.d. From May 1993 the sludge was exposed to the ambient temperatures of 26-36°C. The SMA then dropped from 0.3 g COD/ g VSS.d to 0.21 g COD/g VSS.d in a period of 7 months. Although the SMA of GS did not decrease very significantly during this 7 months stored time, it should be mentioned that a quite long adaptation period is needed. For instance, from the results of the experiment carried out in April 1995, shown in Fig. 3.8.2, it appears that the first feed needed more than 39 days to complete the degradation. Moreover from regularly made visual observations it also appeared that granular sludge gradually disintegrated in small particles.

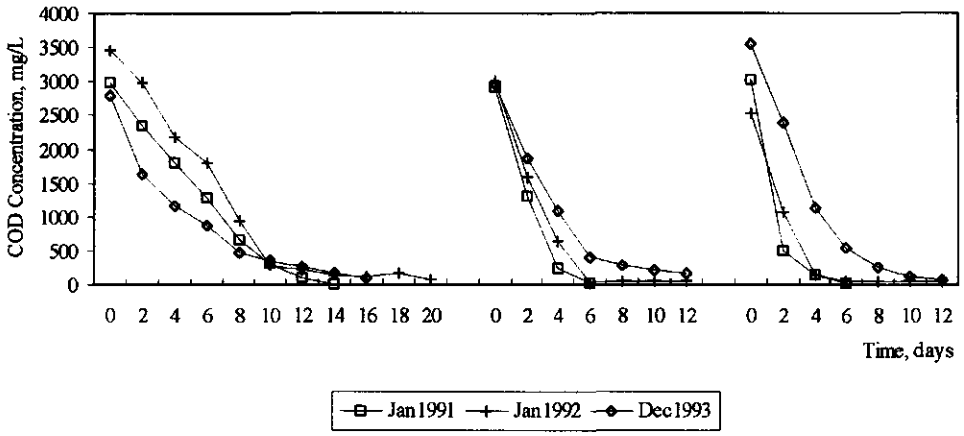


Fig. 3.8.1 The course of the COD reduction in experiments with the granular sludge which has been unfed for different period of time.

From Fig. 3.8.1 it can be seen that in the first feed the degradation rate did not differ significantly for the various unfed storage periods, i.e. amounting to 2-3 years. It can be seen that at the high VFA concentration ranges, the COD reduction rate are very similar. However at the lower VFA concentration range, there apparently exist rather substantial differences in the reduction rate; at relatively short storage period the sludge degrades VFA faster than at longer storage periods. In the continuous experiment (paragraph 4.3) we also found that a fresh DPMS can accept a faster increase of the loading rate than old sludge. It looks like the substrate affinity particulate has been affected upon storage.

An additional experiment was performance with GS and ground GS to assess any possible effect of grinding on the degradation rate on the stored GS. This experiment was carried out in April 1995, consequently after 6 years unfed storage. The experimental results are shown in Fig. 3.8.2.

In the first and second feed, the reduction rate assessed in both reactors was almost the same; they needed 42 days and 27 days, respectively to complete the degradation, while the GS in 1993 needed only 12 days. However in the second feed, a substantially higher reduction rate was found compared to the first feed.

In the third feed, the reduction rate is very similar in both reactors at COD-concentration exceeding 1,400 mg/L and below this concentration the reduction rate of the unground GS is even higher than ground sludge. The GS needed about 14 days to reduce the COD concentration from 3,107 mg/L to 222 mg/L and the ground GS needed about 18 days to reduce the COD concentration from 3,949 mg/L to 270 mg/L. The calculated SMA is the same 0.11 g COD/g VSS for both reactors. It should be noted that the break point of GS in 1995 is about 1,300-1,500 mg/L, while the break point of GS in 1993 is about 250-300 mg/L.

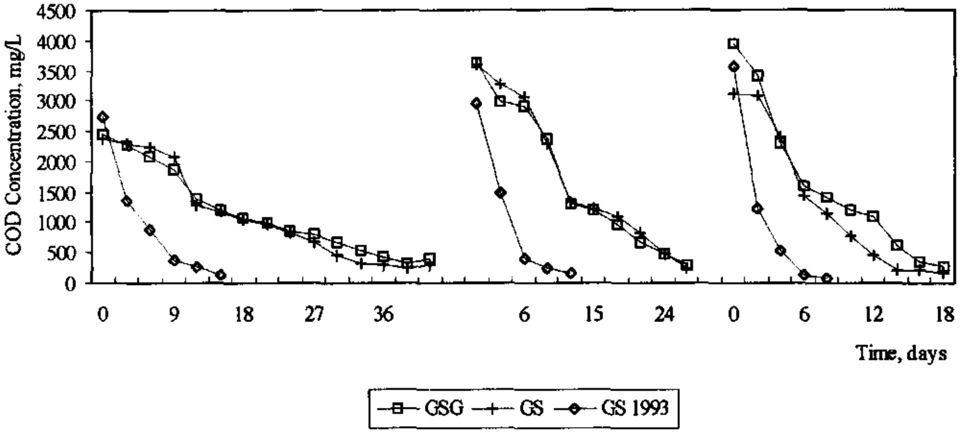


Fig. 3.8.2 Assessed COD reductions in 6 years unfed sludge (at 5 °C) for disintegrated (by grinding) GS and unground GS (carried out 1995).

3.9 CONCLUSIONS

With respect to anaerobic treatment process of RLP wastewater the following conclusions are withdrawn:

- The available seed sludges in Vietnam for UASB start-up comprise:
  + DPMS with SMA of 0.13-0.26 g COD/g VSS.d.
  + CS with SMA of 0.12-0.15 g COD/g VSS.d.
  + STS with SMA of 0.11-0.12 g COD/g VSS.d.

- Based on the SMA and other factors, DPMS is strongly recommended to used as seed sludge, but STS is also available with huge amount in Ho Chi Minh City and other urban areas.

- Most of the organic matter constituents, e.g. proteins, sugars, contained in RLP wastewater are anaerobically readily and rapidly converted into acetate, propionate and very small amount of butyrate and formic acid.

- The rapid and easy conversion of organic matter contained in RLP wastewater into VFA may result in a serious pH-drop in anaerobic systems treating RLP wastewater, and therefore might represent one of the major constraints for unskilled operators in the operation of RPL anaerobic treatment process.

- At least up to 95% (if not higher) organic matter of RLP wastewater is anaerobic biodegradable.

- With specific waste COD concentration the pH of anaerobic system can increase due to the establishment of micro-ecosystem inside batch reactor

- Concerning to standardization of the SMA test, oxygen and mixing does not affect significantly to the result at the COD concentration higher than 300 mg/L. Consequently the following SMAT procedure are recommend for Vietnamese condition:
  + Filling the experimental reactor with a standard substrate, nutrients and trace elements (solution).
  + Closing the reactor airtight.
  + Keeping the temperature as stable as possible.
  + Manual mixing 3 times/day
  + Determination of the course of COD concentration.

- At high temperature condition, the unfed storage time affects not only the SMA of sludge, but physical structure as well.

Chapter 4

Application of the UASB Process to Treat Rubber Latex Processing Wastewater

4.1 INTRODUCTION

Due to a lack of fundamental understanding of the anaerobic digestion process up to the sixties (MacCarty, 1964) anaerobic wastewater treatment was not a popular treatment option. However last two decades the situation improved very significantly, mainly as a result of considerable amount of applied and fundamental research conducted since beginning of the seventies. Nowadays the anaerobic wastewater treatment concept clearly has demonstrated its enormous potentials, viz. excellent performance has been attained at full-scale for a large variety of wastewaters. At present in various countries in Europe, South and South-East Asia and in Latin America anaerobic treatment has been successfully implemented for treating a large variety of industrial wastewaters and for domestic wastewater as well (Lettinga, 1995).

In order to overcome the lack of fundamental understanding of anaerobic process, its microbiology, chemistry and technology, many multidisciplinary studies have been made at lab-scale and pilot-scale, and several anaerobic processes have been developed during the last decades, such as UASB-, EGSB-, UAF-reactors. Of these systems particularly the UASB turned out to be a very successful concept in practice, the UAF found some full scale application and certainly will be more widely applied, possibly in hybrid systems, the EGSB-system very likely has a big future, while some other systems due to their higher investment and operation cost are still in laboratory or pilot plant phase. Like other processes, each anaerobic process has its typical advantages and disadvantages, although a system like the UASB really seems to suffer not seriously from any big drawbacks, which makes that it is becoming increasingly accepted in practice.

At date already over 500 high rate anaerobic wastewater treatment plants have been implemented world-wide, and among them the UASB process by far is the most popular (Lettinga and Hulshoff Pol, 1991). The reasons for its popularity can be found in its excellent performance achieved for a great variety of wastewaters, its relatively plain design, and particularly also its low investment and operational costs. One of the main features of the UASB-concept is that a thick flocculent or granular type of sludge will develop in the system. A characteristic device of the system comprises the Gas-Solid-Liquid separator (GSS) device, installed at top of the reactor. This GSS device is essential for retaining a high amount of viable anaerobic sludge under operational conditions.

Despite the success in practice the UASB system may suffer some problems during first start-up and in the operation with some type of wastewaters. Laboratory studies of UASB on RLP wastewater treatment are very important to prevent serious problems happening in full-scale reactors.

Vietnam has just stepped in "the free market" economy and industrialization and urbanization are developing rapidly, introducing bigger and bigger environmental problems, especially also due to industrial wastewaters. Among the industries, RLP is one of the most important. It is also the most polluting industry and it affects seriously the environment due to discharge of non treated high strength wastewater. At present, only four or five wastewater treatment plants have been constructed, such as particularly stabilization pond systems. However, these systems require a large surface area, normally 2-3 ha for each factory. In stead of ponds conventional treatment systems could be implemented, for instance the aerobic activated sludge process, but these systems are high in energy consumption, give a big amount of (poorly stabilize) excess sludge, need import of expensive equipment and are high in investment cost. Moreover they need skilled operation and maintenance. At the present economic conditions and skill of local technicians these systems are very difficult to operate and to maintain.

Regarding sustainability considerations, a combined treatment system consisting of anaerobic primary and aerobic post treatment looks the best solution to solve the environmental pollution. Anaerobic processes are the core of such a concept because they reduce the pollution of organic compounds quite efficiently while the aerobic post-treatment processes will serve polishing and supplying oxygen to the treated wastewater before discharge to receiving water.

After careful considerations and in comparison with other anaerobic processes, emphasizing especially the economic aspects, i.e. investment and operational cost, the UASB was chosen for this study, in order to assess its feasibility to full scale application in Long Thanh RLP factory.

This chapter will discuss the following main items:

(1) Possibility to get granulation of digested pig manure sludge on rubber latex wastewater.
(2) The feasibility of UASB treatment of rubber latex processing wastewater.
(3) The effect of the pH on UASB performance.
(4) The effect of effluent recicurlation on UASB performance.

4.2 MATERIALS AND METHODS, GENERAL ASPECTS.

Experimental conditions

The investigations of UASB treatment on RLP wastewater were performed both in The Netherlands and in Vietnam. In The Netherlands, all experimental reactors were placed in a temperature controlled (30±2 °C) room, while in Vietnam it was exposed to ambient conditions with temperature ranges 26-34°C. Continuous experiments were used in all investigations present in this Chapter.

Experimental UASB-reactors

All experiments were performed using a perspex laboratory-scale UASB- reactors ranging in size from 2.94 L to 8.55 L. Figure 4.2.1 shows a schematic diagram of the 8.55 liter UASB reactor with a internal diameter of 100 mm, total reactor height of 1115 mm and total volume of 8.55 L. The digestion region height is 935 mm and its volume 7.13 L, the settling region height is 180 mm and its volume 1,42 L. The reactors were manufactured from acrylic pipe. The bottom of the reactor is conical shaped for uniform feed distribution, its height is 50 mm and volume 200 mL. The feed inlet pipe is directed downwards into the conical base of the reactor, which was constructed from PVC pipe adapter. A series of small (10mm) sampling ports were fitted at intervals of 100 mm down the side of the reactor to permit wastewater and sludge sampling. At top of the reactor a Gas-Solid-Liquid (GSS) separator made from galvanized steel with a diameter of 80 mm and a slope of 70° was installed. The treated liquid leaves the reactor via a V notch weir placed at top of the settler compartment. Silicone tube was used to connect the gas collector to an alkaline liquid (5% NaOH) displacement system, where the CO_2 is removed from the gas. The (wet) methane was measured in a wet-test gas meter (Meterfabriek Schlummbergen, Dordrecht). Wastewater was fed to the reactor using a variable speed pump (Watson Marlow, UK). In Vietnam, the reactor was operated at ambient temperature of 26-34°C throughout the whole experimental period and the reactor was covered by black paper to prevent algae growth on the wall. All computations with respect to process performance were calculated based on the volume of 8.55 L.

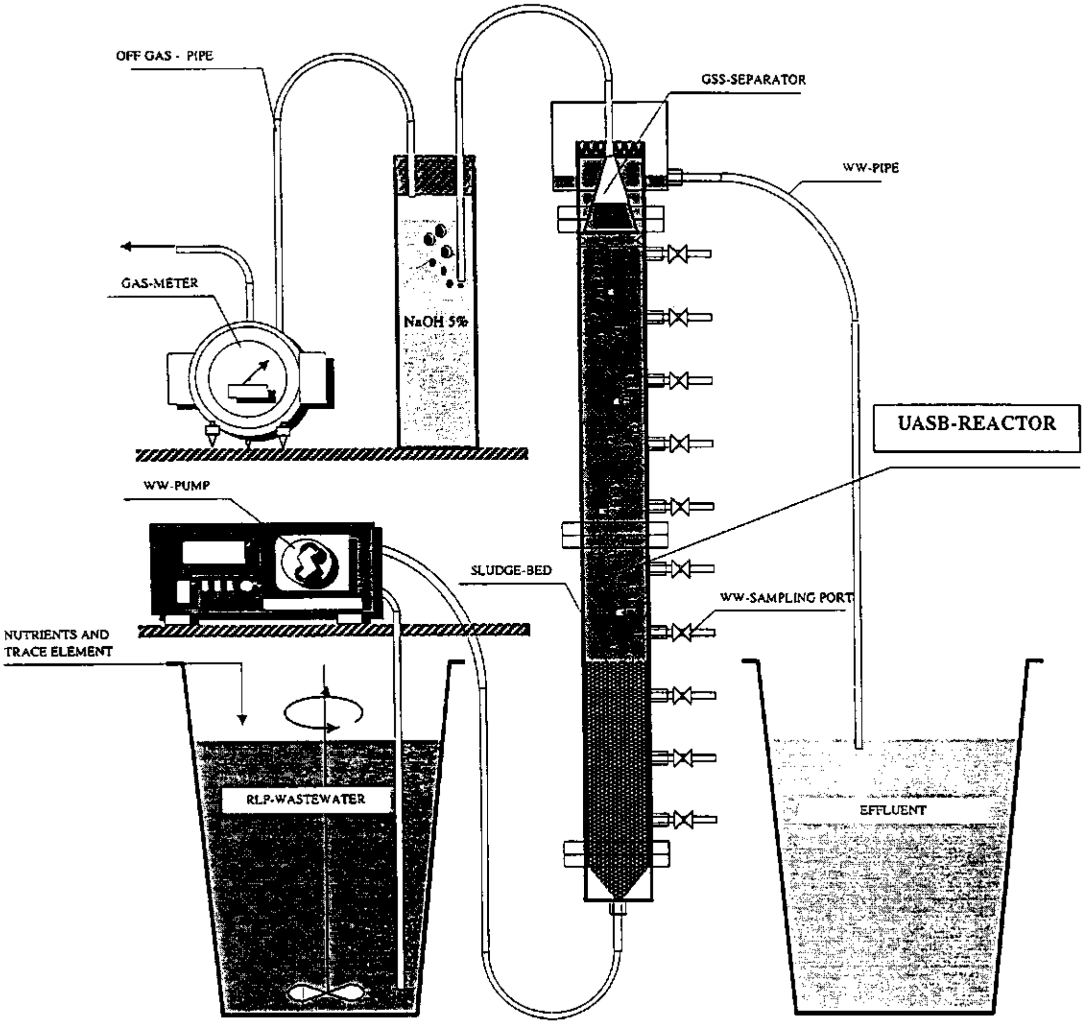


Fig. 4.2.1 Schematic diagram of UASB-reactor.

Wastewater and nutrients

The wastewater used in the experiments was prepared from RLP serum. A serum was obtained after coagulating rubber latex with acetic acid or formic acid (5%). The coagulation process under the laboratory conditions resulted in a relatively low suspended solid concentration in the wastewater (20-40 mg/L).

For the purposes of this study and according to instructions of Hulshoff Pol (1989) concerning the first start-up, the serum solution was diluted with tap water to a influent COD concentration around 2.600-3500 mg/L. A nutrient and trace elements solution was supplied to the influent wastewater by preparing stock solution and use of 6 mL nutrient solution and 0.1 mL trace-solution for 1 L influent. The composition of these stock solution was as follows.

Nutrient solution (mg/L)

NH_4Cl, 1044; K_2HPO_4, 169.8; $(NH_4)_2SO_4$, 169.8; $MgCl_2.6H_2O$, 150; KCl, 270; Yeast, 19.8.

Trace Elements (mg/L)

$FeCl_2.4H_2O$, 0.2; H_3BO_3, 0.005; $ZnCl_2$, 0.005; $CuCl_2.2H_2O$, 0.0038; $MnCl_2.4H_2O$, 0.05; $(NH_4)_6Mo_7O_{24}.4H_2O$, 0.005; $AlCl_3.6H_2O$, 0.009; $CoCl_2.6H_2O$, 0.2; $NiCl_2.6H_2O$, 0.0092; $Na_2SeO_3.5H_2O$, 0.0164; EDTA $C_{10}H_{16}N_2O_8$, 0.1; Resazurine, 0.02; 36% HCl, 0.0001 mL.

Influent wastewater was neutralized to a pH exceeding 6.2 with 6N NaOH solution, except in the experiment which aimed at assessment of the effect of pH on the UASB performance.

Seed Sludge

As explained in Chapter 3, in these experiments digested pig manure sludge (DPMS) was chosen as seed sludge. In Vietnam, the DPMS was obtained from a biogas digester at a pig farm in Ho Chi Minh City, South Vietnam. The seed sludge was screened to remove big particle before it was put in the reactor. The reactor was inoculated with 3-4 kg (wet weight, equivalent 3-4 L, approximately) DPMS which had been stored unfed 6 months at ambient condition. The seed sludge filled up the reactor to a height of 35-45 cm. In The Netherlands, the DPMS was also obtained from a biogas digester and stored at 4°C room until used. The total suspended solid (TSS) and volatile suspended solid (VSS) content of Dutch DPMS was 7.6% (based on wet weight) and 61.9% (based on TSS), respectively (Table 3.3.1), and the maximum specific methanogenic activity could not be determined because the sludge contains a high amount of ammonia, i.e. 10,068 mg $N\text{-}NH_3$/L.

The anaerobic granular sludges (GS) were obtained from a full-scale UASB reactor treating wastewater of a starch factory (Latenstein, Nijmegen, The Netherlands), and from a full-scale UASB-reactor treating wastewater of a sugarcane factory (Puttershock, The Netherlands) were also used in some experiments carried out in The Netherlands and in South Vietnam. Before starting the feeding in the experiments the GSs were exposed to ambient temperature for one day.

Analyses

In order to assess the treatment efficiency and the processes the titrimetric COD_t, COD-VFA, volatile fatty acid (VFA), pH, alkalinity were examined daily or two days each. The samples were centrifuged or filtered before analyzed (see Chapter 3, paragraph 3.3.2). In Vietnam, all parameters, except the COD-VFA and VFA concentrations, are examined according to the "Standard Methods for the Examination of Water and Wastewater" (APHA, 1985, 1992).

Operation of the experimental UASB-reactor

The detailed experimental procedure will be described in each separated paragraph.

4.3 GRANULATION EXPERIMENTS WITH DIGESTED PIG MANURE SLUDGE (DPMS) ON RUBBER LATEX PROCESSING (RLP) WASTEWATER

4.3.1 INTRODUCTION

Considering its big advantages over other processes, the UASB-process has found wide application in the world and the number of wastewater treatment plants using this process increases rapidly. The remaining problem of anaerobic treatment is the start-up of the reactor, especially for the places where no proper sludge is available, such as granular sludge or adapted sludge.

In practice, the period of time required for the first start-up always amounts to several months. However, during this period gradually an increasing fraction of the wastewater will become treated which means that during start-up the environmental situation already is improving gradually significantly. Generally, the highest applicable loading rates in UASB-reactor (viz. up to 40 $kg/m^3.d$) and the best sludge settling characteristic will be achieved if granular sludge is formed in the reactor.

This granular sludge has a very high dense viable biomass and generally an extremely high settling velocity (75 m/h compared to 3-4 m/h for flocculent sludge). The advantages of granular sludge are very obvious. The main problems often happening during the first start-up, viz. the period when still a rather poor quality sludge is present in the system, concerns the high fraction of seed sludge washed out, foaming, overloading, occurrence of a temporary accumulation of VFA, consequently sometimes a pH drop, and the slow development of the required granular.

At present most UASB-reactors are started up using granular sludge obtained as excess sludge from already installed plants. As rapidly more and more UASB are installed, bigger quantities of granular sludge will be needed as inoculum, but obviously also bigger quantities of granular excess sludge come available. Relatively, few studies on granulation of sludge have been carried out in various types of well defined synthetic wastewater, and therefore the information available on granulation on real wastewater is relatively scarce.

Based on the granulation experiments carried out with glucose molasses and citrate wastewater (Weimin Wu *et al.*, 1987), with carbohydrate/protein (Sam-soon *et al.*, 1987), with VFA mixture (de Zeeuw, 1984; Hulshoff Pol, 1989), with food industry wastewater (Oleszkiewicz and Romanek, 1989), with glucose (Sam-soon *et al.*, 1990), with acetate (Morvei *et al.*, 1990) and with ice-cream production waste and methanol (Cayless *et al.*, 1990) the following procedure for granulation can be followed (Lettinga, 1995):

- Initial organic loading rate applied depends on the specific methanogenic activity and the amount of the sludge.
- Influent COD concentration lower 3,000 mg/l.
- Increase the organic loading rate always after at least an 80% reduction in the biodegradable COD has been achieved.
- Start with 12-15 kg sludge VSS/m^3, for thick sludge (>60 kg TSS/m^3) and approximate 6 kg sludge VSS/m^3 with thin seed sludge (<40 kg TSS/m^3).

There is no "fixed" procedure for first start-up reactor for all types of wastewater, but it is well known that granulation will not proceed on wastewaters which contain a high suspended solid concentration, although exact figures in this respect can not be provided, because it also depends on the ratio soluble COD/insoluble COD, and of composition and biodegradability of the fractions.

This study aims at assessing the occurrence of the granulation of DPMS using RLP wastewater. For this purpose lab-scale reactor was operated to obtain data for designing and operating full-scale reactor in practice. The idea is to obtain sufficient insight in the granulation process in order to start-up full-scale reactor in Vietnam, so that the UASB system can be implemented and properly applied.

4.3.2 MATERIALS AND METHODS

Experimental conditions

The granulation experiments using DPMS and real RLP wastewater were performed in Vietnam from 1993-1994 under ambient conditions at temperatures in the range of 26-34°C and in The Netherlands at a temperature controlled room (30±2°C).

Continuous experimental UASB-reactor

Lab-scale reactors with a volume of 2.9 L (in The Netherlands) and 8.55 L (in Vietnam) were used in this experiment. The experimental 8.55 L UASB-reactor configuration is shown in Fig. 4.2.1.

Seed sludge

In Vietnam, DPMS obtained from a biogas digester located in 15th sub-district, Tan Binh district, Ho Chi Minh City was used as seed sludge. The characteristics of DPMS have been provided before.

In The Netherlands, the 2.9 L UASB-reactor was inoculated with an amount of 1000 mL of digested pig manure sludge containing a high ammonia concentration (10,068 mg $N\text{-}NH_3/L$), which is equivalent to appr. TSS 15.2 g and VSS 8.9 g. The sludge bed occupied about half of reactor height.

Wastewater

Wastewater used in the experiments was prepared from RLP serum. Ammonia treated rubber latex was collected in 20 L plastic containers and then brought from the field (*Hevea* forest) to the laboratory and stored at ambient condition. At the laboratory, a serum obtained from coagulation process of the rubber latex using acetic acid was stored in a refrigerator. Before feeding to reactor the serum was diluted with tap water to obtain wastewater with COD concentration of 2500-3500 mg/L, viz. the same COD concentration as in the wastewater of the RLP factories. The coagulation in the laboratory condition resulted in a low suspended solid (20-40 mg/L).

Operation of experimental UASB-reactor

Wastewater was prepared daily by using the stock serum and tap water. The experiments carried out in Vietnam was repeated twice. The initial loading rate was 3 kg $COD/m^3.d$ equivalent to a sludge load of 0.17-0.21 kg COD/kg VSS.d. The loading rate was gradually increased along with the improving COD treatment efficiency, viz. each time when a 75-85% COD reduction or higher was obtained and the pH did not drop down. The increase of loading rate was achieved by increasing the COD concentration of influent and the flowrate was kept constant at 22-37 L/d, consequently at a hydraulic retention time (HRT) of 6.84-9.30 h.

Influent and effluent samples taken once every two days were analyzed for COD, pH, alkalinity, SS in order to assess the treatment performance of the process and the sludge was visually examined weekly for the appearance of the granular sludge particles.

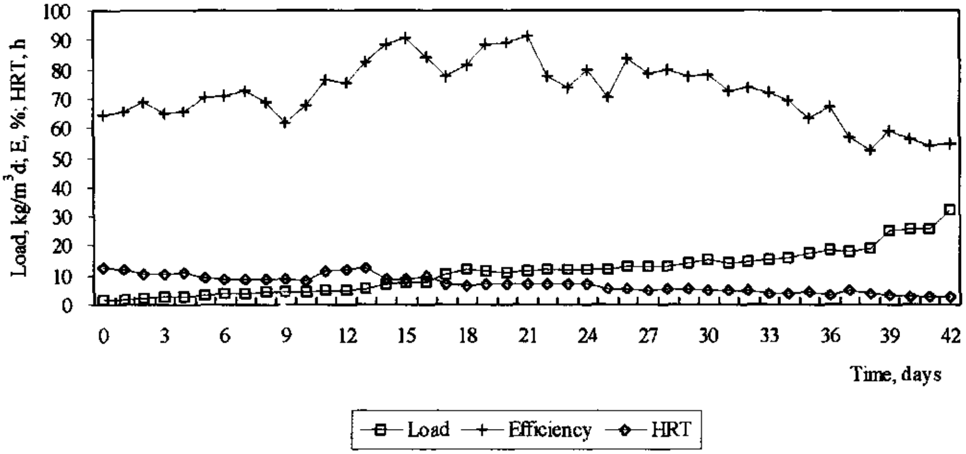


Fig. 4.3.8 The course of loading rate, treatment efficiency and HRT in the experiment carried out in The Netherlands.

4.3.4 DISCUSSION

On basis of results of laboratory experiments and practical experiences it is well known that the mechanism underlying sludge granulation is complex and that up to now no fixed general procedure for granulation is available for all conditions and types of wastewater. On the other hand it is also known that a granular type of sludge will develop on all mainly soluble types of wastewater, provided specific rough guidelines for the first start-up are followed (Hulshoff Pol, 1989; Lettinga, 1995).

In the experiments described here granular sludge was formed applying the following conditions:

- The wastewater contained mainly biodegradable organic matter, i.e. sugar, protein, etc.
- The RLP influent COD concentration generally remained below 3500 mg/L.
- The COD space loading rate during the initial period remained below 3 kg COD/m^3.d and sludge loading rate below 0.17-0.21 kg COD/kg VSS.d. when using DIMS with the SMA of 0.13-0.26 kg COD/kg VSS.d.
- The loading rate was increased stepwise on the basis of the evolution of gas production and the COD treatment efficiency. concentration.
- An imposed superficial liquid velocity in the range of 0.1-0.2 m/h.

Under these conditions the granulation proceeded within a period of 21 days, which is much faster compared to the granulation on the synthetic VFA solutions carried out by Hulshoff Pol (1989), on food industry wastewater (Olcszkiewicz and Romanek, 1989) and on protein (casein) wastewater (Moosbrugger *et al.*, 1990).

Based on the characteristics of the granular sludge, which has high biomass content (80-88% VSS/TS) and exerts a high settling velocity, it is very clear that sludge with a low density and consequently low gravity is not anymore present in sludge bed. This fraction of the seed sludge has been washed out from the reactor as a result of the applied liquid upflow velocity and the gradually increasing mixing conditions. During the first period of time, when the imposed organic loading rate is restricted to prevent the system to become overloaded, the mixing intensity is low, and then mainly the very light fraction of sludge is washed out. Three types of mixing can be distinguished, viz. using mechanical devices and mixing resulting from the liquid flow and from the biogas. Mixing resulting from the biogas is the best because it is a gentle type of mixing (not disrupting sludge aggregates), but still quite effective. Biogas is produced in the sludge bed continuously and released from the sludge bed in the form of smaller and bigger bubbles which move upward with a high velocity, and then gently mix up sludge particles and agglomerates in the liquid phase above the bed, subsequently heavy sludge particles will settle down and the lighter sludge will be washed out. In addition, when gas produced is retained for sometime in the sludge agglomerates/particles they may float up to the GSS, and after releasing the gas here they settles down again rapidly. During this up and down movement particles gradually become polished beads and they grow denser. The observation and experimental data presented very clearly confirm this statement. Within 4 hrs after feeding already the gas production commenced and the sludge bed expanded substantially. The amount of sludge washed out during the first days amounted to 1800-1900 mg/L, and its VSS/SS ratio was 60-70%. It is the very fine fraction of the seed sludge, but not inert matter because its SMA amounted to 0.1-0.15 g COD/g VSS.d. However, it is essential that this fraction is removed from the system, because the main objective of the first-up is to develop a heavy well settling sludge. The heavier sludge particles present in the seed sludge, which start moving up and down and/or stay in the sludge bed, are well retained. It is clear that the amount of sludge retained decreases substantially due to the sludge wash-out, but the treatment efficiency remains the same and gradually improves. After increasing the loading rate, temporary a slight drop in the treatment efficiency will occurs, but then the efficiency will start improving again. Consequently the SMA of the sludge increases. The most important sludge characteristics improving during a proper first start-up are the settling characteristics and the SMA, although latter not clearly could be demonstrated in our experiments. This can be due to the fact that the granular sludge remained unfed for quite a long period of time before conducting the SMA test.

It is therefore clear from the above that the imposed space load should be sufficiently high to produce enough gas for mixing, but the system obviously also should not be overloaded.

The experiments clearly demonstrated that the two reasons causing sludge wash-out during the first start-up are:

1. The gradually increasing "selection pressure" resulting from the higher upflow velocity and the higher gas production later. But all poorly settleable sludge (finely dispersed matter) should be eliminated from the system in order to initiate and enhance the growth of granular sludge.
2. "Piston formation" in the sludge bed due to accumulating gas in the sludge bed as a result of which parts of the bed are lifted and slowly moved upward. This phenomenon is mainly due to small diameter of the laboratory reactor. The slugde block, consisting of well and poorly settleable sludge, occasionally will be forced out from the reactor, unless they collapse before reaching the effluent launder. This phenomenon will not happen in full-scale reactors because entrapped gas will be released relatively easily in that case as a result of the large surface area and the inherently much lower strength of the "sludge bed piston" at increasing surface area..

The first mechanism stimulates the granulation process, while the second one will decrease the treatment capacity of the system. It is obvious that proper measures should be taken to prevent the second phenomenon. In the laboratory scale reactors, e.g. by applying - if possible - intermittent mechanical mixing in the sludge bed.

In these investigations it clearly has been found that sludge granulation with proceed on RLP wastewater which contains up to 80 mg/L SS. During start-up the treatment efficiency should exceed about 70% after each increment of the load, and the influent COD concentration should not be lower than 1000 mg/L.

different flowrates, the influent pH always was adjusted to the values exceeding 6.2.

At the initial space loading rate of 8.0-9.7 kg COD/m^3.d imposed to the reactors at the first day, the influent COD concentration (COD_{inf}) already was reduced from 1241 mg/L to 256 mg/L and then it remained steady at a concentration of 215-235 mg/L (see Fig. 4.4.1), consequently at a treatment efficiency (E) in the range of 77.3-84.6%. For RLP wastewater this is a rather low treatment, which can be due to low activity of the unfed stored DGS. At this loading rate the hydraulic retention time (HRT) and the upflow velocity (V_{up}) were 6.4 m^3/m^3.d and 0.3 m/h (8.4 m/d), respectively (corresponding flowrate (Q) of 55 L/d), the pH increased from 6.27-6.75 to 7.39-7.78 (see Fig. 4.4.2).

Table 4.4.1 Performance data of the 8.55 L UASB-reactor with RPL wastewater and with DGS from Latenstein starch factory as seed (carried out in South Vietnam)

Parameter		Space organic loading rate (kg COD/m^3.d)			
		8.0-9.7	15.5-19.3	20.2-28.5	34.0-37.0
COD_{inf}	mg/L	1241-1500	2560-3000	2784-3422	3770-4067
COD_{eff}	mg/L	215-310	308-480	345-660	812-1095
E	%	77.3-84.6	82.2-86.6	79.8-87.9	59.8-73.1
Q	L/d	55	55	64-78	60-78
L_H	m^3/m$^{3.d}$	6.4	6.4	7.3-9.1	7.0-9.1
HRT	h	3.7	3.7	3.3-2.6	2.9-2.6
V_{up}	m/h	0.3	0.3	0.3-0.4	0.4
pH_{in}		6.27-6.75	6.30-6.56	6.27-6.54	6.45-6.54
pH_{eff}		7.39-7.78	7.68-7.86	7.60-7.87	7.49-7.54
Alk_{in}	mg $CaCO_3$/L	650-930	920-1150	980-1800	1600-1700
Alk_{eff}	mg $CaCO_3$/L	1200-1580	1800-2130	2000-3200	2300-2700

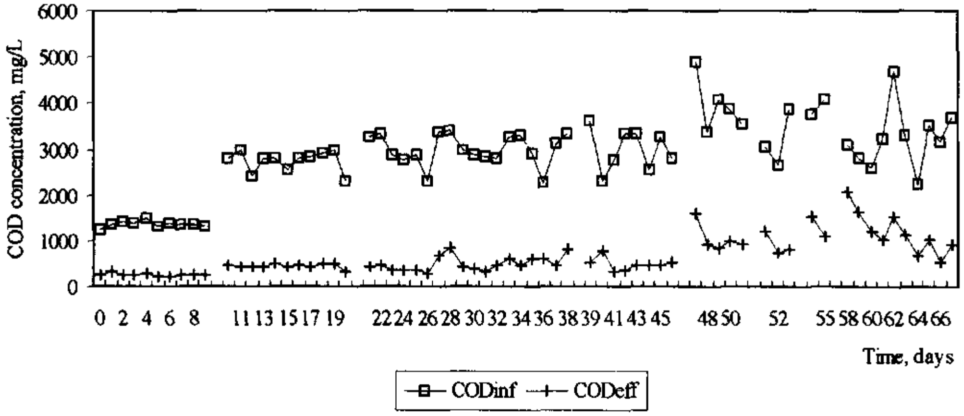


Fig. 4.4.1 COD reduction in UASB treatment of the RLP wastewater using DGS (carried out in South Vietnam).

At the imposed loading rate of 15.5-19.3 and 20.2-28.5 kg COD/m^3.d, the treatment efficiency amounted to 82.2-86.6% and 79.8-87.9%, respectively, consequently slightly different compared with the initial loading rate. However with the COD_{inf} in the range from 2,560-3,000 and 2,784-3,422 mg/L the effluent COD concentration (COD_{eff}) of 308-480 and 345-660 mg/L were higher than before.

During the experimental period the tube connecting the GSS to the sodium liquid adjusted pressure column and to the gas meter frequently became clogged due to rubber scum accumulating at the liquid surface below the GSS and therefore gas production could not be measured accurately.

At a loading rate of 34.0-37.0 kg COD/m^3.d. the treatment efficiency dropped sharply to 59.8-73.1% (see Fig. 4.4.3), and especially the COD$_{eff}$ values of 812-1095 mg/L were rather high, the effluent pH (pH$_{eff}$) is lower than before. The experiment was terminated at this load.

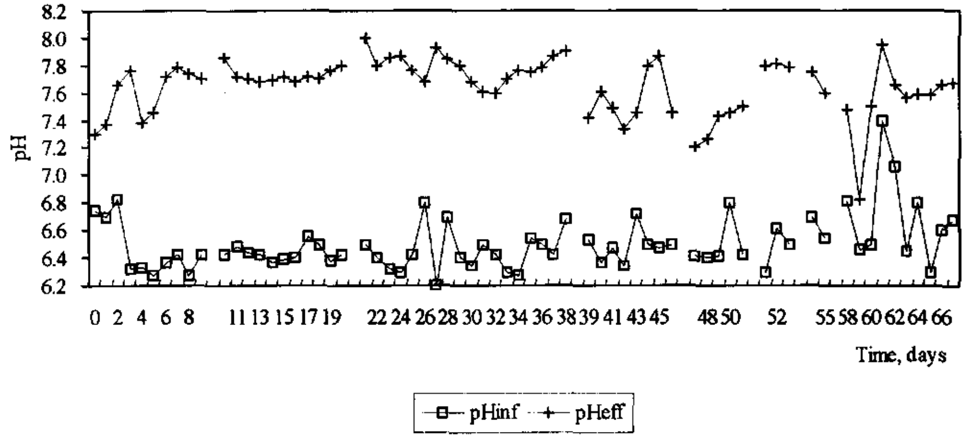


Fig. 4.4.2 pH variation during the first experiment using DGS (carried out in Vietnam).

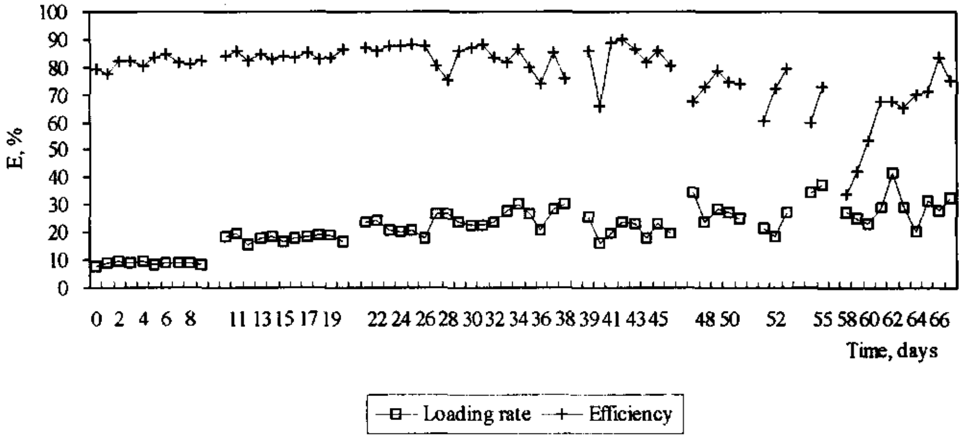


Fig. 4.4.3 UASB treatment efficiency on the RLP wastewater using DGS (carried out in Vietnam)

Visual observation during the experiment revealed that the rubber particles which were left in the wastewater after coagulation process, were coagulated in the reactor, especially in the sludge bed. The reason for the occurrence of this "coagulation" very likely has to be found in degradation of the protein layer surrounding rubber particle. This will result in a de-stabilization of the rubber colloidal matter.

The newly coagulated rubber particles accumulate in the sludge bed and stick to the granular sludge or float up and then they accumulate at the liquid surface below the GSS.

During operation of the UASB-reactor, it is obvious that three problems may happen to the granular sludge. The first problem comprises the wash-out of the granular sludge from the reactor due to the foam forming in the sludge bed, due to which gas could not sufficiently well release, and then the sludge bed is pushed out of the rector. This phenomenon is very similar to that described in paragraph 4.3, and it very likely will not happen in a full scale reactor. The second problem concerns the slow deterioration of the granular sludge during the experiment. As a result the sludge gravity seems to decrease, especially at high organic loading and high influent COD concentration. In the bottom part of the sludge bed, the color of sludge changed from black to grey-white, revealing the fast growth of attached acidogenic bacteria. Moreover granular sludge felt apart into smaller particles and these smaller particles rinse out from the system. At the end of the first experiment the DGS in the reactor became similar in appearance than the sludge obtained in the granulation experiment on the DPMS with the RLP wastewater. The third problem comprises the adherence of fine sludge to rubber particles, which reinforces the buoying tendency of sludge, resulting in an accumulation of sludge-rubber agglomerates at the liquid-gas interface in the GSS which caused clogging of gas tubes and reduced the amount of sludge in the reactor.

The experiment carried in South Vietnam using granular sludge (VGS) cultivated on DPMS. In the second experiment a granular sludge was used obtained in the granulation experiment conducted on DPMS with the RLP wastewater. The performance data obtained in these experiments are summarized in Table 4.4.2

Table 4.4.2 Treatment efficiency of UASB-reactor fed with RPL wastewater and with VGS cultivated on DPMS

Parameter		Space organic loading rate (kg COD/m^3.d)		
		5.1-13.2	13.2-18.6	18.9-22.1
COD_{inf}	mg/L	1088-2689	2608-3576	2704-3302
COD_{eff}	mg/L	112-253	310-607	435-504
E	%	90.6-93.6	79.9-88.9	82.8-85.2
Q	L/d	38-42	38-44	50-59
L_H	m^3/m^3.d	4.4-4.9	4.4-5.1	5.8-6.9
HRT	h	5.4-4.9	5.4-4.6	4.1-3.5
V_{up}	m/h	0.21-0.24	0.21-0.25	0.28-0.33
pH_{in}		6.18-6.43	6.24-6.68	6.31-6.62
pH_{eff}		7.61-7.72	7.43-7.97	7.03-7.83
Alk_{in}	mg $CaCO_3$/L	140-500	800-2600	840-1600
Alk_{eff}	mg $CaCO_3$/L	464-1560	2000-4400	1920-3000

The experiment was also carried out at three organic loading rates, viz. at 5.1-13.2, 13.2-18.6 and 18.9-22.1 kg COD/m^3.d.

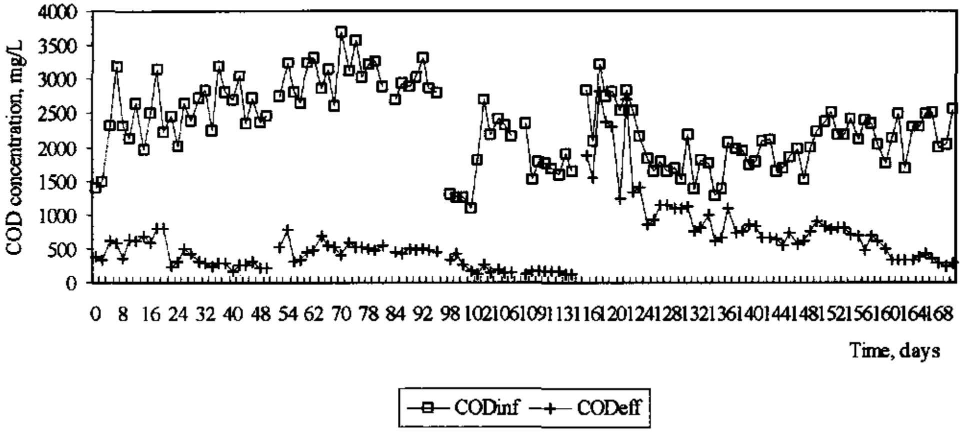


Fig. 4.4.4 COD reduction in UASB treatment of the RLP wastewater using DGS (carried in South Vietnam).

At the imposed loading rate of 5.1-13.2 kg COD/m^3.d, the COD concentration dropped from 1,088-2,689 mg/L to 112-253 mg/L (see Fig. 4.4.4) resulting in a treatment efficiency of 90.6-93.6%, consequently clearly higher than on the granular sludge originating from Latenstein. The pH raised from 6.18-6.43 to 7.61-7.72 (see Fig. 4.4.5).

The treatment efficiency found at organic loading rates of 13.2-18.6 kg COD/m^3.d and 18.9-22.1 kg COD/m^3.d amounted to 79.8-88.9% and 82.8-85.2% (see Fig. 4.4.6), respectively, consequently only slightly different from that at the lower load. The COD_{eff} at the higher loading rate is slightly higher, 310 mg/L compared with 435-504 mg/L.

The applied hydraulic loading rate in the experiment and V_{up} were 4.4-6.9 m^3/m^3.d and 0.21-0.33 m/h (5.04-7.92 m/d), respectively.

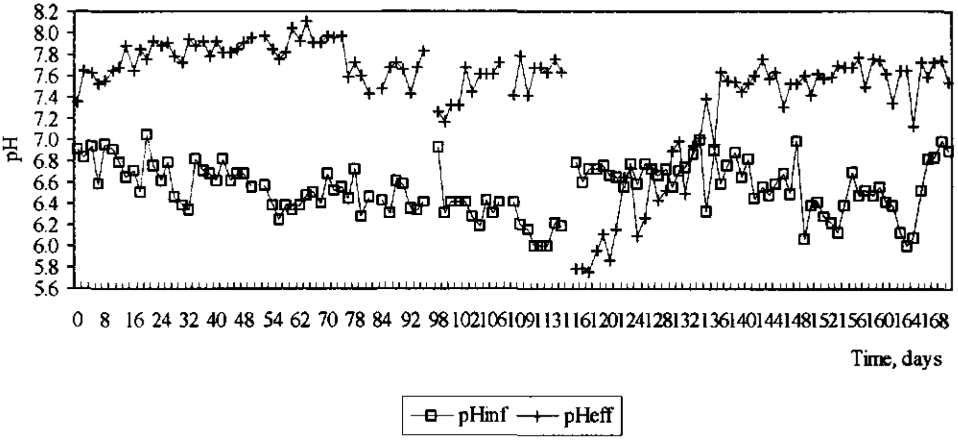


Fig. 4.4.5 pH variation during the second experiment using VGS (carried out in Vietnam).

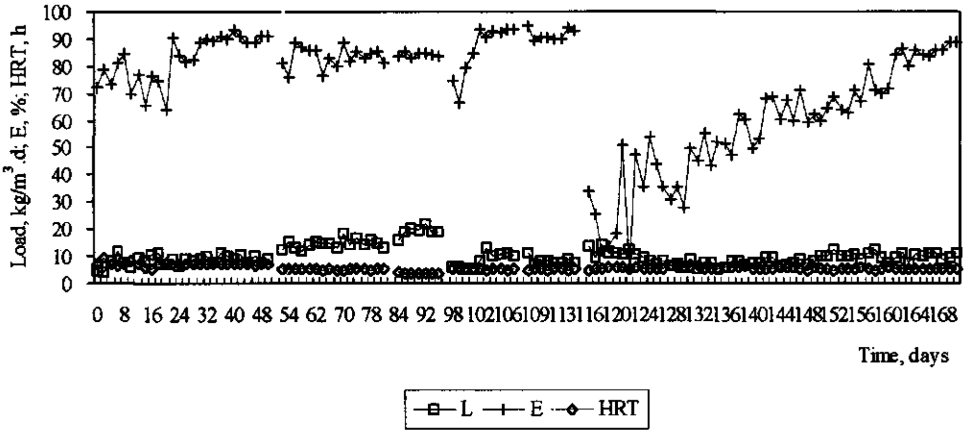


Fig. 4.4.6 The UASB treatment efficiency on RLP wastewater using VGS (carried out in Vietnam)
L: loading rate, E: treatment efficiency, HRT: hydraulic retention time.

After this loading rate, the feeding of the reactor had to be interrupted for one month at a temperature of 26-34°C due to a lack of wastewater. The feeding was resumed at day 93. The experimental data obtained after resuming the feed are shown in Fig. 4.4.7.

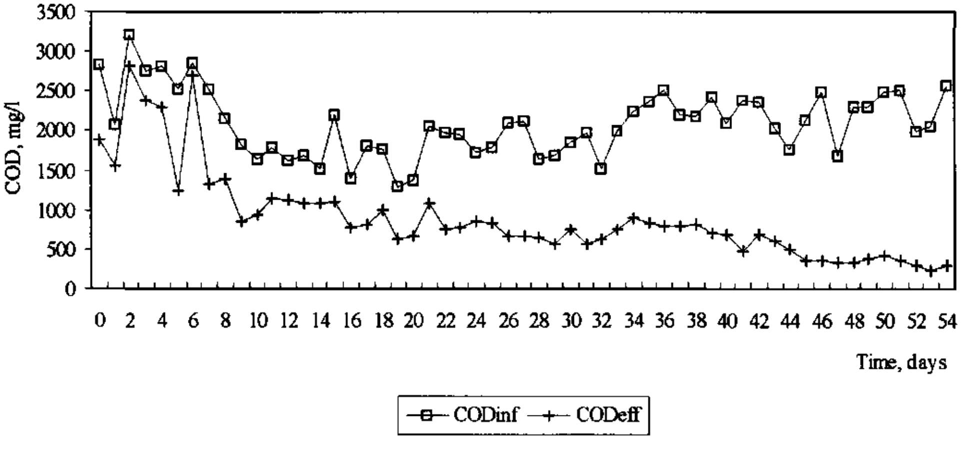


Fig. 4.4.7 COD reduction in the reactor after one month unfed at 26-34°C.

The results reveal that an one month feed interruption at such high temperatures affected the system quite detrimentally. Even despite the rather low applied organic loading rate, i.e. 10.4-14.2 kg COD/m^3.d, viz. only 50% of the loading rate applied before stop, the achieved treatment efficiency of 52.6-34.7% is extremely low (see Fig. 4.4.7). And also the pH dropped from 6.60-6.76 to 5.76-5.96 (see Fig. 4.4.8) indicating that the system was overloaded, consequently a lot of VFA accumulated in the reactor. After the organic loading rate was reduced to 5.3-7.8 kg COD/m^3.d, at day 8 the system recovered slowly. At day 54, at an imposed loading rate of 11.4 kg COD/m^3.d, a hydraulic loading rate of 4.4 m^3/m^3.d and HRT of 5.4h the COD$_{inf}$ was reduced from 2558 mg/L to 288 mg/L resulting COD removal efficiency of 88.7%, i.e. as high as before.

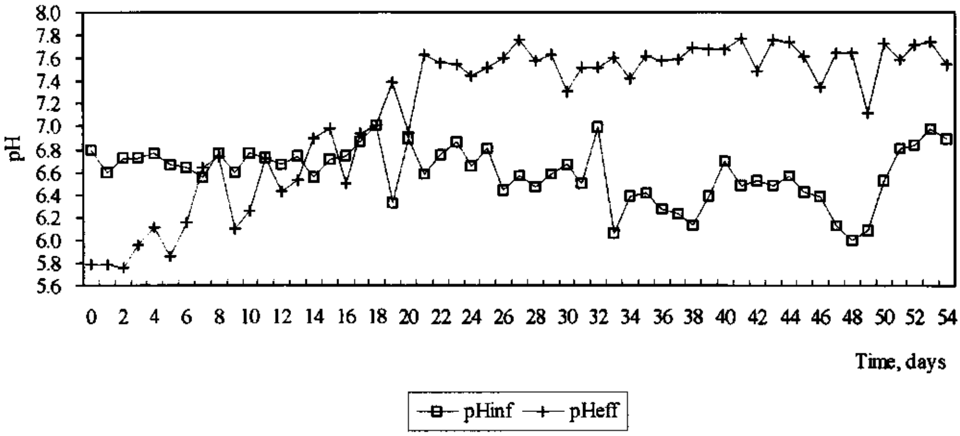


Fig. 4.4.8 pH variation in the reactor after one month unfed at 26-34°C.

During the experiment, the COD and pH profile over the height of the reactor were also measured to assess the "effective" volume of the reactor. The measurements were carried out at two different situations, viz. during a period that the sludge bed was expanded while gas was releasing, and during a situation where the sludge bed remained non-expended after gas was released. The data are shown in Fig. 4.4.9 and 4.8.10.

At the moment when profile samples were taken the height of the sludge bed was about 15-18 cm. The experimental results illustrate that in the sludge bed (to port 2) the COD concentration dropped rapidly and significantly, i.e. from 1,140 mg/L to 301 mg/L, but in the liquid phase above the sludge bed the removal looks negligible, i.e. only from 301 mg/L at port 2 to 104 mg/L at port 11 due to low bacteria concentration and the rather well mixing conditions prevailing here.

During the period that gas was produced the sludge bed expanded from 10-15 cm height to 30-45 cm as a dense block and the sludge blanket reached up to 60 cm height. The COD concentration dropped immediately from 1140 mg/L at influent port (port 0) to 435 mg/L at 10 cm height (port 1). However, the COD came up to 457-483 mg/L from port 3 to port 5 due to the fact that a part of the organic solids accumulated in the sludge bed is released into the solution, ultimately to 155 mg/L at 60 cm, the position of the top of the blanket (port 6). Beyond this point the COD concentration decreased to 104 at effluent port (port 11). pH increased from 6.12 at port 0 to 7.20 at port 2 and 7.71 at port 11, the effluent.

In case of a non-expanded sludge bed, the COD decreased immediately from 1807 mg/L at port 0 (influent) to 257 mg/L at port 2, i.e. 20 cm height where was the top of the sludge bed and to 213 mg/l at port 11. The pH increased rapidly from 6.06 at port 0 to 7.48 at port 2, and to 7.84 at port 11.

The reason for the rapid pH-increases from 6.06-6.12 to 7.20-7.44 can be attributed to the rapid conversion of acetic acid (stronger acid with $K_a = 10^{-5}$) in to methane and carbonic (weaker acid with $K_{a1}=10^{-7}$), according the below reaction:

$$CH_3COOH^- + H_2O \rightarrow CH_4 + HCO_3^-$$

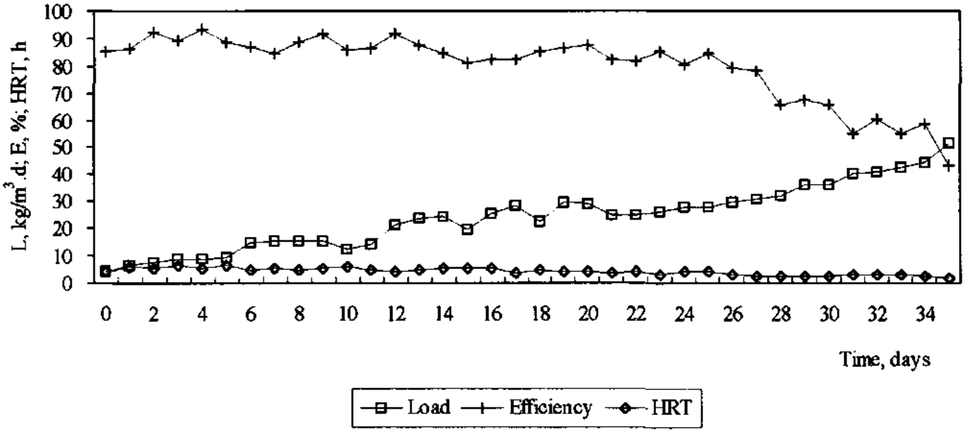


Fig. 4.4.12 The UASB treatment efficiency on RLP wastewater using DGS (carried out in The Netherlands).

4.4.4 DISCUSSION

This experiment was carried with two types of granular sludge, DGS from Latenstein starch factory, The Netherlands and VGS originating from granulation of DPMS on RLP wastewater in Vietnam. The use of granular sludge allows to apply the highest organic loading rate and as well as the highest hydraulic loading rate, i.e. the highest upflow velocity.

The experimental data obtained for both types of sludge reveal that a UASB system is highly feasible for the treatment of RLP wastewater. This could be expected, because the organic compounds and conversion products contained in the wastewater are sugars, proteins and mainly acetate (paragraph 3.6). Therefore RLP wastewater soluble pollutants are readily degraded. With an organic loading rate up to 28.5 kg COD/m^3.d. a COD removal efficiency up to 79.8-93.6% can be achieved corresponding to a hydraulic loading rate up to 6.9 m^3/m^3.d and HRT up to 2.6 h. the upflow velocity applied was up to 0.4 m/h (9.6 m/d), which still is far from the settling velocity of granular sludge (35-75 m/h). In all these experiments a rather shallow sludge bed, i.e. a small amount of sludge was still present in the reactor due to a limited amount of granular sludge available in Vietnam. The data obtained from the COD profile over the height of the rector evidenced clearly that if granular sludge is available, a lot more sludge could have retained in the reactor and then a significantly higher loading rate would be feasible.

At all organic loading rates applied and treatment efficiencies obtained the effluent COD concentration always exceeded 100 mg/L. Therefore, in order to meet effluent standards, some post-treatment is needed for polishing.

In the UASB-reactors, soluble organic compounds such as sugars are converted into acetate and subsequently into methane and carbon dioxide. However, RLP wastewater also contains a biodegradable fraction of a colloidal and suspended matter, i.e. consisting of proteins, lipid, etc., which is not determined in terms of filtered COD, but also this fraction treated in UASB-reactor, and therefore in case of RLP wastewater, the true treatment efficiency of the UASB-reactor is higher.

In the reactor, especially in the sludge bed, the pH can increase up to about 8.0 or higher depending on the treatment efficiency, e.g. the higher treatment efficiency the higher the pH will raise, consequently the higher will become the amount of alkalinity.

Concerning the effluent SS concentration, it should be noted that RLP wastewater contains a colloidal COD fraction consisting of rubber particles covered with a protein layer. After being anaerobically destabilized, the protein is hydrolyzed and converted into amino acids and subsequently into acetate, and rubber particles will coagulate and become suspended solids which might affect the UASB system quite detrimentally and lead to an increase of effluent suspended solids concentration and some part of the suspended solid present in the effluent is not active sludge.

Based on the experimental evidence obtained and the visual observations made it is very clear that the accumulation of freshly coagulated rubber particles in the system may cause big operational problems, viz. a difficulties in maintenance, i.e. retaining a sufficient amount of sludge. After 50 days of continuous operation, rubber particles stick together into blocks in the sludge bed which easily float up to the liquid surface under the GSS and accumulate there forming a very thick layer. This layer obstructs the release of produced gas. Rubber also sticks on the surface of granular sludge particles and due to their lower gravity the mixture floats up and remains in the top of the reactor.

The other serious problem is the deterioration of the (Dutch) granular sludge under the influence of the rubber particles. During the operational period of the experiment, the size of the granular sludge became smaller and smaller. On the other hand at the same time we presume that a new granular sludge developed of very similar characteristics as the granular sludge developing on DPMS in the DPMS granulation experiment.

Furthermore the results clearly reveal that an one month unfed storage of the sludge (due to a feed interruption) at 26-34°C strongly deteriorated the specific activity of the sludge, i.e. a drop of more than 50% occurred. The system needed a quite long period of time for recovery.

4.5 THE EFFECT OF pH ON THE PERFORMANCE OF A UASB SYSTEM

4.5.1 INTRODUCTION

In the digestion process, anaerobic organisms convert organic matter into methane and carbon dioxide. The anaerobic degradation is affected by many factors, such as concentration, type and nature of the organic compounds, pH, concentration of ammonia, trace elements, etc. The pH is a very important parameter because it affects strongly the stability of the system, and therefore the treatment efficiency due to the sensitivity of methanogenic and also acetogenic bacteria. In practice, the cost of chemicals that can be supplied to the influent to maintain the pH at optimum conditions represent a main part of operational cost. Chemicals such as sodium hydroxide, sodium bicarbonate are commonly used to maintain the pH in the optimum range of 6.5-7.5 (Stronach *et al.*, 1986). In the past already several studies were carried out to assess the effect of the pH on anaerobic treatment processes, e.g. in order to find the proper solutions such as supply of alkalinity, recycling of effluent, etc..

Young and McCarty (1967), Cronje (1973) and Capri (1973), in their studies with upflow anaerobic filter in treating protein and carbohydrate wastewater observed a decline in pH at the bottom of the reactor and a recovery of pH in the upper regions of the filter. They reported a drop in the COD removal efficiency when pH declined to values below approximately 6.2.

In a UASB study of Somson *et al.* (1987) treating carbohydrate waste also a decline of pH at the bottom of the reactor was reported and higher pH values in the upper part of the system. It was found that by using of effluent recycle the influent alkalinity requirements could be significantly reduced (Somson *et al.*, 1991).

Many (un)published data carried out at the Department of Environmental Technology, Wageningen Agricultural University, The Netherlands, also reveal a decline of pH in the reactors in treating organic wastewater and the negative effects of a pH drop on the treatment efficiency of the system. However, so far relatively little information is available about possible long term effects of a low influent pH to sludge quality present in the reactor and its effect on important sludge characteristic like the presence of accumulated alkalinity in the (seed) sludge, the rate of recovery of the system when exposed to a low pH shock. It is obvious that this information is of big practical importance for operation and application.

This paper reports results of a study on the effect of pH on the performance of an UASB-reactor and the recovery of the system following a pH-upset.

4.5.2 MATERIALS AND METHODS

Experimental conditions

The experiment was performed at the Department of Environmental Technology, Wageningen Agricultural University, The Netherlands, in a 30 ± 2°C temperature controlled room.

Experimental reactor

The laboratory 8.55 L UASB arrangement used in the experiment is shown in Fig. 4.2.1.

Sludge

Granular sludge (GS) from a wastewater treatment plant of a sugar factory Puttershoek, The Netherlands, with a specific methanogenic activity of 1.5 g COD-VFA/g VSS.d was used as seed sludge. The specific gravity of the sludge was rather high, viz. 1080-1090 kg/m^3, which mainly resulted from its high calcium content. For the purpose of this study the (un-expanded) sludge bed volume was set at 3 L with a bed height of 35 cm, viz. up to a level of sampling port number 4, corresponding to 373.5 g VSS.

Substrate composition

The substrate used in the experiment consisted of rubber latex processing serum, diluted 1:10 with tap water before feeding it into the reactor. The characteristics of the substrate are presented in Table 4.5.1. The rubber latex was imported from (South) Vietnam.

In all experiments a nutrient solution and trace element solution according to de Zeeuw (1984) was added to the influent. During the first phase of the experiment the wastewater was not neutralized in order to investigate the effect of the pH on the performance of the UASB system. During the second phase of the experiment, focussed on the recovery of the system, alkali (NaOH 6N) was added to increase pH of influent up to 6.15-6.42.

Table 4.5.1 Characteristics of the wastewater feeding used in the experiment

Parameter	Unit	Concentration
pH		4.4- 4.6
COD_t	mg/L	1,605-1,980
VFA (C_2)	mg/L	1,300-1,500
$N\text{-}NH_3$	mg/L	170-190
Glucose	mg/L	240-300

Analyses

Titrimetric centrifuged COD_t, Volatile Fatty Acids (VFA), alkalinity accumulated in the seed sludge, gas composition and production, pH profile (12 points) were determined with the methods described in paragraph 4.2.

The experimental procedure

In order investigate the effect of the pH on the UASB wastewater treatment system, e.g. the low pH effect and the recovery of the system, the influent wastewater pH was set at values as low as 4.4-4.6 is applied until the whole system passed in a serious up-set for 1-2 days, and then next the experiment was continued using an influent pH value exceeding 6.2 to assess the recovery of the system on the basic of the COD treatment efficiency and gas production rate.

4.5.3 RESULTS

The experiment was carried out in two phases:

- First phase: to study the effect of low pH on the UASB system, and
- Second phase: to assess the recovery of the UASB system following pH-upset.

The characteristics of the wastewater used in the experiment are presented in Table 4.5.1, and the experimental parameters for both phases are presented in Table 4.5.2.

Table 4.5.2 The experimental parameters used in the experiments conducted at low pH_i and neutral pH^i for recovery

Experimental parameter		Experimental phase	
		Acidified	Recovery
pH		4.45-4.62	6.15-6.42
COD_t	mg/L	1650-1980	1605-1713
COD-VFA	mg/L	1346-1565	1254-1321
C_2	mg/L	1236-1414	1115-1321
Q	L/d	23.0-31.4	24.0-34.0
L, sludge	gCOD/gVSS.d	0.32-0.44	0.27-0.45
L, Space	$kgCOD/m^3.d$	4.58-6.34	3.90-6.27
HRT	h	6.65-9.10	6.14-8.49

The effect of low pH to UASB system

The flowrate during this first phase of the experiment was kept at 23.0-31.4 L/d, corresponding to a COD space load of 4.58-6.34 kg/m^3.d, consequently in fact a low space load and at a sludge load of 0.32-0.44, i.e. a moderate load. The system was operated until the treatment efficiency and gas production dropped down completely, and the pH dropped to values below 6.0.

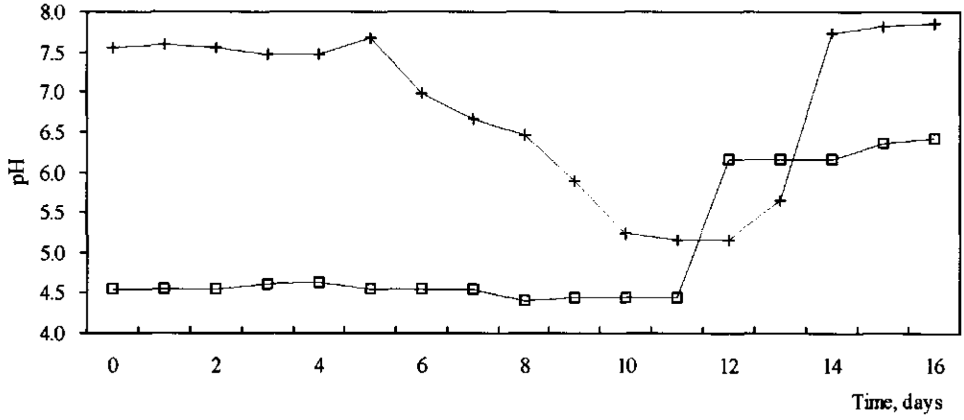


Fig. 4.5.1 The course of the pH in the UASB experiment.

During the first 5 days of operation, the treatment efficiency remained very high, and the pH increased from 4.55-4.62 of the influent to 7.5-7.6 of the effluent (see Fig. 4.5.1). The COD_t concentration dropped from 1650-1980 mg/L to only 84-98 mg/L (see Fig. 4.5.2) amounting to a total COD reduction of 94.8-95.5%. These high values correspond to those (93.3-97.7%) found in the biodegradability studies with RLP (see table 3.4.3). The CH_4 gas production was up to 19.4 L/d (see Fig. 4.5.3). The influent C_2 concentration decreased from 1231-1468 mg/L to 28-56 mg/L in the effluent and any C_3, C_4 and C_5 were not found. The pH profiles shown in Fig. 4.5.4 (day 1-5) reveal that the pH increased rapidly over sludge bed. This can be attributed to two factors, viz. the sludge buffer capacity and the conversion of VFA into methane gas. As a result of these factors the pH remained almost the same from port number 4 (above sludge bed) to 10, but the pH of the effluent increased to 7.81 due to the release of CO_2 to the air.

From Fig. 4.5.1 it is obvious that starting from day 5 the "buffer capacity" of the sludge became exhausted, but up to day 7, at a effluent pH of 6.45 the COD_t concentration of the effluent still remained low, viz. 98 mg/L, amounting to a COD_t reduction of 92.7%. However starting from day 8, the treatment efficiency dropped rapidly, viz. the COD concentration of the effluent raised to 879 mg/L, corresponding to a treatment efficiency E= 50% and at the bottom part of the reactor the system was already in a almost complete up-set (see Fig. 4.5.4, day 8), and the gas production declined to less than 6 L/d.

At day 10 the whole system was in a serious upset. The results in Fig. 4.5.1 and 4.5.2 show that the pH in the reactor increased only very slightly, viz. from 4.5 to 5.9., the VFA concentration increased slightly, viz. from 1,263 mg/L in the influent to 1,344 mg/L in the effluent. This can be due to the fact that the sugars and proteins contained in the wastewater are converted to acetic, propionic and butyric acid, at day 10, resulting in concentrations of 1344, 14.5, 54.5 mg/L, respectively. As during the experiment gradually smaller amount of viable sludge became available to convert these acids into CH_4, it is clear that at some stage, the remaining viable sludge will become overloaded, and consequently the VFA concentration in the effluent irrevocably needs to increase. The pH profiles are shown in Fig. 4.5.4. The system failure was maintained for 3 days, viz. day 9 to 11 using a feed of low pH. At day 12 the pH of the feed was increased to 6.15-6.25.

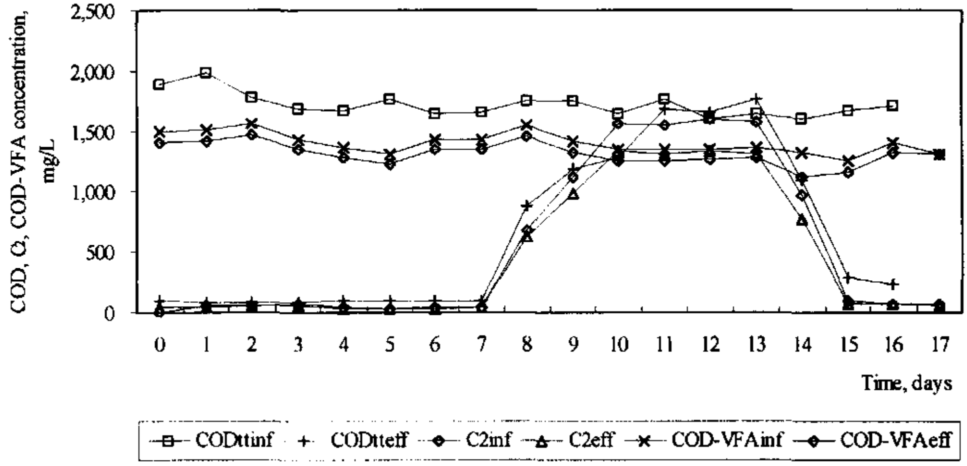


Fig. 4.5.2 COD_t, COD-VFA and C_2 reduction in the experiment.

The high loading potentials of the system even after the serious pH-upset for treating the RLP wastewater were assessed by increasing the COD_t concentration to 3,287-3,357 mg/L, corresponding to the COD loading rate of 0.78-0.83 kg COD/ kg VSS.d (11.2-12.0 kg COD/m^3.d). The COD removal efficiency achieved was 79-88% with the effluent COD concentration of 394-729 mg/L. However after increasing the influent concentration to 5,250 mg COD/L, corresponding to a load of 1.22-1.43 kg COD/kg VSS.d (17.5-20.5 kgCOD/m^3.d) the treatment efficiency dropped down to 37-52%. Fig. 4.5.5 presents the COD-VFA profile at the influent COD concentration of 3,191 mg/L.

4.5.4 DISCUSSION

In anaerobic digestion, as result of VFA conversion into methane and carbon dioxide according to the overall reactions shown below, protons are removed from the solution, i.e.:

for acetate,

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$$

for propionate,

First step $CH_3CH_2COO^- + H^+ + H_2O \rightarrow CH_3COO^- + H^+ + 3H_2 + CO_2$

In this step no acid proton donor is removed.

Second step $CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$

Third step $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

for butyrate,

First step $CH_3CH_2CH_2COO^- + H^+ + 2H_2O \rightarrow 2CH_3COO^- + 2H^+ + 2H_2$

In this step a proton donor is produced.

Second step $CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$

Third step $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

In anaerobic digestion ultimately a relatively strong acid (VFA) with pK_a=4.74 is replaced by a relatively very weak acid, viz. H_2CO_3, because carbon dioxide reacts with water to form carbonic acid, and then it dissociates according to:

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^- \quad K_{a1} = 4.3 \times 10^{-7}$$
$$HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-} \quad K_{a2} = 5.6 \times 10^{-11}$$

Once neutralized VFA have been removed, an equivalent amount of bicarbonate alkalinity generally will be present in the solution.

From the above reactions, it is clear that after anaerobic biodegradation the effluent is neutral or even may be alkaline in pH (Samson *et al.*, 1991), because bicarbonate alkalinity is produced.

In case of RLP wastewater, which mainly contains acetic acid, complex sugars and proteins, acetic acid, the complex sugars and proteins are first hydrolyzed and then acidified into VFA, which then are converted in methane and carbon dioxide. The following reactions are involved:

for sugar,

$$\begin{aligned} &C_6H_{12}O_6 &&\rightarrow 2CH_3CH_2OH + 2CO_2 \\ &CH_3CH_2OH + 2H_2O &&\rightarrow CH_3COOH + 2H_2 \\ &CH_3COO^- + H^+ &&\rightarrow CH_4 + CO_2 \\ &4H_2 + CO_2 &&\rightarrow CH_4 + 2H_2O \end{aligned}$$

for protein (glycine),

$$\begin{aligned} &4CH_2NH_2COOH + H_2O &&\rightarrow 3CH_3COOH + 4NH_3 + 2CO_2 \\ &CH_3COO^- + H^+ &&\rightarrow CH_4 + CO_2 \\ &4H_2 + CO_2 &&\rightarrow CH_4 + 2H_2O \\ &NH_3 + CO_2 + H_2O &&\rightarrow NH_4^+ + HCO_3^- \end{aligned}$$

The above reactions show that in the anaerobic degradation, one mole $C_6H_{12}O_6$ produces 3 moles CH_4 and 3 moles CO_2, and from 4 moles glycine 3 moles CH_4, 5 moles CO_2 and 4 moles NH_3 are produced. The production of ammonia increases the amount of bicarbonate alkalinity in the solution, therefore the buffer capacity of the system.

When treating a wastewater of pH lower than 5.8 (like RLP wastewater), the anaerobic system can be affected adversely because particularly the methanogenic step is quite susceptible for acidic pH. Especially in poorly mixed UASB system the low influent pH may affect the bottom part of the sludge bed. As the buffer capacity is far from sufficient at the influent pH lower than 6.0, the pH may fall to much lower pH levels due to rapid VFA formation from sugars, and then acetogenic and methanogenic bacteria become progressively inhibited. In case of poorly buffered wastewater the buffer capacity of the sludge becomes of crucial importance, i.e. its accumulated alkalinity, especially in the form $CaCO_3$. $CaCO_3$ reacts with VFA, e.g. CH_3COOH according to:

$$\underset{\text{(insoluble)}}{2CaCO_3} + \underset{\text{(soluble)}}{2CH_3COOH} \rightarrow Ca(HCO_3)_2 + Ca(CH_3COO)_2$$

The hydraulic conditions in a UASB-reactor affect significantly the buffer capacity of the system. Plug flow conditions may prevail in the digestion zone (sludge bed and liquid phase) during periods with very low gas production. Liquid back mixing then is very low (Hulshoff Pol, 1989). On the other hand completely mixed conditions may prevail in the digestion zone during periods with heavy gas production. In a normal functioning completely mixed anaerobic digestion system generally the bicarbonate alkalinity consumption is virtually zero or even negative (i.e. "net production") so that any alkalinity has not to be supplied to maintain the pH above 6.2. But this is not the case for poorly mixed system.

And since the effect of a low pH on the anaerobic treatment processes is quite detrimental, as was clearly demonstrated in the present investigations,, special measures have to be taken in poorly mixed UASB-reactors.

From the above discussion it therefore should be clear that the pH tolerance of a UASB treatment system depends on: 1) the amount of buffer alkalinity present in the sludge, and 2) the extent of liquid back mixing in the system (paragraph 4.6).

In case liquid back mixing is low (or at a low effluent recycle factor), the acid zone (with free VFA) irrevocably will move up from the lower part of the sludge bed and the free VFA present in the liquid will react with $CaCO_3$ present in the sludge to form $Ca(Ac)_2$ and $Ca(HCO_3)_2$. The $Ca(Ac)_2$ produced will be converted in upper layers into soluble $Ca(HCO_3)_2$ which will be removed from the system with the effluent. In absence of liquid back mixing conditions the rate at which the low pH zone will move upward through the bed can be calculated, consequently also the amount of sludge remaining in "active condition" based on the amount of sludge supplied to the reactor, the amount of $CaCO_3$ present in the sludge, the concentration of VFA in the wastewater from origin plus the amount formed as a result of acidification, and the wastewater flowrate to the reactor, according to the equation:

$$[M^{2+}] = t \times Q \times [C_n]$$

where, $[M^{2+}]$ - total amount of Ca^{2+} accumulated in the sludge
t - time of operation, day
Q - upflow of wastewater, m^3/d
$[C_n]$ - amount of VFA reacting with Ca^{2+}.

The amount of sludge required to degrade the imposed daily load can be estimated on the basis of the original sludge activity.

In case there is back mixing the $Ca(HCO_3)_2$ present in the "treated" solution will react with the HAc present in the feed and depending on the extent of back mixing, the concentration of $Ca(HCO_3)_2$ present in the back mixed solution (which depends on the treatment efficiency) and the free VFA concentration in the influent, the pH in the lower part may remain in the optimal pH for methanogenesis.

It will be also clear that, in case of a insufficient back mixing, especially the sludge in the lower part of the sludge bed will have been exposed to the low pH for quite a long period of time, while this is not the case for the sludge in the upper part of the bed, provided the sludge bed remained unmixed.

In the present experiment, with 500 mg $CaCO_3$/kg of granular sludge accumulated alkalinity in the sludge the system could maintain a very high treatment efficiency for 6-8 days. However, the measured pH profiles clearly reveal that pH dropped rapidly in the lower part of the sludge bed, and from the before going it is clear that this situation will lead to a definite upset, because the acid zone irrevocably will move upward. In the experiments the extent of back mixing was too low for the relatively very acid influent. One should consider that at an influent pH = 4.55, 50% of the C_2 present is present as free acetic acid.

Very interesting for practice is the observation that the system is able to recover completely from an acid pH-shock within a relatively short period of time, i.e. within three days. The sludge, atleast the sludge present in the upper part of the sludge bed, apparently did not deteriorate. On the other hand it also is clear that the sludge completely lost its buffer capacity. A new exposure to a too low influent pH therefore rapidly will result in a new upset, which might be more serious, as demonstrated in an experiments. It indicates that a prolonged exposure of the sludge to a low pH. i.e. as was the case for the sludge in the lower part of the bed, may lead to more serious deterioration in the activity.

It is clear from the results obtained that contrary to some reports in literature (e.g. Young and McCarty, 1967; Samson *at al,* 1991) which mentioned that a pH of 6.2 is the lowest permissible influent pH, in fact distinctly lower influent pH can be accommodated provided the extent of back mixing remains sufficiently. Otherwise effluent recycling should be applied.

4.5.5 CONCLUSIONS

From the experiments conducted concerning the effect of low RLP influent pH to the stability of an UASB system seeded with granular sludge, and particularly also the recovery of system after a pH-upset, the following conclusions can be drawn:

- The period of time passing before the detrimental effect of low pH to UASB system depends on the buffer capacity of the sludge (alkalinity present in the sludge), and the pH and the VFA-content of the influent, and the amount of non acidified organic matter present, the imposed loading rate applied (treatment efficiency) and the extent of back mixing prevailing in the system and/or effluent recycle factor applied.

- In case the acidic zone will move upward through the sludge bed due to insufficient back mixing, the sludge will loose its buffer capacity completely.

- Sludge can recover from an acidic pH-upset, although the period of time required for and possibly also the extent of recovery depends strongly on:

  + Wastewater characteristics,
  + Alkalinity of the sludge,
  + Load.

4.6 THE EFFECT OF EFFLUENT RECIRCULATION ON UASB PERFORMANCE

4.6.1 INTRODUCTION

In the rubber latex processing factories in South Vietnam, acetic or formic acid are normally used for coagulating rubber latex to produce block rubber (Chapter 2). After the coagulation process most of the acid used in the process is discharged into wastewater.

Two problems caused by the low pH of wastewater manifested clearly during the operation of the anaerobic treatment systems, i.e.:

1. Combined with the anaerobic acidification of organic matter, i.e. sugar, proteins and lipids present in the wastewater, the free acids in the wastewater (acetic/formic acid) lead to a drop of the pH in the reactor, which then seriously inhibits acetogenic and methanogenic bacteria. After degradation of the free VFA, the pH of the wastewater will increase (Hulshoff Pol, 1989). However during the initial stages of the anaerobic digestion process of RLP wastewater may be hampered due to a lack of buffer capacity, because then the pH may fall to values below 5.8. Therefore, as explained in paragraph 4.5, a certain amount of alkalinity should be supplied in some way or an other to the influent to maintain the pH in the reactor at values exceeding 6.2. However at full-scale plant operation the supply of alkalinity would incur significant operational cost, and therefore a better option is to apply effluent recycle in order to meet the influent alkalinity requirements. Samson *et al.* (1991) found that to treat a carbohydrate waste, the minimum influent alkalinity requirement is about 1,2 mg as $CaCO_3$/mg influent COD, is based on a VFA production of 2.4 meq. per 100 mg COD, which looks quite overestimated. However the influent alkalinity requirements can be reduced significantly, frequently even completely, by imposing effluent recycling.
2. From theoretical consideration it can be explained that in the anaerobic degradation of formate the pH of the solution can increase to values exceeding 9.4, consequently to values which inhibit acetogenic and methanogenic bacteria. Results obtained in laboratory experiments indeed confirmed this theory. Those problems so far have not been sufficiently reported in literature. This lack of information may be attributed to reasons like a) difficulties in reliable analyses of formic acid using an FID equipped gas chromatograph, because for the VFA analyses by GLC the samples generally are prepared using formic acid, while wet chemical methods to determine formic acid in a mixture of volatile fatty acid are quite laborious (Grobicki and Stucky, 1989); 2) formate as intermediate is not very important in the anaerobic digestion.

Since the pH problems generally imply a cost factor in the operation of the anaerobic system, the present investigations were focused on using effluent recirculation to improve the performance and also the economy of UASB-reactors treating RLP wastewate containing either formic acid or acetic acid.

4.6.2 MATERIALS AND METHODS

Experimental conditions

The experiments were carried out in The Netherlands and in (South) Vietnam. In The Netherlands synthetic wastewater was used and the reactor was placed in a temperature controlled room (30+2°C). The experiments in South Vietnam were conducted using real wastewater and the reactor was exposed there to ambient conditions, i.e. temperatures in the range of 26-34°C.

Experimental reactor

In South Vietnam a 8.55 L UASB-reactor (see Fig. 4.2.1) was used and in The Netherlands a 2.25 L UASB-reactor (see Fig. 4.6.1). A peristatic pump (Watson Marlow) was used to pump wastewater into the reactor. The design of the GSS was the same in both reactor. In both cases a sodium hydroxide solution was used to adjust the pressure and to remove carbon dioxide.

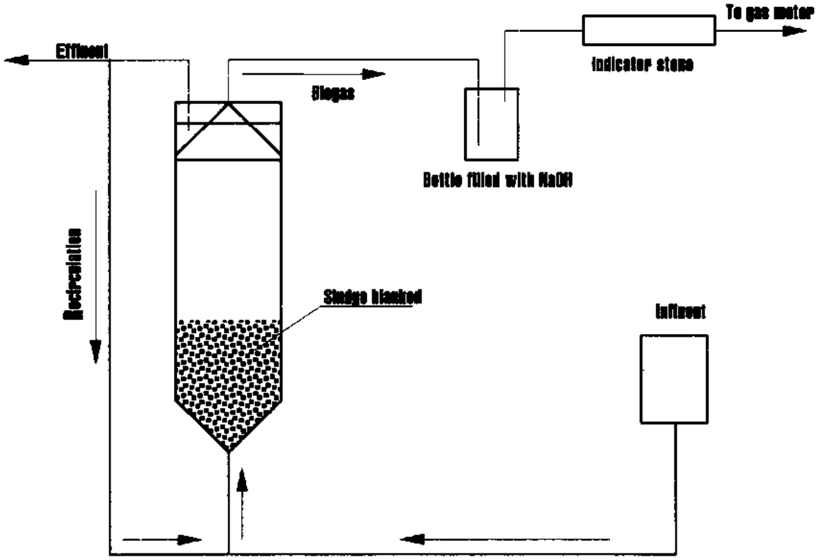


Fig. 4.6.1 Schematic diagram of the 2.25 L UASB-reactor.

Seed sludge

The experiment in The Netherlands

In the experiments 1.65 L of digested pig manure sludge (DPMS) was used as seed material, VSS content of 98.6 g/L and N-NH^{+}_{4} content of 6.46 g/L.

The experiment in South Vietnam

Stored granular sludge obtained from the starch factory Latenstein was used as seed sludge. The characteristics of the GS were presented in paragraph 3.3.

Wastewater, Nutrient and Trace Elements

The experiment in The Netherlands

A synthetic wastewater composed of formic acid (10 g/L) and glucose (1 g/L) was used as influent. The influent was stored in a refrigerator.

The experiment in South Vietnam

The real wastewater was used in this experiment. The wastewater was prepared from serum obtained in coagulation of rubber latex with acetic acid and tap water as mentioned in paragraph 4.4.

Nutrient and trace elements were used in both experiment according de Zeeuw (1984) and Hulshoff Pol (1989).

Analyses

In order to assess the performance of the system the pH, the influent and effluent COD concentration, the formic acid and VFA concentration (in The Netherlands) and gas production were determined. The analysis methods are presented in Chapter 3, paragraph 3.2.

Experimental procedure

The experiment in The Netherlands

The influent flowrate was kept constant during the whole experimental period. In order to buffer out the imposed extremely low pH values, an effluent recirculation factor of 4 was applied. The experiment was started using a influent pH of 4.2 and later pH values imposed were (see Fig. 4.6.3):

- Day 0 - 33: pH = 4.2;
- Day 34 - 64: pH = 3.6;
- Day 65 - 71: pH = 3.2;
- Day 72 - 74: pH = 3.9;
- Day 75 - 77: pH = 4.8.

The influent pH values were lowered when the effluent pH exceeded 8.5 and raised when the effluent pH dropped below 6.2.

The experiment in South Vietnam

Similarly to the experiment carried out in The Netherlands, constant influent flowrate was applied and the effluent recirculation of factor 4.

4.6.3 RESULTS

The experiment carried out in The Netherlands

The experiment carried out in The Netherlands lasted for 77 days and the operational data are summarized in the Table 4.6.1.

Table 4.6.1 The operational data in the experiment carried out in The Netherlands in 1991

Parameter	Duration				
	00-33	33-64	65-71	71-74	75-77
C_1	7.1-10.1	6.7-10.2	9.4-9.5	9.4	9.4
C_1-COD	2.5-3.7	2.3-3.5	3.2-3.3	3.3	3.3
$(C_1 + C_6)$-COD	3.4-4.7	3.3-4.5	4.2-4.3	4.2	4.2
COD_n	3.8-4.0	3.8-4.8	4.6-4.8	4.4	4.6
pH	4.0-4.3	3.5-3.7	3.2	3.9	4.5-4.8

All parameters are expressed in g/L, except pH.

C_1	*- the formic acid concentration of the stock solution;*
C_1-COD	*- the influent C_1-COD concentration of the mixture, i.e. effluent and supplied stock solution;*
(C_1+C_6)-COD	*- the influent COD concentration of formate and glucose*
COD_n	*- the influent COD concentration examined by micro method.*

During the whole experimental period it was attempted to maintain the flowrate of the stock solution constant at about 1 L/d, but due to fluctuations of the stock solution pump, the influent flowrate fluctuated from 1.10 L/d to 1.37 L/d, corresponding to a hydraulic retention time of 49.1h to 39.4h. And the total influent flowrate, i.e. stock solution flowrate plus the effluent recirculation flowrate, was in the range 2.2-7.2 L/d, corresponding to a hydraulic retention time of 24.5-7.5 hours.

During the period day 1-33 little if any formic acid was found in the effluent (see Fig. 4.6.2). Apparently sufficient activity was present in the seed sludge to convert formate.

However, during the first days of the experiment the ability of the sludge to convert glucose into fatty acids, apparently was minimal, because the differences between the values of COD-VFA (C_2, C_3 and C_4) and the values for centrifuged COD_t show that the soluble (centrifuged) COD concentration exceeds 2,000 mg/L (see Fig. 4.6.2). While almost no fatty acids are present in the effluent.

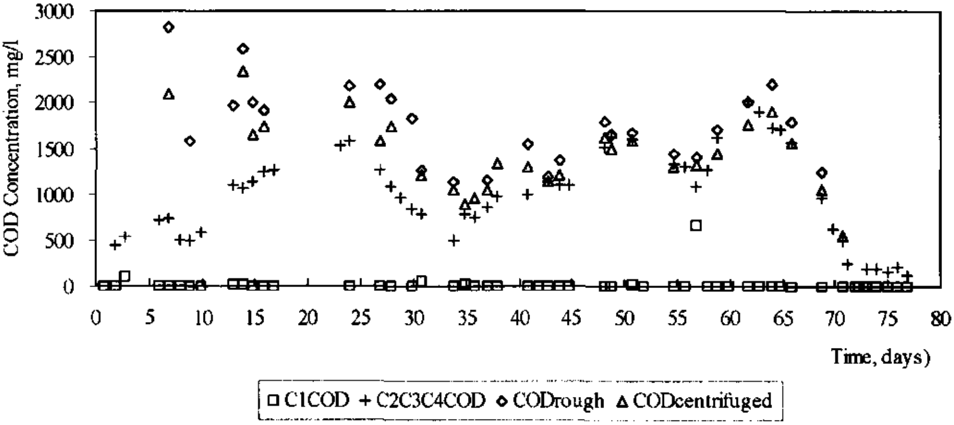


Fig. 4.6.2 The variation of the effluent COD concentration during the experiment carried out in The Netherlands.

It should be mentioned that due to the high concentration of NH_4^+ in the seed sludge, the initial NH_4^+-concentration in the effluent was rather high, i.e. up to 5.47 g NH_4^+-N/L, but within one week it dropped appr. 500 mg/L (see Fig. 4.6.3) as result of dilution with the lower ammonia concentration of influent. The high ammonia concentration during the first days affected the sludge activity (paragraph 3.3 and 4.3).

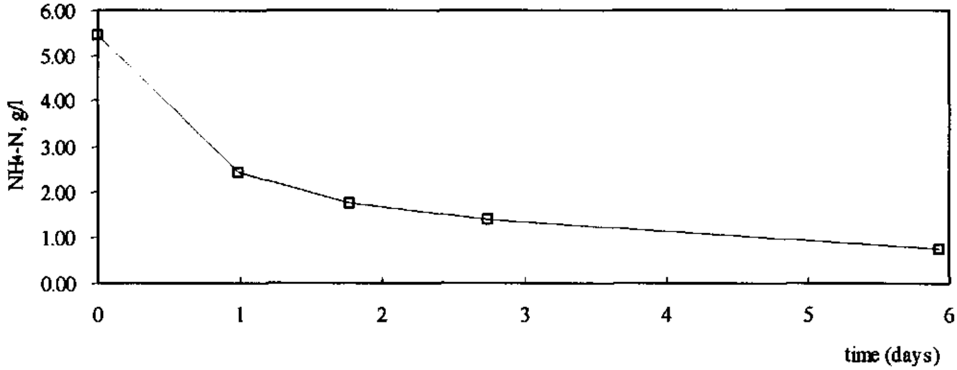


Fig. 4.6.3 A decrease of the ammonia concentration during the period of operation.

At day 7, the sludge bed in the reactor had decreased from 1,50 L (start-up) to 1,25 L, indicating ±17% sludge wash-out.

The ability of the sludge to convert glucose in fatty acids, gradually improved, as a result of growth-in of fermentative and hydrogenotrofic bacteria. As a result the VFA concentration in the effluent gradually increased, contrary to the effluent COD_{tt} concentration, because it even started to decrease. This can be attributed to a decrease in the wash out of fine matter present in seed sludge. As a result of growth-in of hydrogenotrofic bacteria, the hydrogen concentration decreased from ±1,000 ppm at the first day to almost zero at day 10.

At day 24, the COD-VFA concentration in the effluent amounted to ±1,550 mg/L, which in fact is more than expected on the basic of the glucose conversion (1 $gC_6H_{12}O_6/L$ = 970 mgCOD/L). Consequently also some conversion of formic acid into acetate might have occurred.

Following day 24, the COD-VFA concentration in the effluent gradually decreased to 505 mg/L at day 34, which can be explained by the growth-in of acetotrofic methanogenic bacteria. At that time, the biogas consisted of 95% CH_4 and 5% CO_2. (see Fig. 4.6.4)

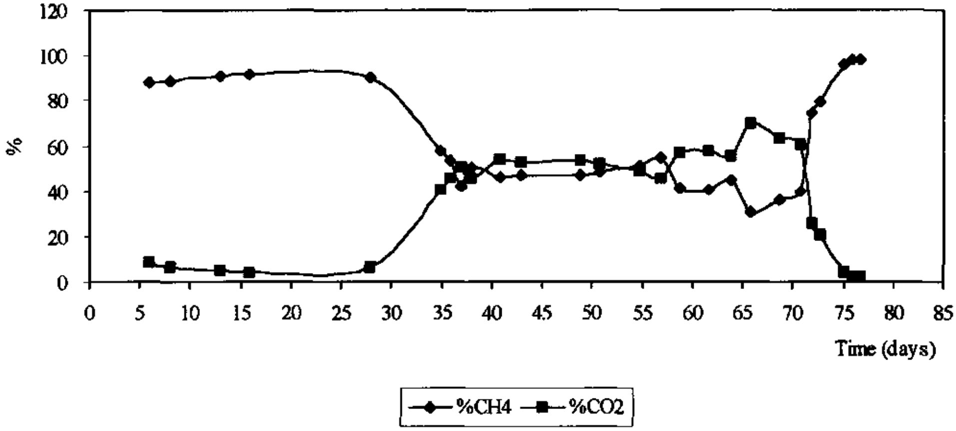


Fig. 4.6.4 Gas composition.

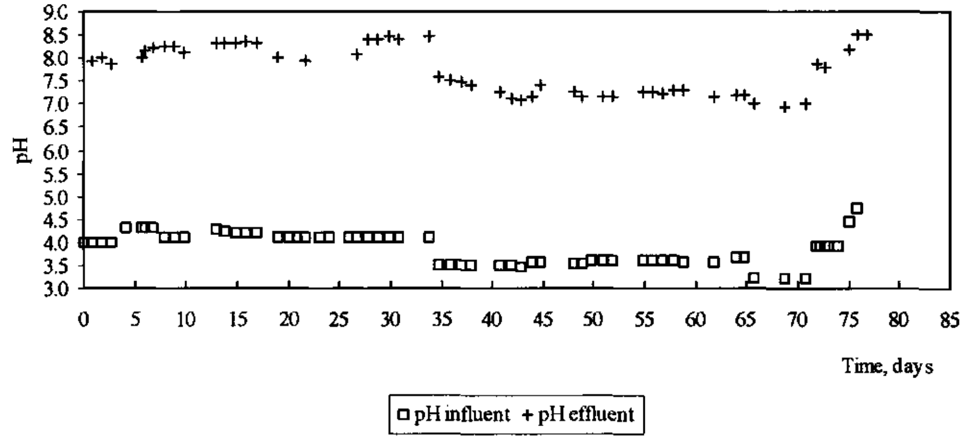


Fig. 4.6.5 The influent and effluent pH during experiment carried out in The Netherlands.

Along with the decreasing concentration of VFA, the effluent pH slowly increased to a value of 8.5 (see Fig. 4.6.5), which in fact is too high for methanogens. Considering this, it was decided at day 29 to lower the influent pH to 3.6, which in fact also means that only about 60% of the amount of NaOH was needed compared to the proceeding situation.

However, this lowering of the influent pH changed the situation dramatically, because the COD-VFA effluent concentration increased slowly to ± 1,500 mg/L at day 42 and up to 1,618 mg/L at day 49, while at the same time the gas production increased. Latter can be attributed to the fact that the gas consisted for only 45-50% of CH_4 and 50-55% of CO_2 (see Fig. 4.6.4), while in the proceeding period the gas contained 90% CH_4 and less than 10% CO_2. Following day 49 the effluent VFA-COD tended to decrease.

At day 57, due to a failure in the effluent recirculation the sludge in the reactor had to accommodate an pH of 3.6. The system responded immediately and for the first time (although very temporary) formic acid was measured in the effluent and also the effluent VFA concentration increased. Methanogenesis became seriously disturbed, leading to the presence of more than 20,000 ppm of hydrogen in the biogas.

After the recirculation was resumed, the formic acid degradation immediately recovered, i.e. no or almost no formic acid could be detected anymore in the effluent. However, methanogenesis still did not proceed satisfactory. The VFA concentration continued increasing further and at day 62, still more than 10,000 ppm of hydrogen was found in the biogas. At day 62, the effluent COD-VFA concentration amounted to about 2000 mg/L. It therefore can be concluded that an influent pH of 3.6 the conditions for methanogenesis are seriously disturbed

At day 65, taken into account the overcapacity of buffer in the recirculated system, it was decided to lower the influent pH even to 3.2. Such low pH is acceptable, regarding the buffer capacity. There still is enough bicarbonate in the recirculated effluent to buffer the influent in order to obtain a proper pH and reactor pH.

After lowering the pH, a quick decrease of fatty acids in the effluent occurred. Apparently under these conditions a more optimal reaction pH prevails in the system. The biogas composition changed to ±30% CH_4 and ±70% CO_2 (see Fig. 4.6.4), whereas at the same time the total amount of produced methane increased.

While having achieved now an efficient removal of COD, it was decided at day 60 to increase the effluent pH step by step (see Fig. 4.6.5), up to situation almost no carbon dioxide can be found in the biogas and the reactor pH reaches a value of 8.6. Despite this high effluent pH, the effluent VFA concentration remained very low.

The experiment carried out in South Vietnam

A effluent recirculation factor ranging from 3.6 to 5.5 was also applied for the experiment carried out in South Vietnam, mainly due to fluctuations of treatment efficiency and pump. During the whole experiment, except the first three days, the raw and mixed influent flowrate was kept in the range of 10-16 L/d and 60-62 L/d respectively, corresponding to a hydraulic retention time in the range of 20.5-12.8h and 3.4-3.3h, respectively. The imposed COD loading ranged from 5.5 to 22.5 kg COD/m^3.d. The pH and COD concentration of raw wastewater were 4.4-4.9 and 3,300-9,600 mg/L, respectively. After mixing the effluent and the raw wastewater the pH and COD concentration of influent mixture were about 6.2-6.9 and 980-3,800 mg/L, respectively.

The experimental results obtained reveal that the treatment efficiency remained rather low over whole experiment period, particularly during the first day at a low organic load. The effluent COD was often higher than 1000 mg/L (see Fig. 4.6.6) except during period 9-16 when the imposed organic load was lower than 5 kg COD/m^3.d. The poor performance can be attributed to the low activity of seed sludge which had been exposed for a long period of time, i.e. 3-4 months, to tropical temperatures under unfed conditions, and to the imposed relatively high loading rate. Nevertheless, the gas production (see Fig. 4.6.8) slowly increased from 1.2 L/d during the first few days to 20-27 L/d at day 14. A peak value in the gas production of 60 L/d was reached at day 48. However from day 65 onwards the gas production decreased from 27 L/d to 7.4 L/d at day 68. This decline very likely is caused by the relatively very high loading rate applied, i.e. 24-30 kg COD/m^3.d. The results of the measured pH in the raw wastewater, the effluent-wastewater mixture and the effluent (see Fig. 4.6.7) reveal that high pH values up to pH=8 merely prevailed in the system when the pH of the raw wastewater was around pH=6.5 (period 40-50).

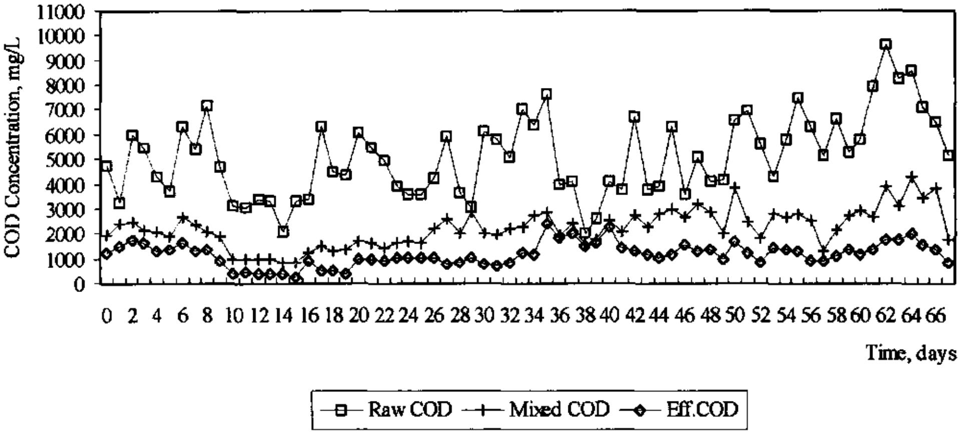


Fig. 4.6.6 The COD reduction in the experiment carried out in South Vietnam.

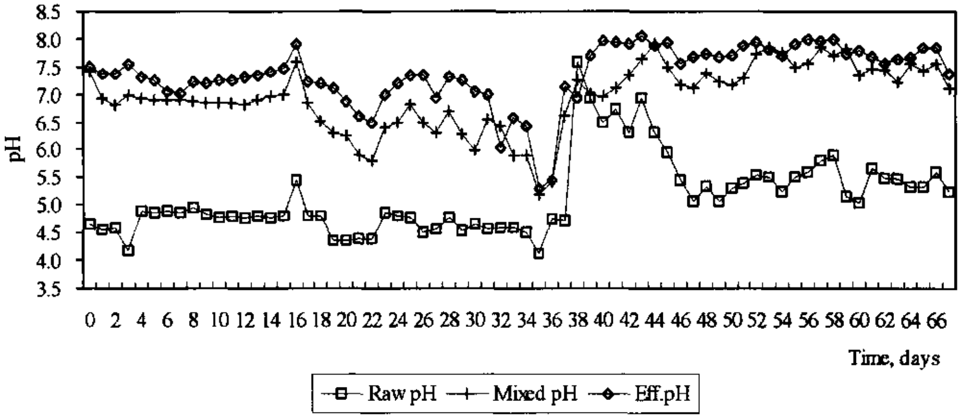


Fig. 4.6.7 The course of the pH values in the experiment carried out in South Vietnam.

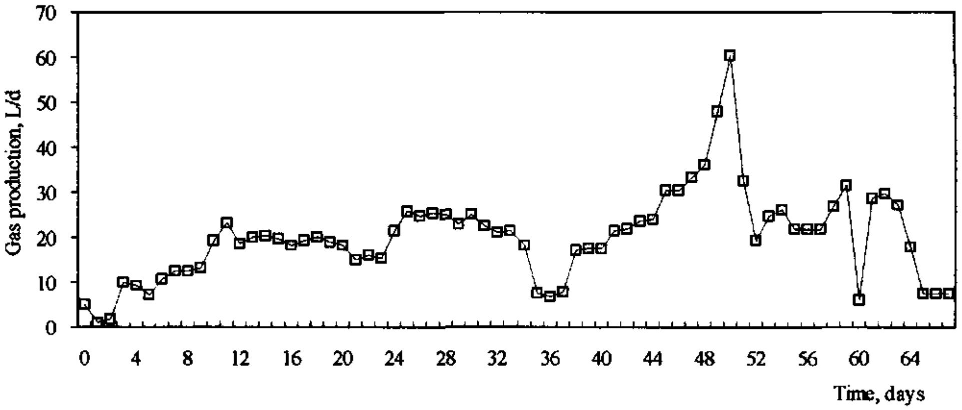


Fig. 4.6.8 Gas production.

4.6.4 DISCUSSION

It is well known that the pH is one of the most important factors that influence the rate of biochemical reactions, especially in anaerobic processes. In many industrial wastewaters, pH problems may be encountered. In the case of RLP wastewater treatment, especially for formic acid containing wastewater, the system can become seriously affected by both by low and by high pH values. In the case of formic acid RLP wastewater the following chemical and biochemical reactions should be considered:

1. The dissociation of formic acid

$$HCOOH \rightarrow HCOO^- + H^+ \qquad (1)$$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = 1.77 \times 10^{-4} \qquad \text{at } 25^{\circ}\text{C} \qquad (2)$$

2. The anaerobic conversion of formic acid

The following reactions can be involved:

$$4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O \qquad (3)$$

a. Non neutralized formic acid:

$$HCOO^- + H^+ + 3H_2 \rightarrow CH_4 + 2H_2O \qquad (4)$$

according to Grobicki and Stucky (1989) this reaction provides more energy than methanogenesis from H_2/CO_2 (reaction 6) or cleavage of formate into H^2/CO_2 (reaction 5).

b. Neutralized formic acid

$$HCOO^- + H_2O \rightarrow HCO_3^- + H_2 \qquad (5)$$

and also,

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad (6)$$

The protons required for the conversion of the neutralized formic acid ($HCOO^-$) are obtained from the dissociation of H_2O. As formic acid (presented by HCOOH in above equation) is converted into methane and carbon dioxide (3), the carbon dioxide formed needs to neutralize the cations from the original formate present in the influent, which can be accomplished via the dissociation of carbonic acid.

3. Dissociation of carbonic acid

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (7)$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.45 \times 10^{-7} \quad \text{at } 25^\circ C \qquad (8)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \qquad (9)$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad \text{at } 25^\circ C \qquad (10)$$

From the equations (7) and (8) it is obvious that the concentration of the different forms (H_2CO_3, HCO_3^-, CO_3^{2-}), which are part of one system, merely depends on the pH. A change in pH will shift the relationships.

Based on the above reactions and equilibrium the discussion of the pH problems in the anaerobic degradation of the formic acid containing wastewater can be explained as below.

It can be seen from equilibrium (1) that at any pH value, the dissociation ratio of formic acid ($HCOO^-$ /HCOOH) can be calculated based on the dissociation constant (equation 2).

During the whole experimental period, the influent formic acid concentration was kept constant at 10 g/L which is equivalent 0.22 moles HCOOH/L, consequently

$$[HCOOH] + [HCOO^-] = 0.22 \text{ moles/L}, \quad \text{or } [HCOOH] = 0.22 - [HCOO^-] \text{ and}$$

substituting this in (equation 2) gives:

$$\frac{[H^+][HCOO^-]}{[0.22 - [HCOO^-]} = \frac{[10^{-pH}][HCOO^-]}{[0.22 - [HCOO^-]} = 1.77 \times 10^{-4},$$

From the dissociation of formic acid (eq.1) and (eq.2) it is clear that at the influent $pH_{inf} = 3.75$:

$$pH_{inf} = 3.75 \quad \rightarrow \quad [HCOO^-]_{inf} = [HCOOH]_{inf} \qquad (16)$$

and at high influent pH:

$$pH_{inf} > 3.75 \quad \rightarrow \quad [HCOO^-]_{inf} > [HCOOH]_{inf} \qquad (17)$$

It therefore will be clear that for a safe reactor operation, a pH<3.75 and exceeding the minimum influent pH value is recommended. The curves presented in Fig. 4.6.10 show the minimum and maximum pH in relation to recirculation factor. It should be noticed that the curve expresses the minimum acceptable influent pH depending on the applied recirculation factor (0-10) and the straight line expresses the maximum acceptable influent pH value, which depends on the recirculation factor. The shadow area can be seen as the safe influent pH region. From Fig. 4.6.10 it also can be concluded that at a recirculation factor 1, the minimum influent pH is the same as the maximum. So the minimum recirculation factor amounts to one.

In the experiments carried out in South Vietnam with RLP acetic acid containing wastewater, any pH problems didn't happen. This can be explained on the basis that acetate instead of formate is present in the wastewater. It is obvious that in the hydrolysis and acidogenic processes, as well acetogenic processes, sugars and proteins are converted mainly via acetic acid. The conversion of acetate into methane and carbon dioxide follows from the reactions shown below:

1. Non neutralized acetic acid

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (18)$$

and CO_2 reacts with water,

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

2. Neutralized acetic acid

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^- \qquad (19)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (20)$$

$$CO_2 + OH^- \rightarrow HCO_3^-$$

It is obvious that the system will become slightly alkaline. From these experimental results it also can be seen clearly that at recirculation factor 4-6 the influent pH increases to values exceeding pH = 6.2, i.e. quite favourable for the anaerobic-process, even when the treatment efficiency would remain low.

4.7 CONCLUSIONS

From the studies presented above, the following conclusion can be drawn:

- The UASB process can be quite profitably applied to treat RLP wastewater
- A COD loading rate up to 15-20 kg COD/m^3.d (or higher when more amount of seed sludge supplied to the reactor compared to experimental conditions) can be used for design.
- The HRT can be in the range of 2-6h.
- The sludge can contain sufficient buffer capacity to accommodate low influent pH-values at least temporarily in poorly mixed systems.
- The recovery of sludge following the low pH upset needs about 2-3 days.
- In treating a wastewater with formic acid as main pollutant acidic influent pH-values, combined with effluent recycle, have to be applied in order to maintain stable conditions in the reactor and to achieve a high treatment efficiencies.
- The pH problems can be solved by the effluent recirculation and the influent pH control.

Chapter 5

Post-Treatment Process, Waterhyacinth and Algae Treatment of Rubber Latex Processing Wastewater

5.1 INTRODUCTION

In the recent years, rubber latex processing (RLP) industry developed rapidly in Vietnam. Concentrated effluents with COD = 1,811-9,962 mg/L, BOD = 1,720-8,780 mg/L, pH = 4.98-6.12, VFA = 860-5,600 mg/L from rubber latex processing (coagulation, milling and cutting) has been discharged directly to receiving water thus causing heavy environmental pollution (Chapter 2).

The UASB process is undoubtly highly feasiblely to treat the RLP wastewates. However the experimental data obtained in the lab-scale experiments presented in Chapter 4 show that the COD concentrations of the UASB effluent always exceeded 150 mg/L, which is higher than the Vietnamese national effluent standards. Therefore post-treatment is essential for polishing the UASB effluent before it is discharged into waterway.

At present, aerobic systems and stabilization ponds, with or without aquatic plants (van Buuren *et all.*, 1993; Catunda *et all.*, 1994), have been suggested to polish the UASB effluent. The aquatic plant (waterhyacinth and algae) pond system was chosen to investigate its feasibility for polishing the UASB effluent treating the RLP wastewater in South Vietnam, because it offers some important advantages compared to conventional treatment processes:

- Low construction and maintenance cost,
- Very simple operation,
- Low energy requirement (if any at all),
- Low production rate of sludge,
- Use of local materials,
- Low requirements in terms of nutrients and chemicals for neutralization,
- High shock-loading capacity due to a huge volume,
- Aerobic condition in the effluent as a result of photosynthesis by algae..

In the world, specially in tropical countries such as Brazil, Thailand, Malaysia, China, Vietnam, and also in United State aquatic plants pond systems have been applied widely to treat several types of wastewater: vegetable oil wastewater (Viet, 1987), piggery effluent (Finlayson *et al*, 1987), palm oil mill effluent (Moi & Chong, 1988), petroleum wastewater (Triet *et al.*, 1989), heavy metals containing wastewater (Jain *et al*, 1988, 1989), domestic sewage (Kumar and Garde, 1989; Tchobanoglous and Burton, 1991). The pond systems are also used to treat the effluent from rubber latex processing factories, especially in Malaysia. However they need a long time to complete degradation of organic compounds, i.e. 20 days for anaerobic digestion and 40 days for aerobic digestion, to give an effluent that meets specifications for discharge into a waterway (Webster and Baulkwill, 1989).

There are some references demonstrating the feasibility of waterhyacinth (WH), *Eichhornia crassipes* (Mart) Solms, and algae (ALG), *Chlorella*, for industrial wastewater treatment. The applied loading rates were up to 220 kg/ha.d in domestic wastewater (Kumar & Garde, 1989) and 1,256 kg/ha.d in vegetable oil wastewater treatment (Viet, 1987). According to Tchobanoglous and Burton (1991) an organic loading rate of 45-90 kg BOD_5/ha.d at a detention time of 10-36 days can be applied for waterhyacinth treatment system and with the effluent BOD_5 concentrations in the range of 130-180 mg/L the effluent BOD_5 concentration less than 20 mg/L and the concentration of SS less than 20 mg/L can be expected.

The main drawbacks restricting significantly the application of aquatic plant pond systems are their large area requirements, i.e. in Malaysia the land area requirement for each RLP factory to treat approximately 2,000 m^3/d is about 8-10 ha in the series of 3-6 ponds, their low tolerance for high concentration of pollutants and the high evapotranspiration rate of waterhyacinth, especially when the effluent is reused for irrigation, i.e. up to 70-120 m^3/ha.d (Viet, 1987) which depends greatly on the ambient temperature, humidity, a density and metabolism rate of waterhyacinth. Therefore some system configurations have been studied and suggested in order to overcome these weak points. Among them is a combined system of Upflow Anaerobic Sludge Blanket (UASB) as primary treatment step and an aquatic plants pond system as post-treatment step, which could represent an attractive and feasible concept (van Buuren *et al.*, 1993). The UASB-process in this concept is responsible for the reduction of the organic matter (COD) concentration and the aquatic plant pond system completes breaking down organic compounds and takes care for the supply of oxygen to the water by photosynthesis of algae. The aquatic plants pond system produces an additional breakdown of organic compounds, brings about some N and P removal and most import gives room for removal of pathogenic organisms. After these processes the treated wastewater is expected to meet the effluent standards for discharge to the environment.

In this investigation, lab-scale experiments were carried out to assess the ability of waterhyacinth (WH) and algae (ALG) for 1) treating raw rubber latex processing (RLP) wastewater and 2) act as a post-treatment process for UASB effluent. Another important aspect of these experiments is to establish the design criteria for aquatic plant ponds treating RLP wastewater.

5.2 MATERIALS AND METHOD

Experimental conditions

The experiments were carried out with lab-scale reactors at ambient conditions, in the laboratory of the Department of Environmental Engineering, Ho Chi Minh University of Technology during the period 1991-1992. The experimental temperature applied in these experiments ranged from 26-34°C. All reactors were exposed directly to sunlight.

Experimental reactors

Batch reactor. In order to investigate the tolerance of WH and ALG to RLP wasterwater, 6 plastic containers marked from R_1 to R_6 each 20 L in total volume and 15 L in wet volume, with a depth of 15 cm and surface area of 0.063 m^2 were used to simulate an experimental reactor. WH was planted with a density of 15 kg/m^2 and ALG was cultured at a concentration of 100-120 mg/L in reactor R_1 to R_5 and reactor R_6 was the control, e.g. without waterhyacinth or algae. The amount of water evapotranspiration in each of the reactors was recorded during the experimental period by measuring the decrease in volume and then next tap water was added to keep the same volume in the reactors before sampling for analysis.

Continuous flow reactor. Continuous flow reactors made of glass with WxLxH = 0.4x1.2x0.6 m were used to simulate aquatic ponds for determining the treatability and admissible rate of loading of WH and ALG in RLP wastewater. The total surface area and volume were 0.48 m^2 and 288 L, respectively, with a wet volume between 144-244 L depending on the depth of water (0.3-0.5 m). Baffles were installed at a distance of 10 cm from the beginning and the end of the tank to skim floating matter (rubber). Wastewater was pumped quantitatively into the ponds by Heidolph pumps and the overflow rate of effluent was measured daily using plastic containers. In order that the system only receives sunlight through the top surface the side windows of the aquarium were covered with black paper.

Also smaller experimental glass aquariums (WxLxH = 0.4x0.6x0.4 m) were used and wastewater was fed to them from 20 L plastic containers by gravity. This experimental configuration at that time was very suitable for Vietnamese conditions because there was no electricity to drive pumps.

Aquatic plants

Waterhyacinth (*Eichhornia crassipes)* and algae (*Chlorella*) were chosen to investigate the treatability of RLP wastewater because of the following reasons (Viet, 1987):

- Both grow abundantly in the South of Vietnam,
- They are highly tolerant to many pollutants as compared to other types of aquatic plants, like duck weed, waterlily, etc.,
- They are easy to culture and to control and at low cost,
- Algae produce oxygen by photosynthesis, which is enhancement in a post-treatment system.

WH was taken from city canals and immediately put into the experimental reactors at a density of 15 kg/m^2 (wet weight). WH was not harvested during experimental period, but only removed after they had died and then they were replaced by new WH plants to maintain the same WH density.

ALG were cultured in the laboratory or taken from natural ponds and put into the reactors at an initial concentration of 100-120 mg/L. The identification of algae were carried out using Olympus microscope.

Wastewater

Two types of wasterwater were used in these experiments 1) wastewater prepared from serum (effluent of latex coagulation process) diluted with tap water, 2) the effluent from an UASB-reactor (lab-scale).

To simulate the practical conditions no nutrients and trace elements were added to the influent and the pH was kept at that of original wastewater, e.g. no chemicals were used to neutralize wastewater. The compositions of the wastewater used can be referenced in Chapter 4.

Analyses

The recorded parameters were COD, pH, DO, SS. Composed samples were taken during the period of examination and all these parameters were analyzed immediately after sampling according to standard methods (APHA, 1985, 1992). Visual observation was also brought about for quick assessment of the plant conditions.

The COD concentration was analyzed using the closed reflux, titrimetric method. The sample was oxidized with potassium dichromate 0.0167 M in sulfuric acid (18 M) under pressure at 150°C in closed borosilicate 25 ml vessel for 2 h. Oxidized samples were titrated with standard ferrous ammonium sulfate (FAS) titrant 0.1 M. Samples for soluble COD, especially in ALG experiment, were centrifuged at 5000 rpm for 5 min. in a centrifuge model HERAEUS labofuge A (Germany) or filtered using Whatman filter paper GF/A No 54 with pore size of 45 μm. The open reflux method was also used to analyze the samples when the COD concentration of the effluent dropped lower than 50 mg/L.

The pH was measured immediately after sampling using pH meter WPA 2100 or Hach 2000 and combined gel electrode. The titrimetric method with a 0.2 N sulfuric acid solution was used to determine alkalinity. pH measurement was used to indicate the equivalence points.

DO was measured using a WP 90 DO meter (England) or by titrimetric method according to Winkler method mentioned in the *Standard Methods* (APHA, 1985).

Due to a lack of the equipment the climate parameters, i.e. wind speed, sunlight intensity, rain and humidity, were not measured, however they were observed and qualitatively recorded.

Experimental procedure

Batch experiments. In the first feed, the serum was diluted to concentrations ranging from 72 mg/L to 434 mg/L (Table 5.1) and poured into the plastic containers. No nutrient and trace elements were supplied and no chemicals were used for neutralization. And then WH and ALG were cultured in the reactors at a density and concentration as mentioned above and they were immediately exposed to the ambient conditions. Evaporated water loss was compensated daily by adding tap water before sampling.

In the batch experiment eight feeds were applied (Table 5.1). In each feed the experiment was continued until a steady state situation had established and they then were continued until the aquatic plants could not stand anymore the wastewater. The COD concentration in each of the reactor was increased stepwise, i.e. up to 2,256-4,256 mg/L, following the concentrations mentioned in Table 5.1 after termination of the previous feed.

Continuous flow experiments. These experiments were carried out in two periods. During the first period the experiment was performed using RLP wastewater prepared by diluting serum with tap water and during the second period the lab-scale UASB effluent was used. Flowrates were adjusted to control the organic (COD) loading rate in the range of 4-20 g COD/m^2.d and the hydraulic retention time in the range of 6-10 days. The COD concentrations of the influent varied from 100-300 mg/L. In the case using RLP wastewater, after termination of each loading rate applied the supernatant layer was discharged completely and the new wastewater with a higher COD concentration was replaced. In the case of using the UASB effluent the supernatant layer was kept in the reactors. At each loading rate the experiment was carried out until a steady state situation had established and the COD loading rates were increased until the treatment efficiencies were low or aquatic plants could not stand.

Table 5.1 Batch experimental program with WH and ALG treatment of RLP wastewater

		Initial COD_I (mg/L)					
Feed	T	R1	R2	R3	R4	R5	Ctrl
01	5	72	151	234	319	434	nd
02	7	159	236	448	520	631	289
03	13	322	400	560	600	780	408
04	11	460	620	720	820	940	640
05	21	752	802	1084	1084	1267	580
06	20	1039	1234	1640	2033	2480	1536
07	24	1361	1851	2721	2912	nd	2281
08	nd	2256	2688	3360	4256	nd	2972

R_1, R_2, R_3, R_4, R_5, *Ctrl* - *reactor number 1, 2, 3, 4, 5 and control, respectively*
T - *experimental duration, days*
nd - *not determined*

5.3 RESULTS

Batch experiment. The batch experiments were used to investigate the tolerance of WH and ALG systems for RLP wastewater. In each of the reactors the COD concentration was increased gradually to assess the adaptability of WH and ALG to RLP wastewater. The batch experimental results obtained during the eight feeds are summarized in Table 5.2.

Waterhyacinth

In the first feed of the batch experiment the initial total COD concentrations (COD_i) in the 15 L reactors ranged from 72 mg/L to 434 mg/L (see Table 5.1). The COD concentration dropped rapidly to 8-42 mg/L within 2 days in R_1, 4 days in R_2 and 5 days in R_3, R_4, R_5 (see Fig. 5.1), corresponding to the COD removal efficiencies of 88.5%, 89.4%, 91.5%, 91.8% and 90.3% in R_1, R_2, R_3, R_4 and R_5, respectively. In all the reactors the pH increased slightly from 5.6-6.0 to 6.4-6.8 (see Fig. 5.2) and the SS concentrations were lower than 20 mg/L at an initial SS concentrations in the range of 65-90 mg/L. In the first day a rubber film developed at the surface of water and it disappeared in the next few days. No smell was detected and the water became very clear. During this period WH grew very well, viz. increasing in the rank R_3, R_4, R_1, R_2 and R_5. No explanation can be found for this rank. In R5 some leaves became dry and yellow because a rubber film coated the root of WH obstructing the transportation of water from the root to the leaves. The amount of water evaporated was of 3.1-9.7 $L/m^2.d$. The more healthy were the plants the higher the amount of water evaporated water.

In the second feed the COD_i was in the range 159-631 mg/L for R_1 to R_5. In this experiment a control reactor without WH or ALG was used as a reference, i.e. to compare treatment efficiencies. The COD removal efficiencies now ranged from 79.1% to 91.2%, but it does not range with the rank of COD_i (see Table 5.2), i.e. at day 7 the COD removal efficiency of R_3, R_4 and R_5 with an COD_i of 448, 520 and 631 mg/L were 87.9%, 91.2% and 88.4%, respectively (see Fig. 5.1). The SS concentration dropped from the initial concentration of 80-120 mg/L to 3-8 mg/L, which is very low and consequently it was not determined in the next batches. The amount of evaporated water amounted to 1.3-7.1 $L/m^2.d$.

Also in this feed, the COD_i of the control reactor was 289 mg/L which could be compared to the initial COD_i of the R_2. At day 6 the COD concentration of the control reactor (R_6) dropped to 30 mg/L corresponding to a COD removal efficiency of 89.6% (see Table 5.1). However, the sample of the control reactor had to be centrifuged before being analyzed because visual observation showed that rubber particles were present in the solution and the scum accumulated at the surface of water. Offensive smell was detected.

In the third feed the total COD concentrations in the reactors were in the range of 322-780 mg/L. A main part of organic matter was removed during the first three to five days (see Fig. 5.1). And after 12 days the COD concentrations of all reactors dropped to less than 100 mg/L and the pH came up from 6.3-6.4 to 7.6-8.0. During the first three days some waterhyacinths in the reactor R_2 and R_3 died and the color of their roots became black and then they detached from the plant body and settled down at the bottom. However, after few days young leaves and new roots appeared. The quantity of evaporated water amounted to 1.1-7.8 $L/m^2.d$. In the control reactor at day 11 the COD concentration dropped from 408 mg/L to 98 mg/L, and the COD reduction rate was slightly higher than the R_2. Microscopical observation showed that ALG, i.e. *Chlorella* and *Spirulina*, were present in the water.

Table 5.2 The treatment and adaptation capacity of WH on RLP wastewater (batch experiments)

	COD, mg/l					
	R1	R2	R3	R4	R5	Ctl
1. First feed						
C_I	72	151	234	319	434	-
C_e	08	16	20	26	42	-
E	88.9	89.4	91.5	91.8	90.3	-
t	02	04	05	05	05	-
2. Second feed						
C_I	159	236	448	520	631	289
C_e	41	42	54	46	73	30
E	79.1	84.0	87.9	91.2	88.4	89.6
t	06	07	07	07	07	06
3. Third feed						
C_I	322	400	560	600	780	408
C_e	53	57	66	80	97	77
E	83.5	85.8	88.2	86.7	87.6	81.1
t	10	09	09	13	13	13
4. Fourth feed						
C_I	460	620	720	820	940	640
C_e	52	60	70	60	91	92
E	88.7	93.3	90.3	92.7	90.3	85.6
t	07	09	09	11	11	11
5. Fifth feed						
C_I	752	802	1084	1084	1267	580
C_e	56	44	80	87	94	65
E	92.6	94.5	92.6	92.0	92.6	88.8
t	14	16	16	16	21	19
6. Sixth feed						
C_I	1039	1234	1640	2033	2480	1536
C_e	70	80	101	240	-	207
E	92.3	93.5	94.0	88.2	-	86.5
t	16	18	20	20	-	18
7. Seventh feed						
C_I	1361	1851	2721	2912	-	2281
C_e	70	96	150	283	-	250
E	94.7	94.8	94.8	90.3	-	89.0
t	16	16	16	24	-	21
8. Eight feed						
C_I	2256	2688	3360	4256	-	2972
C_e	887	1452	1974	3086	-	1909
E	60.7	46.0	41.3	27.5	-	35.8
t	04	04	04	04	-	04

C_i, C_e *- initial and the end* COD_t *in the reactor, mg/L*
E, % - treatment efficiency, $(1- C_e/C_i)100$ *%*
t - experimental time, days

In the fourth feed about 7-11 days were needed to reduce the COD concentration from 460-940 mg/L to 52-91 mg/L and the pH increased from 5.5-5.6 to exceeded 7.2. During this experimental period of time several young leaves and new roots developed, specially in R_1, R_2 and R_3, which resulted in an increase of the amount of evaporated water to 1.9-11.4 L/m^2.d indicating the adaptation of WH in RLP wastewater. In the control reactor the ALG grew abundantly, consequently the data are presented in the ALG experiment below.

The best WH growth was observed in the fifth feed with the COD_i in the range of 752-1,267 mg/L. More than 90% COD was removed in all the reactors and complete degradation needed 14-21 days with a quantity of evaportranspiration water amounted from 2.4 to 6.4 L/m^2.d. At the end of this experimental period the COD_e of all the reactors, as well as the control reactor, were lower than 100 mg/L.

In the sixth feed conducted at an COD_i of 2,480 mg/L most of WH of R_5 died in the first day, all leaves became yellow and dry and the roots dropped to the bottom, although a few small branches survived. *In the* R_1, R_2, R_3 *conducted at an* COD_i *of* 1,039, 1,234 and 1,640 mg/L, respectively, the waterhyacinth grew very well, i.e. with beautiful green leaves and the amount of evaporated water increased. The WH in reactor 4 (COD_i of 2,033 mg/L) was not healthy. At day 12 in all the reactors including reactor 5 young leaves grew and the amount of evapotranspirated water amounted to 1.6-11.1 L/m^2.d.

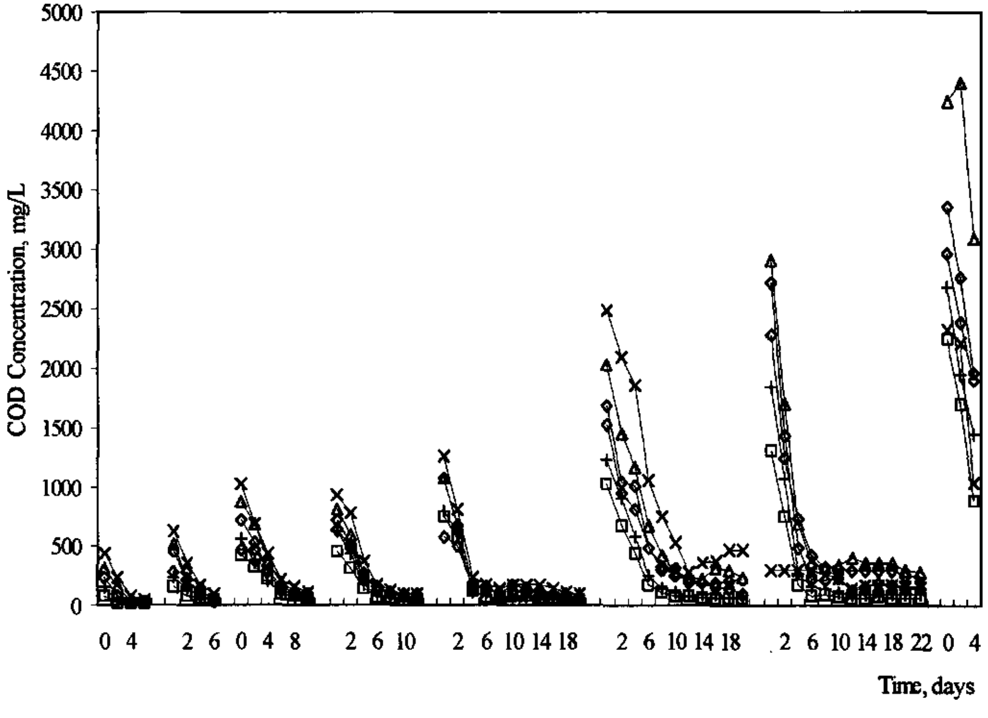


Fig. 5.1 The COD reduction in the batch experiment with waterhyacinth.

It is surprising that in the seventh feed the WH in reactor 4 still grew and could tolerate a the COD_i of 2,912 mg/L, i.e. a higher COD concentration than in R_5 that caused a death of WH in the sixth feed. And WH of reactor 5 grew very well and created beautiful green bunches. The amount of evaporated water was up to 23.8 L/m^2.d.

In the last feed conducted at an initial COD_i concentration ranging from 2,256 to 4,256 mg/L the condition of WH in all the reactors became very poor, the leaves turned yellow and dry and the color of the roots became black. At day 4 all waterhyacinth died. Despite the WH grew very poorly, the COD concentrations continued to drop, because the high COD concentration does not affect bacteria who have main responsibility to break down the organic matter contained in the wastewater.

The experimental results obtained also revealed that 50-70% of the organic matter (COD) was broken down during the first few days (2-5 days), 11-20 days were needed to complete the degradation. Moreover, the higher the initial COD concentration the more time is needed to complete the degradation. At the beginning of each feed a white rubber film formed at the surface of water for some days. During this period of time the WH grew not well in all the reactors.

Except the first feed, the pH in all reactors increased rapidly to 7.7-7.8 and the maximum pH recorded was 8.3 in the sixth feed conducted at an initial COD_i concentration of 1,234 mg/L in the R_2 (see Fig. 5.2).

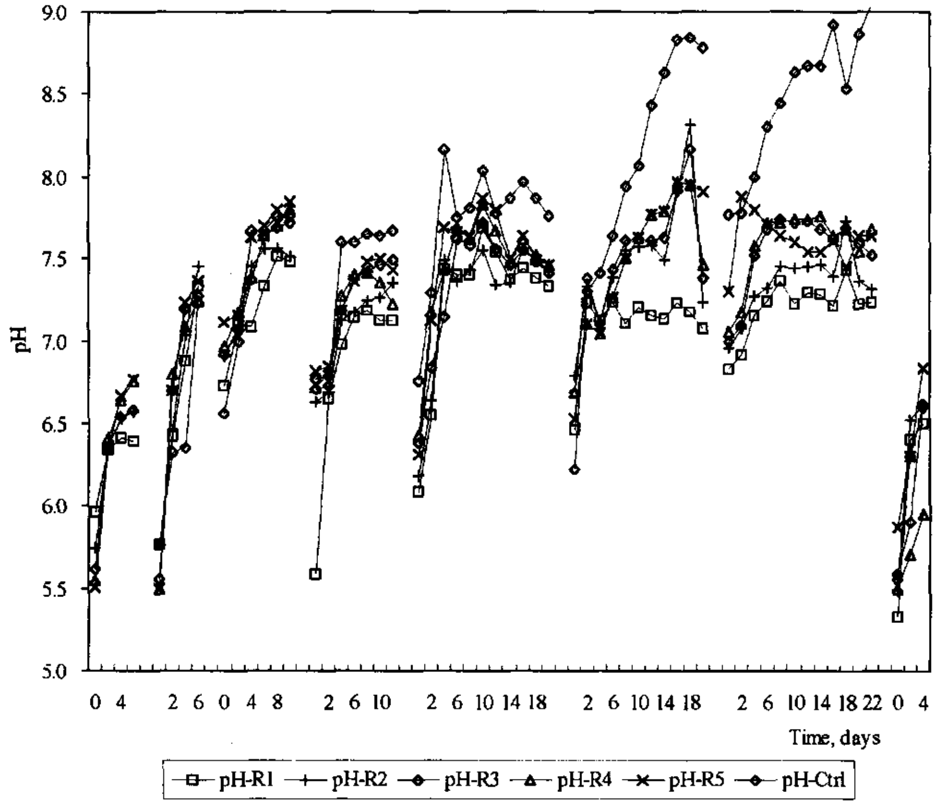


Fig. 5.2 The pH variation during batch experiment with waterhyacinth.

Algae

Unfortunately, using the same COD concentrations in the batches with WH, ALG could not accommodate RLP wastewater even not at an initial COD concentration of 100 mg/L. In all the batches the color of the ALG changed from green to grey and they accumulated at the surface of water in blocks causing a special smell. The problems can be attributed by rubber particles sticking to the surface of the ALG. Therefore the experiment was terminated.

However, in the third feed of the batch experiment carried out with WH, algae were capable to grow in the control reactor (without WH) and this resulted in an increase of the treatment efficiency and the pH (see Fig. 5.1 and 5.2 at the control reactor). Microscopical observations showed that algae present in the water were not only *Chlorella*, but *Spirulina* as well. In the fourth, fifth and sixth batch the COD removal efficiencies in the ALG reactor (the control reactor of the batch experiments with WH) were 85.6%, 83.4% and 85.4%, respectively, slightly lower than found in the WH reactors. Due to the photosynthesis of algae the pH increased significantly during these experiments, i.e. the maximum pH recorded was 8.8 at day 16 of the sixth feed. In the seventh feed algae could not grow healthy anymore and almost all of them died all in the eighth feed.

Continuous flow experiment. The continuous flow experiments were carried out in order 1) to determine the organic loading rate for WH and ALG ponds using the wastewater prepared from diluted serum, 2) to assess the feasibility of WH and ALG ponds to polish the UASB effluent, at least for SS removal and oxygen supply.

Determination of Organic Loading Rate

A number of continuous flow experiments using a RLP wastewater prepared from the serum were conducted to determine the organic (COD) loading rate for a waterhyacinth and algae pond, and also to establish the proper operational procedures for aquatic plant pond systems. The experiments were carried out at an organic loading rate (OL) and hydraulic retention time (HRT) in the ranges of 40-200 kg/ha.d and 6-10 days, respectively.

In the first experiments OLs of 40, 80, 100, 120 and 160 kg/ha.d were applied with an HRT of 10 days approximately. The analyses carried out consisted of COD, pH, SS and DO. The data obtained allow assessment of the treatment efficiencies of WH and ALG ponds. The treatment efficiencies calculated at HRT 10 days and at the steady state conditions are summarized in Table 5.3.

Table 5.3 Treatment efficiency of WH and ALG in RLP wastewater (continuous flow experiment)

OL	Waterhyacinth			Algae		
	C_{inf}	C_{eff}	E	C_{inf}	C_{eff}	E
40	96	25	74	98	30	69
80	212	35	84	189	35	82
100	260	35	87	280	45	84
120	293	35	88	448	75	83
160	579	60	90	528	50	85

OL - *organic loading rate, kg/ha.d,*
C_{inf}, C_{eff} - *influent and effluent COD concentration, mg/L,*
E - *treatment efficiency, %* $(1-C_e/C_i)100$.

At an OL of 40 kg/ha.d the COD concentration dropped rapidly from 96-98 mg/L to 33-37 mg/L during the first two days in both WH and ALG reactor and the pH raised from 5.8-6.0 to 7.3-7.5. At steady state conditions the COD_e ranged from 22-30 mg/L in the WH reactor and 22-38 mg/L in the ALG reactor which are not significant different. In the first day a rubber scum with whitish milk color accumulated on the surface of the water, but it disappeared after few days. During this period of time some WH near the feed inlet point died and leaves were dry due to a rubber film covering the roots, which obstructed water transfer from the root to the leave. When WH died the roots became black in color and detached from plant body and settled down to the bottom. In the ALG reactor during the first few days ALG accumulated on the surface of the water and the color also changed from green to grey and this was accompanied with a very special smell. The concentration of SS was very low in the effluent, 4-22 and 30-60 mg/L for WH and ALG effluent, respectively. At day 6, the WH and ALG apparently became adapted to the RLP wastewater and they started growing again.

After the experiment at an OL of 40 kg/ha.d the OL of the system was increased step by step to successively 80, 100, 120 and 160 kg/ha.d. At an OL of 80 kg/ha.d the treatment efficiencies were 84% and 82% for WH and ALG, respectively, and the effluent COD concentrations were more or less the same as found at an OL of 40 kg/ha.d. The pH in the ALG reactor was always higher that in the WH reactor. The treatment efficiency found at an OL of 100 kg/ha.d was 87% and 84% for WH and ALG, in fact even higher than those in lower loading rate. At an OL of 120 and 160 kg/ha.d, the treatment efficiency of WH still was 88% and 90% and the pH increased from 5.8 to 7.1-7.8, respectively, while in the ALG reactor, the treatment efficiency was 83% and 85% under these conditions, respectively and in both OLs the pH raise to 7.8.

When OL was increased further at the area surrounding the inlet point of the aquarium the whitish rubber films always appeared, accumulating at the water surface, but it disappeared after a few days. This rubber film caused the death of WH at the beginning part of reactor, but WH at the center of reactor grew very well. At an OL of 120 kg/ha.d the ALG could not flourish and the color of ALG changed to dark green, and also the WH did not grow well, and at an OL of 160 kg/ha.d the WH only could survive for a few days.

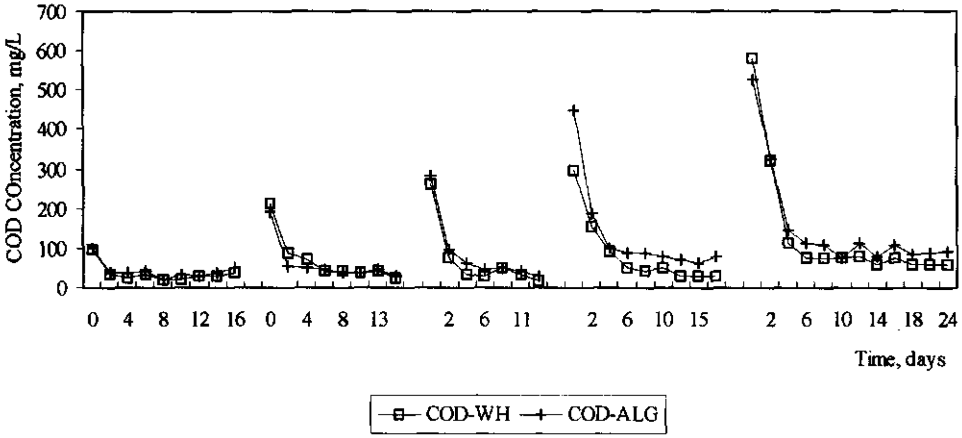


Fig. 5.3 The COD reduction in continuous flow experiments using RLP wastewater with WH and ALG at various organic loading rates (in kg COD/ha.d).

It is clear that treatment efficiencies increased with increasing OL and influent COD concentration, for instance, in case of WH the assessed efficiencies at OLs of 40, 80, 100, 120 and 160 kg/ha.d were 74, 84, 87, 88 and 90%, respectively. In the same way the treatment efficiencies increased in ALG-reactor, but the effluent COD concentrations of the ALG-reactors were always higher than those of the WH pond, while the pH was higher. And statistic data also show that the pH increased with an increase of influent COD concentration and treatment efficiency.

The experiments with ALG conducted with an influent COD concentration of about 300 mg/L and at HRT, 10, 8, 6 days, and at an OL of 74, 92, 122 kg/ha.d were also carried out to assess the effect of HRT on the treatment efficiency and the oxygen production. The results obtained show that the influent COD concentrations dropped down from 311, 320 and 303 mg/L of reactor 1, 2 and 3, respectively, to 75, 59, 70 mg/L at day 6. The experiment lasted for 30 days. At the end of the experimental period (day 30) the effluent COD concentrations were almost the same for three cases, 45, 43 and 48 mg/L. It is surprising that in this continuous flow experiment ALG could tolerate an OL of 122 kg/ha.d.

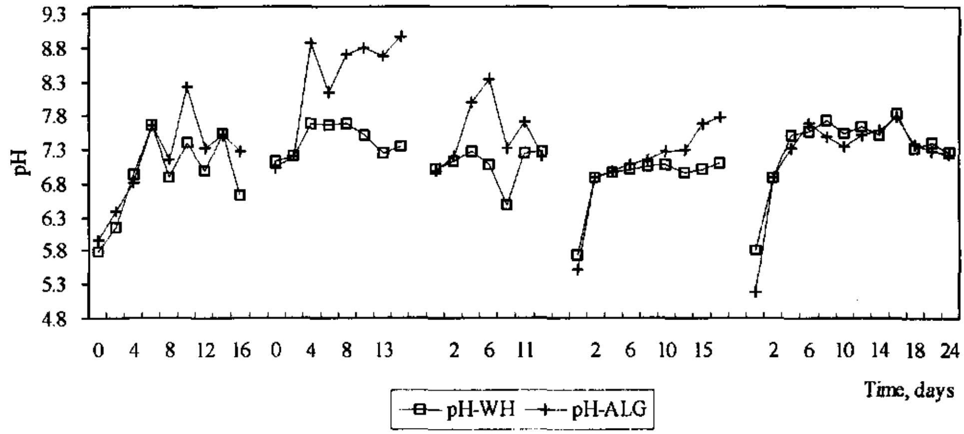


Fig. 5.4 pH variation in continuous flow experiment with WH and ALG at various loading rates.

The pH increased from 6.0, 5.9 and 6.1 to 7.3, 7.4 and 7.4, respectively. The maximum pH measured was 9.00 which was recorded at day 16 in reactor 3 with OL of 122 kg/ha.d (see Fig. 5.5). During period day 11 to day 18 of the ALG experiment the ALG concentration raise up to 100-124 mg/L and the pH went up to values higher than 8. In this experiment the highest DO measured was 54 mg/L (900% higher saturation of oxygen dissolved in water, 6 mg O_2/L at 32°C) which was measured at 2 pm.

Polishing of UASB effluent

In some additional continuous flow experiments WH was used to investigate the post-treatment of UASB effluents, e.g. emphasizing the removal efficiency of SS. In these experiments the OL varied from 100 to 160 kg/ha.d at an HRT of 6-10 days, and the experiment was carried out for a period of 40 days. The results are shown in Fig. 5.6 and 5.7.

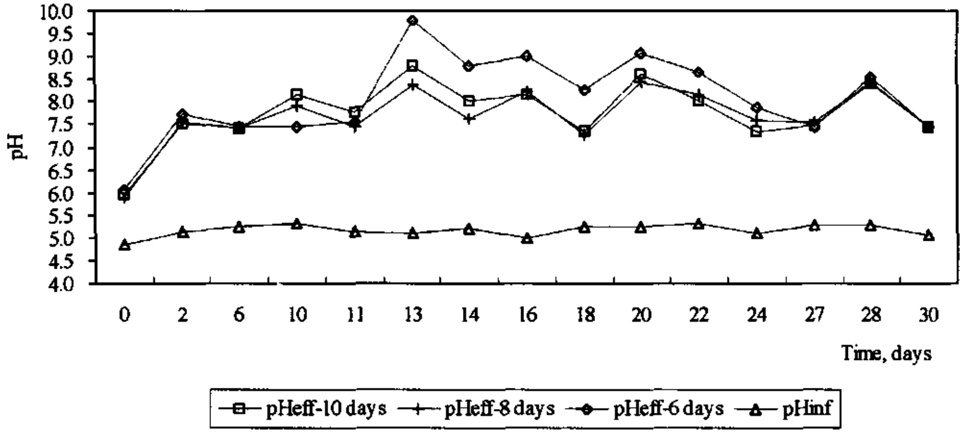


Fig. 5.5 The pH variation in the continuous flow experiment with ALG at different HRT.

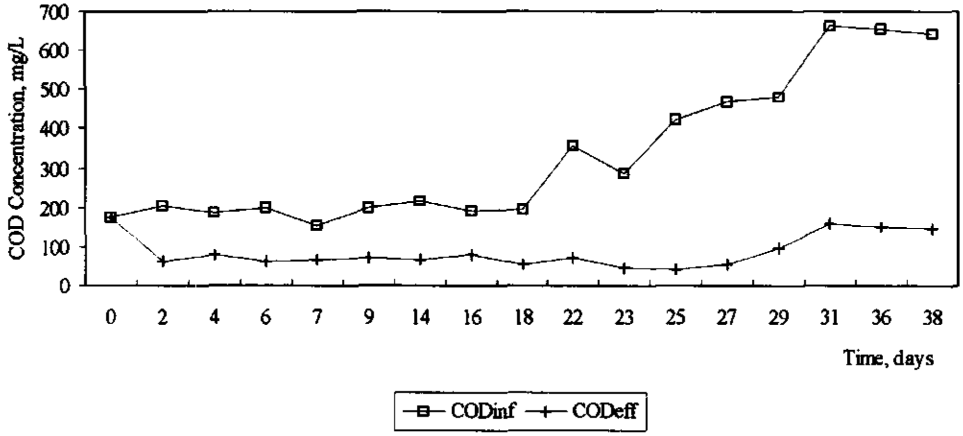


Fig. 5.6 COD removal efficiency of WH polishing the lab-scale UASB effluent.

In the first two days the COD and SS concentration dropped from 205 mg/L and 65 mg/L to 64 mg/L and 20 mg/L, respectively. With the influent COD concentrations in the range of 155-216 mg/L and at an OL of 100 kg/ha.d the treatment efficiency ranged from 68-79.6% and the effluent COD concentration could be maintained at low values of 44-60 mg/L. With such low COD concentrations the treated wastewater indeed can be discharged to receiving water. The WH grew not healthy in this period of time.

When the OL was increased to values exceeding 100 kg/ha.d the COD_{inf} dropped from 469-479 mg/L to 43-93 mg/L in the effluent, corresponding to the treatment efficiency of 80%. But at this loading WH also grew not well. When OL exceeded 120 kg/ha.d at an influent COD concentration of 640-663 mg/L, the COD_{eff} raised up to 144-158 mg/L (see Fig. 5.6) and WH could survive only for a few days. During the whole experimental period the effluent SS concentrations remained in the range 15-20 mg/L (see Fig. 5.7).

In addition, the results of the experiment with WH at an HRT of 2-3 days show that effluent COD concentrations of 41-69 mg/L could be obtained. However, the WH died after 6-7 days.

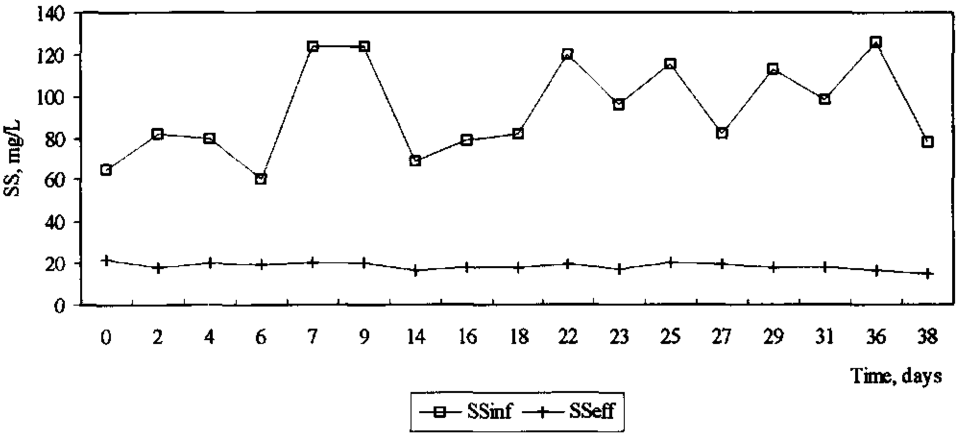


Fig. 5.7 SS removal efficiency of WH polishing the lab-scale UASB effluent.

It should be noted that the control reactor in the continuous flow experiments, e.g. the reactors without WH and added ALG, became already contaminated by ALG in the first few days.

5.4 DISCUSSION

It is well known that in aquatic plant ponds treating wastewater the ecological system consists of both bacteria and aquatic plants. Except for the algae population, the biological community in the ponds is similar to that present in the activated-sludge systems, i.e. consisting of a suspended bacterial growth system but in case of pond systems also with algae and with attached growth in the presence of waterhyacinth. Bacteria mineralize organic matter to simple compounds (and CO_2) which serve as nutrients for aquatic plants. Aquatic plants have a different function. ALG use the products of bacterial degradation, such as nutrient salts and they use sunlight energy for their activities in photosynthesis. ALG produce oxygen for aerobic microbial activity to break down organic matter (Tchobanoglous and Burton, 1991). Differently to ALG, WH can supply only very little oxygen through their stems and roots to water (Orth, 1988), but it is believed that the main contribution of WH is to provide surface for attached bacterial growth. Therefore it should be understood that bacteria play the most important role in the degradation process, while WH and ALG provide only better conditions for this bacterial degradation process.

The tolerance of waterhyacinth & algae in the RLP wastewater

Basically, the most important purpose of the experiments was to determine the tolerance of aquatic plants for the RLP wastewater because as discussed above bacteria break down organic matter and aquatic plants mainly provide better conditions for bacteria. Therefore if aquatic plants can survive in wastewater, both more oxygen and a higher bacterial population are available in the water and the treatment efficiency therefore would increase, while also aerobic conditions will establish in the effluent.

Experimental data and visual observations show that WH and ALG can be used in stabilization ponds to treat the RLP wastewater or to polish the UASB effluent. WH can tolerate RLP wastewater COD concentrations up to 2,480 mg/L, and in some cases even up to 2,900 mg/L. The admissible capacity of ALG is lower than 2,280 mg/L, but it is recognized that the maximum admissible capacities of both WH and ALG depend significantly on the adaptation procedure applied. Once adapted at lower COD concentration WH can also accommodate higher COD concentrations. On the other hand ALG added to dilute wastewater already died at a COD values as low as 100 mg/L. However, ALG naturally grown in were found to grow at wastewater concentrations up to 2,280 mg/L. It looks that rubber particles are the most important pollutant fraction affecting the admissible capacity of WH and ALG because in other types of wastewater WH and ALG can live healthy at much higher COD loading rate.

The knowledge of admissible capacity of WH and ALG obviously also is necessary in the design of the UASB-reactor. Based on the data obtained in the present investigations, the admissible effluent COD concentration of UASB can be chosen.

The experimental results (see Fig. 5.2) also indicate that aquatic plants, especially algae, improve the pH of treated wastewater. High pH values, viz. up to 8.9, have been observed when ALG grew very well and at high COD concentration. Since both WH and ALG use carbon dioxide in their photosynthetic activity, removal of carbon dioxide must be responsible for the development of such high pH conditions, i.e. according to the following equilibrium (Saywer and *et al*, 1994):

$$M^{2+} + 2HCO_3^- \rightarrow CO_2 + CO_3^{2-} + H_2O.$$

After CO_2 is removed by ALG, the pH will raise, because the pK_1 of carbonic acid is high.

Concerning to the WH culture, visual field observations carried out in South Vietnam and in Thailand (Viet, 1987) showed that WH growing in a rich nutrient water have shorter, smaller and less dense roots and a lower admissible capacity than WH growing in a poor nutrient water. Therefore, at the beginning of the operation of an aquatic plant pond wastewater treatment system it is advised to take WH from poor nutrient receiving body.

Mechanism of the treatment of waterhyacinth and algae ponds systems for RLP wastewater and UASB effluent.

The mechanism of the treatment of RLP wastewater in an aquatic plant pond system as based on:

1. Sorption of non-soluble and soluble matter present in the wastewaters to the surface of the roots of WH, via a mechanism similar to the biosorption process proposed by Hajanis and Ronade (1994). This process proceeds rapidly therefore - as found in the experiment - the COD concentration drops down very rapidly during the first few days and also the effluent SS drops to low values. However some pollutants in RLP wastewater form a film on the root surface which causes the death of aquatic plants, presumably due to the fact that water and nutrients can not pass through this film. The characteristics of the root surface affect the absorption capacity. Due to the sorption the COD concentration continues to drop down even after WH died.

2. The roots of WH provide a good medium for bacterial immobilization. Therefore the microbial population at the root surface is much higher than in the bulk of the wastewater, which will result in a higher treatment efficiency compared to the system without WH. However, more important is that the root surface has high absorption capacity which will result in a rapid reduction of the SS concentration.

3. When ALG are present, during day time oxygen is produced and the aerobic bacteria present will consume oxygen and oxidize organic matter. In stabilization ponds ALG can create much higher concentrations of dissolved oxygen than in conventional aeration processes and also oxygenation proceeds faster, because the size of the oxygen bubbles produced in algae cells is significantly smaller than that of air bubbles produced by air diffuser.

From the experimental data obtained it is clear that WH and ALG can be used to treat both RLP wastewater and UASB-effluent and to create the aerobic conditions in the effluent. Organic loading rate up to 100 and 120 kg/ha.d can be applied for ALG and WH pond. At the lower loading rates WH and ALG grow very well in RLP wastewater provided the system is well adapted to the wastewater. The reason for death of WH and ALG can be found in the formation of a rubber film at the surface of WH roots and ALG. It is well recognized that a part of WH at the beginning of pond can be used as barrier to prevent a high concentration of rubber particles in the rest of WH pond. On the basis of a proper culture procedure, e.g. the collection of the proper area where WH can grow well, enough WH will grow-in to compensate the amount of WH that died.

ALG obviously contribute to the suspended solid content of the effluent and sometimes the amount of ALG even is such high that it affects the effluent quality quite negatively. In order to overcome this problem WH could be cultured at one third from the outlet of aquatic plant pond.

An advantage of using aquatic plant pond systems is that no chemicals are needed to neutralize wastewater, because an ALG pond is able to increase the pH from 4.9-5.2 to 7.2-8.3, sometimes even up to 8.9-9.0. The mechanism underlying this phenomenon is:

1. At day time, WH and ALG use carbon dioxide because of the photosynthesis processes therefore the alkalinity of the system increases.

2. As a result of the high alkalinity of treated water and because of the big volume of the pond wastewater will be diluted and therefore neutralized.

The results of experiments carried out at full-scale (see Chapter 6) will show that the treatment capacity of an aquatic plant pond system is different compared with those of the lab-scale experiment. Based on experiments obtained in the practical operation of a full scale RLP wastewater treatment plant another advantage of the pond system is that in case of calamities, such shut down of electricity, obstruction of pumps, a pond system offers a good buffer capacity to protect the environment from pollution.

5.5 CONCLUSIONS

The experiments were performed in order to assess the ability of aquatic plant pond system to treat directly RLP wastewater and the UASB effluent, consequently as a post-treatment step so that the effluent standards for discharge to receiving water can be met.

In case of the RLP wastewater, WH can accommodate COD concentrations up to 2,480 mg/L, and some cases even up to 2,900 mg/L, while the admissible concentration for ALG is lower than 2,280 mg/L, depending on the adaptation procedure.

Suspended rubber particles constitute the main pollutant fraction in RLP causing rapid death of WH and ALG due to the fact that these particles stick as a film the roots of WH and ALG cells, so preventing the transfer of water and nutrient to the leaves or cell.

A big amount of water is lost daily due to evapotranspiration, viz. amounting from 10 m^3/ha.d to more than 100 m^3/ha.d depending on ambient temperature, humidity, wind velocity and the growth of WH.

An OL up to 100-120 kg/ha.d can be applied in WH and ALG ponds. An influent COD concentration of up to 300 mg/L gives an effluent COD concentration of less than 100 mg/L. In the ALG pond a low OL has to be chosen because at organic loading rate exceeding 14 kg/ha.d no oxygen will be present in the effluent.

In aquatic plant ponds organic matter is removed very rapidly (during the first few days) as a result of a biosorption process.

When operated in series, a WH pond has to be the first step and ALG pond the second. A WH barrier at the beginning and at the end of pond is essential to remove rubber particles from the influent and ALG from the effluent.

6.1 INTRODUCTION

In present, 29 RLP factories in South Vietnam annually discharge about 4.2-5.1 mill. cubic meter of wastewater to the environment, equivalent 8.5-9.5 mill. ton COD/year, which pollutes an huge amount of fresh water of streams, rivers, canals and lakes, and is also causing heavy air pollution. According to the country's planning, rubber (*Hevea* tree) forest will be expanded from 200,000 ha in 1995 to 500,000-700,000 ha in 2005 and rubber production (block and concentrated rubber) will increase from 135,000 ton/year in 1995 to 200,000 ton/year in 2005. In the past, the capacity of the RLP factories was small and they used an outdated technology and produced a small amount of wastewater. Therefore the wastewater affected the environment not too badly because of the natural self-purification capacity of receiving water bodies. Since 1990, all RLP factories have been expanded. The environmental pollution caused by RLP wastewater has become a serious problem not only for water bodies but for the air as well. The application of appropriate technologies in all RLP factories to treat their wastewater is an urgent need and essential for sustainable development

Five years (1990-1995) of study on a feasibility of the anaerobic wastewater and of post-treatment processes for RLP wastewater on lab-scale experiments in The Netherlands and in Vietnam have been conducted in order to find out the design parameters, the proper operation procedure and the effects of some important factors on the treatment processes, e.g. seed sludge, pH, etc. The experimental data obtained were applied to design a pilot plant at the Lai Khe RLP factory, Binh Duong province and a full-scale wastewater treatment plant with capacity approximately 1800-2100 m^3/d at the Long Thanh RLP factory, Dong Nai province. The design was completed in 1993 and it took two years more to construct and install the equipment due to lack of funding. The wastewater treatment plant was completed at the end of July 1995 and since August 1995 the system has been operated.

This chapter presents the design of the Long Thanh RLP wastewater treatment plant and the experimental results during 4 months (August - December 1995) are presented, and the operation problems experienced during this period of time will be discussed. A comparison between lab-scale and full-scale experimental results are also made. Every year, the operation of RLP factories is interrupted for two months (from the end of December to the end of February because of the season for leave change).

6.2 DESIGN OF FULL-SCALE RUBBER LATEX PROCESSING WASTEWATER TREATMENT PLANT

The RLP wastewater treatment technology

According to the original planning, the lab-scale experimental results would have been used to design and to operate the pilot plant installed at the Lai Khe factory, and then based on pilot plant experimental results, a full-scale plant would be designed. But due to problems at the Lai Khe factory and lack of financial support, the pilot plant after completing its construction could not be operated and, therefore, all the design parameters for the full-scale plant in Long Thanh virtually are based merely on the available lab-scale experimental data.

The RLP wastewater treatment technology is based on the following considerations:

1. Quantity of wastewater and regime, (Q, m^3/d).
2. Characteristics of raw wastewater and the required characteristics of the feed to the UASB (based on insights obtained from lab-experiments).

3. Design criteria of UASB-reactor (Lettinga and Hulshoff Pol, 1991) and data established from lab-scale experiments.
4. Characteristics of the receiving water.
5. Local circumstances, e.g. investment capacity, technical level, environmental legislation and regulations, effluent standards and possibilities of reuse recovered rubber and treated wastewater.
6. Land area available.
7. Requirements of the Long Thanh RLP factory.

After carefully considering all the above factors and surveying a site where the wastewater plant would be located, i.e. soil structure, the slop of ground surface, etc., the following wastewater treatment technology is chosen:

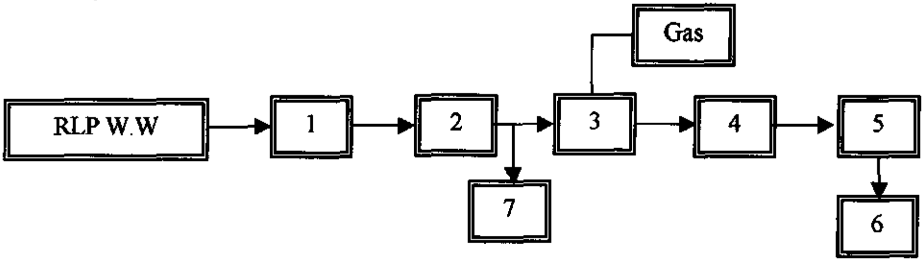


Fig. 6.1 Schematic diagram of the wastewater treatment technology.
1. Skimming tank; 2. Pumping station; 3. UASB; 4. Facultative pond; 5. Oxidation pond with aquatic plant; 6. Receiving water (stream); 7. Chemical for neutralization; RLP W.W. rubber latex processing wastewater

The functions of the various units in the wastewater treatment configuration are as follows:

Skimming tank. This tank in fact serves as a pre-treatment step because it is responsibility for the removal of uncoagulated rubber particles and further for the equalization of fluctuations in the wastewater flow and the concentrations of pollutants. After the skimming tank the wastewater should contain mainly organic soluble matter in order to provide proper conditions for the anaerobic treatment process.

The UASB-reactor. It is applied to break down biodegradable organic matter in the wastewater and to convert this to methane for energy recovery. The main part of the biodegradable organic pollutants should be eliminated in this step from the wastewater. This is the core of the wastewater treatment plant and its treatment efficiency affects greatly the following step, e.g. ponds system.

Stabilization pond system. In order to meet effluent standards and to overcome a possible upset of the anaerobic process, the main function of the stabilization pond system is to polish the UASB effluent by means of a) COD reduction as a result of supply of oxygen through the photosynthesis of algae growing in the ponds and b) the removal of the SS concentration through the barrier of the waterhyacinth roots.

After treatment, the effluent should meet the environmental standards and therefore be allowed for discharge to the receiving water.

The design of RLP wastewater treatment plant

Pumping station and channels were designed based on available experiences. Initial and therefore considerations had to be given to the design of the main units:

- Skimming tank
- The UASB-reactor
- Stabilization ponds.

Skimming tank

The volume and dimensions of the skimming tank were calculated based on the hydraulic retention time (HRT) which has to be sufficiently long for rubber particles to recoagulate and to float up to the surface of the tank.

$$V_{sk} = Q.HRT\ (m^3)$$

where, V_{sk} = volume of skimming tank, m^3
Q = average flowrate of wastewater, m^3/h, $Q = 90\ m^3/h$
HRT = hydraulic retention time, h, $HRT = 8\text{-}12$ h

A depth of 1.4 m was selected for the tank. According to the design, it was intended to collect the scum layer by a mechanical device. However due to limitation of funds provisions had to be made to collect the scum manually.

The UASB-reactor

The applicable organic space loading rate was used as design parameter to estimate the volume of the UASB-reactor (V_{uasb}) (Lettinga and Hulshoff Pol, 1991) as follows:

$$V_{uasb} = \frac{Q \cdot C}{L_{space}}\ (\mathrm{m}^3)$$

where, Q = average flowrate of wastewater, m^3/h, $Q = 90\ m^3/h$
C = COD concentration of wastewater, mg/L, $C = 2{,}500\text{-}3{,}000$ mg/L
L_{space} = applicable space organic loading rate, kg COD/m.d, which was set at 12-15 kg COD/m^3.d at 28-30°C. This figure is based on the results of lab-scale experiments (see Chapter 4) and of available full-scale performance data (see Chapter 1).

The UASB-reactor consists of 6 separate compartments to be operated in parallel and the reactor tank is constructed in concrete, and the Gas-Solid-Liquid separators (GSS) were made from an acid resistant composite material. The gas exhaust pipes of the GSS were connected to a water seal tank, from which the gas tentatively would be released to the air. Due to lack of funds a gas meter was not installed. Wastewater was fed into UASB-reactors through a distribution system consisting of four plastic pipes for each compartment (1 pipe per 4 m^2), releasing the wastewater at the bottom of the rector. The effluent was collected via a V notch weir in a launder. A more detailed design is shown in Fig. 6.2.

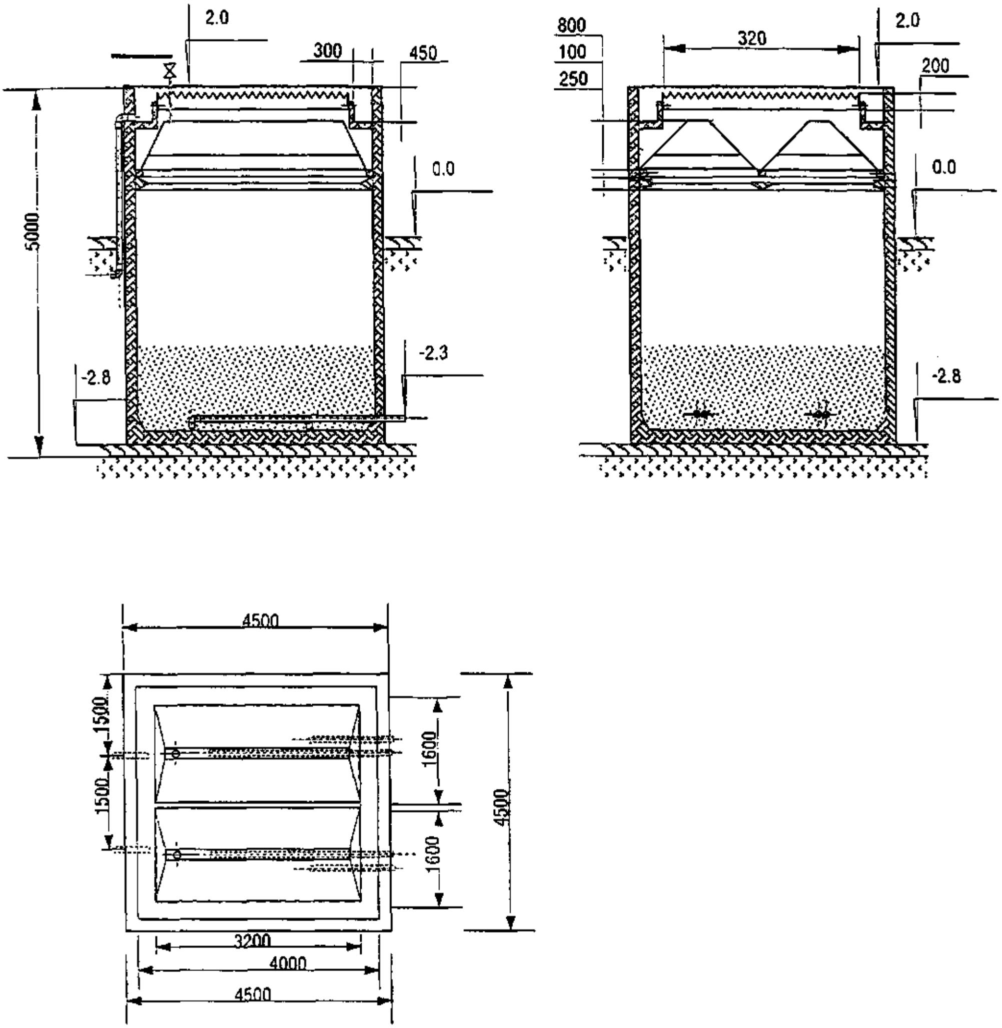


Fig. 6.2 The design of UASB-reactors.

Stabilization pond system

The area and volume of stabilization ponds was estimated on the basis of the applicable surface loading rate and hydraulic retention time, i.e. using

$$S = \frac{Q \cdot C}{L_{sur}} \text{ (ha) and}$$

$$V_p = Q.HRT \text{ (m}^3\text{)}$$

where, S = applicable surface area of the pond, ha

Q = average flowrate of wastewater, m^3/d, $Q = 1,800\ m^3/d$

C = COD concentration of the UASB effluent, (mg/L), $C = 50\text{-}400$ mg/L

L_{sur} = applicable surface organic loading rate, kgCOD/ha.d. According to the experimental results obtained for the conditions expected at the pond site, a load of 100-120 kgCOD/ha.d can be applied

V_p = volume of pond, m^3

HRT = hydraulic retention time, days, which should be in the range 6 to 8 days (see Chapter 5).

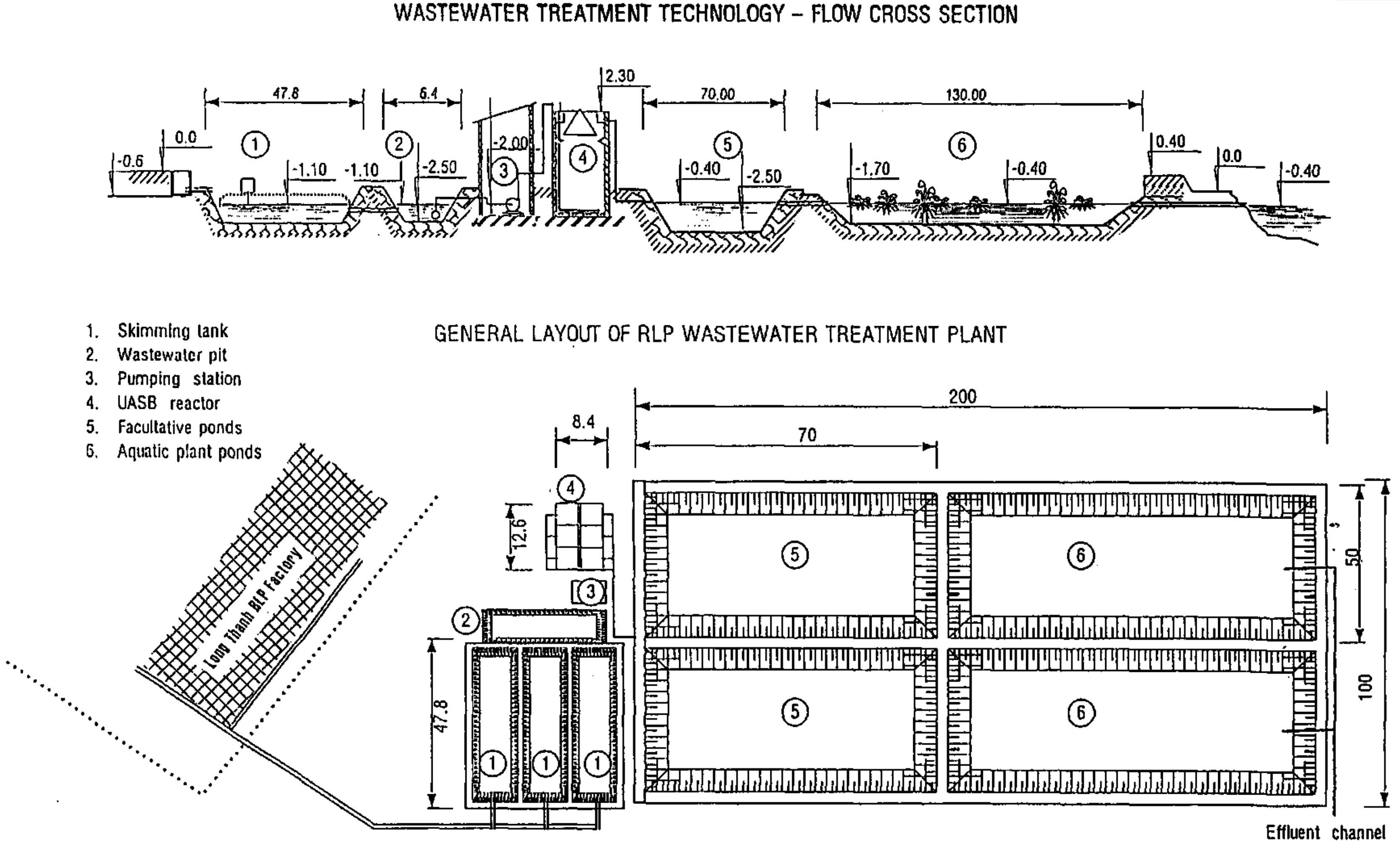
The dimensions of treatment facilities are described in Table 6.1

Table 6.1 The dimensions of various treatment facilities in the Long Thanh RLP wastewater treatment plant

Parameter	SK	UASB	FP	UP
Flowrate, m^3	2100	2100	2100	2100
BxLxH, m	6.5 x 47.8 x 1.4	4 x 4 x 4.5	30 x 70 x 2.1	30 x 130 x 1.3
Units	3	6	2	2

SK - skimming tank; UASB - UASB-reactor; FP - facultative pond; OP - oxidation pond.

The general design is shown in Fig. 6.3.



WASTEWATER TREATMENT TECHNOLOGY – FLOW CROSS SECTION

GENERAL LAYOUT OF RLP WASTEWATER TREATMENT PLANT

1. Skimming tank
2. Wastewater pit
3. Pumping station
4. UASB reactor
5. Facultative ponds
6. Aquatic plant ponds

Fig. 6.3 The Long Thanh RLP wastewater treatment plant.
(general plant)

The wastewater treatment plant operation mode

In the factory, the processing wastewaters are collected in a sewer system. The wastewater is conveyed to the skimming tank by an open channel. In this tank, as a result of anaerobic biodegradation (i.e. acidification), the pH drops down. Because of the applied long retention time (e.g. 8-12h) in the tank rubber particles coagulate here and then partially float up or settle down. The scum layer formed tentatively is removed manually, because mechanical devices could not be installed so far. It was expected that all the suspended solid in the skimming tank would be removed and consequently that in this way good conditions for UASB would be created.

Following the skimming tank, the wastewater is pumped into the UASB-reactors. Prior to start the feeding to UASB-reactor (volume 96 m^3) was inoculated with approximately 24-26 m^3 digested pig manure sludge as seed sludge, corresponding to 0.98-1.07 tons VSS/reactor or 10.2-11.1 kgVSS/m^3. The seed sludge filled up the reactor to a level of about 1.5-1.7 m height, i.e. one third height of the UASB-reactor. The characteristics and the specific methanogenic activity (SMA) of the seed are similar to the sludge used in the experiment presented in Chapter 3, i.e. about 0.13-0.26 g COD/g VSS.d at 28-34°C. The start-up procedure applied in the full-scale UASB-reactors was very similar to that applied in the lab-scale UASB-reactors (see Chapter 3, paragraph 3.3), consequently according to the guidelines for the UASB start-up (Lettinga, 1995). Immediately after starting the feeding, only a small amount of the wastewater (77-80 m^3) was pumped into each UASB-reactor (compared to 300-350 m^3 at design loading rate) in order to maintain the initial space loading rate at approximately 3 kg/m^3.d or sludge loading rate at 0.09-0.20 g COD/g VSS.d. The remaining part of the wastewater was discharged directly to the stabilization ponds during this start period. The UASB-reactor in fact is the heart of the wastewater treatment plant. If the UASB-reactor is operated properly, especially during the start-up period, the COD concentration can drop to 250-300 mg/L which then provides very good conditions for the stabilization pond system and any offensive smell problem can be avoided. According to the plans the UASB-reactors should remove up to 90-95% of the organic pollutants and consequently the COD concentration of the effluent should drop to values as low as 300-400 mg/L. The effluent of the UASB flows by gravity into the stabilization ponds for post-treatment, where as a result of the combined activities of bacteria and algae, and supply oxygen to water, the COD concentration then should decrease further to values allowing discharge to receiving surface water. Algae developing in the pond are removed by the waterhyacinth barrier at grading in the last one third part of the oxidation ponds.

6.3 RESULTS AND DISCUSSION

Immediately after completing the construction, the wastewater treatment plant was put in operation. Additionally, as mentioned above, because of the limitation of land and finance only 2 ha is available, although in fact for a satisfactory effluent quality 6-7 ha for the pond system would be required. The stabilization pond system therefore is overloaded. During the first four months the attention was focussed on the start-up of the UASB-reactors. The results presented in this chapter will deal mainly with those obtained from the UASB experiment, particularly also during the start-up.

Skimming tank

It was difficult to determine from the available data the amount of rubber particles removed from the wastewater in the skimming tank, because uncoagulated rubber particles are present in the wastewater in colloidal form, and these particles pass a glass fibre filter paper with pore size bigger than 45 μm used to determine the SS concentration in wastewater. And when using a membrane filter paper with pore size of 0.2 μm to determine the colloidal fraction, it is difficult to distinguish between rubber particles and other colloidal matters. In the skimming tank, proteins, carbohydrates and lipids are subject to acidogenesis. Since the applied long retention time is quite long (8-12h), a considerable part of these compounds will acidify, and as a result the pH will drop into the acidic range. Due to this pH drop colloidal rubber particles then will coagulate. Part of the coagulated particles will float up to the surface, due to the gas formation in anaerobic degradation, while an other part will settle down to the bottom of the skimming tank, e.g. after the particles released the entrapped gas. From the observations made with full-scale installation it became clear that rubber scum layer appeared over about 60-80% of the effluent part of the skimming tank. The labors could collect about 350-400 kg/d (wet weight) floating rubber depending on the season. So during the high season more rubber is collected and during the rain season less rubber is collected, because then a higher fraction of the rubber settles down, mainly due to the rain. According to the observations made it appeared that at longer retention times the amount of scum becomes higher, but its quality then is worse.

As mentioned in Chapter 2, the pollutant concentration of the wastewater, COD, SS, etc., discharged to the skimming tank fluctuate in term of widely depending on hydraulic retention time. In order to evaluate the treatment efficiency of this tank, and also to assess the wastewater characteristics of the UASB influent, samples of the skimming effluent were taken to be analyzed periodically. The results presented in Fig. 6.4. show that the course of the pH of the skimming tank compared to the influent pH of 5.6-6.7 the pH of the wastewater had dropped significantly (4.8-5.2) due to acidification process. The course of the COD_{fil} and SS concentration of the skimming effluent are presented in Fig. 6.5, they ranged from 1,794-3,100 mg/L and 137-368 mg/L, respectively. The comparison of the total COD_{tt} and filtered COD_{fil} and SS concentration shows that the difference between the COD_{tt} and COD_{fil} concentrations in the effluent were about 138-956 mg/L, which gives with determined values a wide range for the COD of SS, i.e. 0.76-4.35 mg COD/mg SS. While the COD of natural rubber compound is 3.29 mg COD/mg natural rubber, according to the oxidation reaction of natural rubber:

$$C_5H_8 + 7O_2 \rightarrow 5\ CO_2 + 4\ H_2O$$

The observation made in practice combined with the wastewater discharged from factory during the working time also showed that the volume of the skimming tank suffices to equalize the fluctuation of the flow over a period of longer than 12 hours, but the SS concentration with 137-368 mg/L still is high, particularly because it will affect the UASB process detrimentally. However, from the experimental data it could be seen that rarely rubber particles were completely removed from the wastewater.

From the results of the full-scale experiments it is recognized that in the full-scale skimming tank a big amount of organic matter including also rubber particles accumulated at the bottom and gas produced in the anaerobic degradation of these organic brings a lot of finely dispersed SS to solution, consequently the UASB influent, which will affect adversely the UASB performance.

It should be mentioned that the COD_t concentration is affected by the SS concentration present in both the influent and the effluent of the skimming tank. The accuracy of the COD_t concentration depends greatly on the sampling, e.g. when samples were taken with a high amount of the SS the COD_{tt} concentration were high. For this reason the COD_{fil} concentration was determined more frequently to assess the process performance.

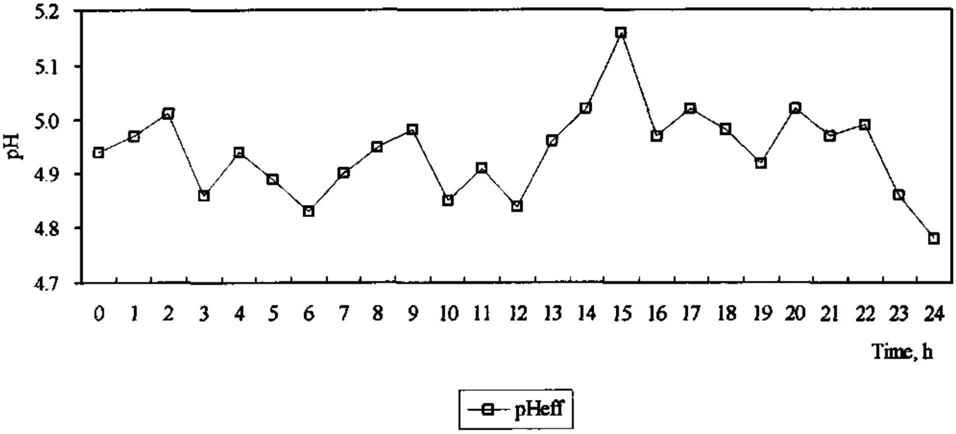


Fig. 6.4 The variation of the pH in the wastewater after the skimming tank, the feed of the UASB-reactor.

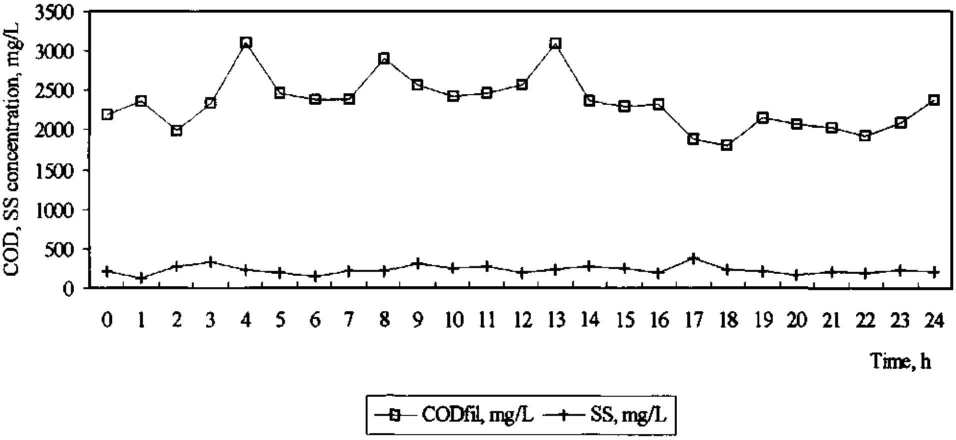


Fig. 6.5 The variation of the filtered COD concentration and amount of dispersed SS in the wastewater after the skimming tank, viz. the feed of the UASB-reactor.

The UASB-reactor

After the skimming tank, the wastewater is pumped into the UASB- reactors. Before introduced in the UASB-reactor the wastewater is neutralized to pH=6.2 using a solution of 5-10% sodium hydroxide. Samples were taken from the influent of the UASB-reactor during a period of 18 weeks wastewater (viz. before the alkali injection point) for measurement of pH, and analyses of COD_{tt}, COD_{fil} and SS.

As explained before, only a part of the wastewater was pumped into the UASB-reactors during the start-up period, i.e. 77-80 m^3/UASB-reactor, which means an OLR of 3-4 kgCOD/m^3.d and HRT of 20-24 hrs. The rest of the wastewater was discharged directly to the stabilization ponds. Along with the start-up of the reactors the amount of wastewater fed into the UASB-reactors was increased and consequently the amount directly introduced in the ponds became smaller gradually. During its start-up period the effluent was not recycled. The experimental results obtained during 18 successive weeks of operation at the HRT of 20-19 h are presented in Fig. 6.6 and Fig. 6.7.

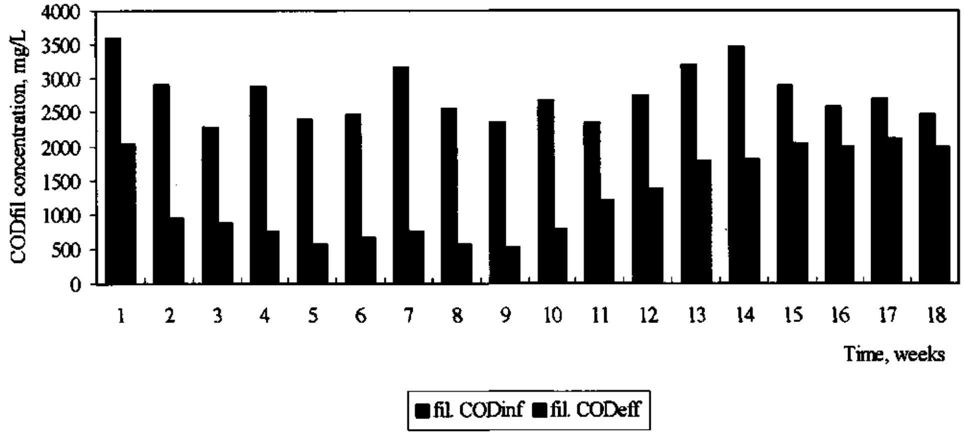


Fig. 6.6 The influent and effluent COD concentration of the UASB system during a period of 18 weeks operation (the start-up period).

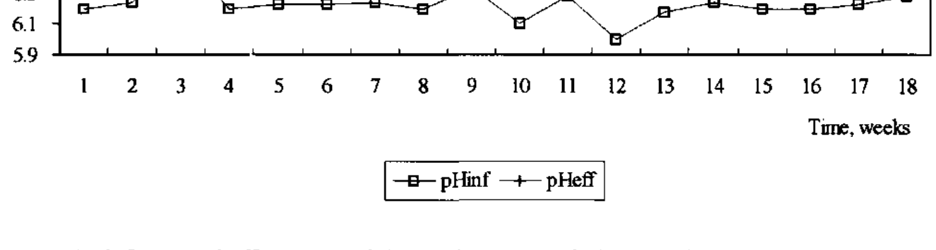


Fig. 6.7 The influent and effluent pH of the UASB-system during a period of 18 weeks operation (the star-up period).

During the first week of operation the COD_{fil} concentration dropped from 2,500-3,000 mg/L to 800-900 mg/L, and the effluent became clear, i.e. the SS concentration amounts to 94-210 mg/L, which means a SS reduction of 60-70%, and no scum layer appeared on the surface of the stabilization ponds and bad smell was not a big problem. During the second and third week the COD_{fil} concentration even dropped further to 500-700 mg and the effluent SS concentration remained stable at a concentration of 60-90 mg/L, corresponding to a treatment efficiency of 67-78% (based on COD_{fil}). At that time the preceding period the organic space loading rate was 3 kg/m^3.d and sludge loading rate 0.1-0.2 g COD/g VSS.d. The highest COD treatment efficiency of 78% was obtained at week 9 and the pH then raised to 7.16-7.56. However, in week 10 the effluent COD$_{fil}$ concentration raised to 1,300-1,700 mg/L, the effluent pH became appr. 6.5. In week 11 the treatment efficiency dropped to 48.5% and in week 17-18 to only 18.8%, and the system turned into a complete upset. At that stage it was decided to lift the GSS for control inspection of the action beneath this GSS. It appeared that a thick layer of rubber particles up to about 40-50 cm had accumulated at the liquid surface under the GSS and also that a substantial amount of sludge had stuck on the rubber. Moreover, it also appeared that the sludge left in the reactor had dropped to a very small amount.

The reason for the observed upset of the UASB-reactors very likely can be found in the fact that the skimming tank was unable to remove the rubber particles sufficiently, consequently a too high amount of uncoagulated rubber particles remained in the wastewater. When exposed to the active anaerobic biomass present in the UASB- reactor first of all the protein layer surrounding the rubber particles will be attached and very likely degraded and then as a result the particles will coagulate. However, to the high adhesive characteristics of the rubber surface, anaerobic sludge particles and bacteria will stick to the rubber and then they buoy up to the surface due to entrapment of gas bubbles and low density of the rubber where they accumulate, and possibly partially will be washed out from the system. It is clear that when the amount of sludge retained in the reactor becomes too small, the COD reduction will decline rapidly.

It is very clear that part of the seed sludge was washed out of the reactor during the start-up. The amount of sludge washed out can be estimated on the basis of measurement of the effluent SS and the flowrate. However also quite a big fraction had stuck on the rubber layer under the GSS and during the operation of the plant it is almost impossible to determine. However, unfortunately also the daily amount of sludge washed out was not assessed due to a lack of operation experience at site. Instead of composite effluent samples grab effluent samples were taken, and consequently an accurate estimate can not be made from available data.

On the other hand, in the lab-scale experiments, the same phenomena happened. Also in these relatively very small reactors occasionally aggregates rubber up to a size of 0.5-0.7 mm were observed in sludge bed. These rubber aggregates either were retained in the sludge bed or float up to the liquid surface, where they then accumulate. It was observed that a certain amount of sludge particles or even granular sludge stuck to the rubber surface and was entrapped in the rubber aggregates. In order to remove the rubber aggregates present in the sludge bed it was found that applying a liquid up flowrate up to 2 m/h is successful. These rubber agglomerates accumulate beneath the GSS device. In order to enable the release of the biogas produced in the sludge bed via the GSS device is necessary to lift for removing the scum layer.

Although it was well understood that the gas production rate can be used to assess in an easy and quick manner the performance situation of the UASB-reactor, unfortunately, due to a lack of equipment and the production of a too large volume of gas – at least in the initial phase of the start-up - it was also not possible to install the proper devices to measure the gas production sufficiently accurately.

Although too little reliable data could be collected, sufficient information has become available to take the adequate measures for preventing these problems in a next start-up.

Stabilization ponds. At the beginning, due to their big volume (20,000 m^3) the effluent COD concentration of the pond remained sufficiently low even in case of high fluctuation in the COD concentration of UASB effluent. The effluent COD values ranged from 400-600 mg/L for the facultative ponds to 250-300 mg/L for the oxidation ponds. The algae concentration ranged from 120-200 mg/L.

However, despite that bad smell is a problem. This can be due to overloading of the pond system, especially during periods when the UASB-reactor does not perform properly. The BOD/COD load of the facultative pond then comes up to 6,000 kg/ha.d or 0.32 kg/m^3.d, while according to available insight only the maximum BOD/COD load for these systems is 56-210 kg/ha.d (Tchobanoglous and Burton, 1991). Scum layers especially appeared during period where wastewater was discharged directly to the ponds. These layers gradually covered the total surface of facultative ponds starting from then bad smell diffused from the pond to the air and up to 4-5 km in the surrounding these nuisance problems were prevailing. Surprisingly, after a period of 3-4 days interruption of the operation, the scum layer appeared to accumulate at one side of the pond. This could be attributed to wind. As a consequence of this "removal" of the scum layer, algae could grow again healthy in the facultative pond, and then, after a period of appr. 7 days or longer, no smell in the pond. The bad smell problems clearly can be prevented by introducing oxygen in the liquid phase.

6.4 CONCLUSIONS

A four months period of start-up operation the biological wastewater treatment systems installed at the Long Thanh rubber latex processing factory obviously is far too short to draw definite conclusions, the more so because sufficient performance data could not be collected. A lot of experimental work still should be done to complete the insight in the observed phenomena and to improve the treatment efficiency. But at this stage already some preliminary conclusions can be drawn and recommendations can be made from the available performance data of full-scale experiment:

1. The volume of the skimming tank looks sufficient for equalizing fluctuations in the flow and the COD concentration of the influent wastewater.
2. In the skimming tank, the pH values drop due to acidification.
3. The skimming tank is unable to remove sufficiently the amount of dispersed rubber particles present in the wastewater and since these particles affect significantly and adversely the performance of the UASB process, it is clear that it is essential to improve the performance of the skimmer in this respect.
4. In order to provide the proper characteristics of the wastewater fed into the UASB-reactor an improved method for pre-treatment should be developed. Such a pre-treatment process could consist of flotation or an anaerobic biosorption process, because when exposed for a period of time to anaerobic conditions the "emulsion" destabilizes. Use can be taken from this phenomenon to remove the rubber particles.
5. The anaerobic seed sludge can adapt to rubber wastewater within a very short period of time and then a satisfactory treatment efficiency is obtained. In order to improve the treatment efficiency - further and more important - to provide the good environmental conditions for UASB application, an appropriate method for removing SS is essential.
6. Under the presently prevailing conditions in the Long Thanh factory, the stabilization pond system still comprises a good post-treatment, because it at least acts as buffer step in case of the UASB-reactor performance is poor, because it then provides a good quality effluent to be discharged to environment.
7. The origin and character of the malodour nuisance formed from the degradation of sulfate containing proteins needs to cleared, while also adequate measures should be developed to overcome these problems.

Chapter 7

Summary and Discussion

7.1 INTRODUCTION

Since 1990, Vietnam has expanded economically rapidly as a result of the transition from a purely command towards a more market oriented economy. This enormous and rapid economic development, especially several in industrial zones and urban areas, has not been accompanied with a sufficient attention to the detrimental side-effects, most notably for deterioration. Vietnam suffers from a variety of environmental ills which to a major extent originate from the too rapid industrial development. These negative side-effects certainly have been well recognized by the central government and regional administrations.

The rubber latex processing (RLP) industry is, among several other industries, one of the industrial branches contributing with a high production capacity quite heavily to environmental pollution.

Annually, more than 29 RLP factories with capacity of 170,000 ton/year (Chapter 2) discharge approximately 4.2-5.1 million cubic meter of wastewater with high pollutant strength to environment. This causes a severe pollution to receiving water bodies, and also to ground water and to the air. This pollution obviously quite detrimentally affected the people living in the surrounding of these factories.

In order to solve the water pollution caused by RLP wastewater, in recent years it has been attempted to implement wastewater treatment systems like conventional aerobic activated sludge process and stabilization ponds. However these processes have quite serious disadvantages, such as in the aerobic activated sludge process a high energy demand, production of a huge amount of excess sludge, and in the stabilization pond systems the very large land requirements, mal-odour nuisance problems. Considering these drawbacks, high rate anaerobic wastewater treatment systems, especially the UASB-process, might represents an attractive alternative.

This study aims at assessing the feasibility of the UASB-process for treating RLP wastewater under conditions prevailing in South Vietnam. Complementary to anaerobic treatment, attention has been paid to post-treatment of the UASB effluent in order to meet the Vietnamese national effluent standards.

The studies were carried out in The Netherlands during November 1990-May 1991 and May 1993-October 1993, and in South Vietnam during 1991-1995.

7.2 OBJECTIVE OF THE THESIS

The main objective of this PhD-thesis is to assess the applicability of UASB process for treating RLP wastewater and the feasibility of some adequate post-treatment processes for the effluent of the anaerobic treatment process.

Chapter 1 reviews the anaerobic wastewater treatment processes and in chapter 2 a survey is presented of the quantity and quality of RLP wastewater. This survey is based on measurements and observations made at six RLP factories. In addition also the rubber latex process is also described in this chapter.

Chapter 3 presents the results of the preliminary investigations made on the feasibility of the anaerobic process for treating RLP wastewater. For this purpose sets of batch experiments were conducted for assessment of 1) the specific methanogenic activity of four types of potential seed sludges available in South Vietnam, 2) the anaerobic biodegradability of RLP wastewater, 3) the anaerobic biodegradation of protein, 4) the effect of pH on the anaerobic digestion process, 5) the effect of oxygen and mixing condition on the specific methanogenic activity (SMA) test, and 6) the effect of the storage time on the

SMA of sludge.

Chapter 4 presents the experimental results obtained in laboratory scale UASB-reactor experiments with RLP wastewater, and of experiments dealing with the effect of pH on the performance of the UASB-process, including also the effect of effluent recirculation on UASB performance.

Chapter 5 deals with experiments concerning the post-treatment of anaerobic effluents using stabilization pond systems with aquatic plants like waterhyacinth and algae.

Chapter 6 describes the design of the full scale RLP wastewater treatment plant at the Long Thanh RLP factory, Dong Nai province and the experimental data during the first four months of operation.

7.3 CHARACTERISTICS OF RUBBER LATEX PROCESSING WASTEWATER IN VIETNAM

The survey of the data obtained in six RLP factories situated in South Vietnam, reveal that RLP wastewater originates particularly from two main processing steps, viz. the coagulation step (serum) and the milling, cutting step. Most of these data were collected in the Long Thanh factory. This factory has a production capacity of 10,000 tons/year (dry weight), mainly consisting of block rubber.

The serum wastewater is high in COD-content, viz. up to 5,015-9,962 mg/L, and its pH-values is low with values in the range of 4.95 to 5.24. The total quantity of the serum wastewater at the Long Thanh factory amounts to 224-300 m^3/d, but there exist high fluctuations in the amount.

The quantity of wastewater produced in crushing and milling amounts to 1,500-1,800 m^3/d at the Long Thanh factory, i.e. contributing up to 80-90% of the total amount of wastewater. However, the COD-content of this wastewater is lower, viz. 1,800-2,400 mg/L, and the pH is higher with values in the range 6.12-6.43. At the milling step, the wastewater flowrate amounts to 8.64-25.92 m^3/h during working time and only depends on the working number of milling machines.

The RLP wastewater contains mainly readily biodegradable organic matter, such as volatile fatty acids (acetic/formic acid), and sugars, proteins and lipids, and in addition mineral salts. Considering the presence of these compounds the RLP-wastewater in principle is quite suitable for biological treatment. However, the raw wastewater also contains uncoagulated rubber particles at concentration up to 350 mg/L. As these particles may affect an anaerobic biological process quite adversely, these ingredients therefore should be removed prior to subjecting the wastewater to the treatment process.

In view of the high fluctuation in both the pollutant strength and flowrate, it is necessary to install an equalization tank in front of the wastewater treatment plant. It is possible to combine the equalization tank with a skimmer to remove floating rubber particles.

7.4 FEASIBILITY STUDIES OF THE UASB-REACTOR FOR TREATMENT OF RUBBER LATEX PROCESSING WASTEWATER IN VIETNAM

Based on information available concerning the start-up procedure of the UASB-process (Lettinga, 1995), four types of potentially attractive seed sludge available in South Vietnam were selected, viz. fresh pig manure (FPM), digested pig manure sludge (DPMS), city polluted canal sludge (CS) and septic tank sludge (STS). These sludges were investigated in a lab-scale UASB-reactor for their suitability for reactor start-up, while also in one case the start-up was followed in a full-scale wastewater treatment plant in order to save time for accomplishing its first start-up.

The experimental results revealed assessed specific methanogenic activities for DPMS, CS, STS and FPM amounting to 0.13-0.26 g COD/g VSS.d, 0.12-0.15 g COD/g VSS.d, 0.11-0.12 g COD/g VSS.d and negligible values, respectively. In principle the first three sludges can be used as seed sludge for UASB-reactor start-up, but we selected DPMS as the most attractive seed sludge for full-scale UASB-reactor start-up, regarding its advantages compared to the others, i.e. being:

1. It is available in a large amount in South Vietnam,
2. Its relatively high specific methanogenic activity,
3. Its low harmful hygienic risks.

Except problems in finding a proper seed sludge, it is well known that another important aspect for the feasibility of anaerobic treatment comprises the biodegradability of the organic pollutants contained in RLP wastewater. Most of the organic matter contained in RLP wastewater, i.e. consisting of sugars, proteins and lipids, is first converted into VFA, mainly consisting of acetate, and relatively little propionate and butyrate. In the experiments we found a biodegradability of RLP organic matter amounting to 90-95%. However, some proteins in wastewater, viz. hevein, was found to be very stable, poorly biodegradable. From the results it was obvious that the anaerobic process offers high potentials for the treatment of RLP wastewater.

Using a SMA test, which is simpler and therefore more adequate for use in developing countries like Vietnam, additional experiments were conducted with the aim to assess the effect of pH, oxygen and mixing conditions. In addition also the effect of the sludge storage time was investigated.

7.5 LAB-SCALE UASB TREATMENT OF RUBBER LATEX PROCESSING WASTEWATER IN VIETNAM

In order to determine the design parameters for pilot and full-scale RLP wastewater treatment plants some lab-scale continuous flow experiments were carried out.

From the results obtained in these experiments it appeared that the UASB-process can be applied for RLP wastewater at an organic loading rate up to 28.5 kg COD/m^3.d., providing a COD removal efficiency in the range of 79.8-87.9%. The corresponding hydraulic loading rate are up to 7.3-9.1 m^3/m^3.d at a HRT as low as 3.3-2.6 h. and an upflow liquid velocity up to 0.4 m/h (9.6 m/d). In all experiments, the height of sludge bed in the reactors was 12-15 cm at the termination of the experiments, indicating that in fact higher organic loading rate can be applied, simply by increasing the amount of sludge (height of the sludge bed) in the reactor, e.g. by using more seed sludge. Moreover by following the proper operation procedure (Hulshoff Pol, 1989; Lettinga, 1995) it was possible to cultivate with RLP wastewater as feed, and within a period of 21-24 days, a good quality granular sludge when using digested pig manure sludge as seed sludge.

A quite adversely effect of low pH values of the RLP wastewater (i.e. as low as pH=4.8) was found on the UASB-reactor performance. The period of time passing before the detrimental effect of low pH on the performance of the UASB system will manifest depends, apart from the pH of the influent and the amount of non acidified organic matter present in the feed solution, particularly on the buffer capacity of sludge bed (i.e. on the accumulated amount of alkalinity in the sludge) and the loading rate imposed to the system. However, it was also found that the system, consequently the sludge, can recover quite well and sometimes even in a relatively short period of time from an acidic pH-upset. The period of time required for recovery depends strongly on:

- Wastewater characteristics,
- Characteristics of the sludge,
- Imposed load.

In the experiment presented, the UASB system recovered completely within 2-3 days when using feed pH values in the range of 6.0-6.2.

The low influent pH, i.e. 4.5-4.8, and high effluent (consequently also the reactor) pH-value that can be reached, viz. in the range of 8.5 to 9.4, may represent true problems in the operation of a UASB-reactor for RLP wastewater, when acid formic is used in the plant for coagulation of latex. These problems can be overcome by using effluent recirculation or - if possible - by limiting formate concentration in the wastewater.

7.6 AQUATIC PLANT POND SYSTEM, POST-TREATMENT

Water hyacinth (WH) can accommodate COD concentrations in RLP wastewater up to 2480 mg/L, and some cases up to 2900 mg/L and the admissible concentration for algae (ALG) anyhow is lower than 2280 mg/L, depending significantly on the adaptation procedure applied.

The main pollutant in RLP-wastewater causing rapid death of WH and ALG is rubber. Rubber particles stick in a film to the roots of WH and the surface of ALG-cells, so preventing the transfer of water and nutrient to the leaves or cell.

In the ponds a big amount of water is lost daily due to evapotranspiration, i.e. it can amount to values varying from 10 m^3/ha.d to more than 100 m^3/ha.d depending on ambient temperature, humidity, wind velocity and the growth of WH.

Organic surface loads (OL) up to 100 and 120 kg COD/ha.d can be applied for design of ALG and WH ponds respectively. At influent COD concentrations below 300 mg/L effluent COD concentrations will be achieved below 100 mg/L. In order to have oxygen in the effluent, in ALG pond low OL should be used.

When operated in series, WH-ponds should precede and come after the ALG-pond. An WH barrier at the beginning and at the end of the pond is essential to remove rubber particle from the influent and ALG from the effluent.

7.7 FULL SCALE RLP WASTEWATER TREATMENT PLANT

Laboratory experimental data were used to design a pilot and full scale wastewater treatment plant in Lai Khe (Binh Duong province) and Long Thanh (Dong Nai province) Rubber Latex Processing Factory. The full scale wastewater treatment plant in Long Thanh has been operated for 4 months, starting in August 1995.

The wastewater treatment plant consists of the skimming tank, a UASB-reactor composed of 6 compartments, an aquatic plant pond system and a pumping station to transfer wastewater from the skimming tank to the UASB-reactor.

The volume of the skimming tank sufficed for equalizing the fluctuations in the flow and composition of the wastewater. However, this certainly was not the case for an effective removal of rubber particles. The particles affect quite detrimentally the performance of the UASB-process. With a wastewater

7.1 INLEIDING

Sinds 1990 is Vietnam, als gevolg van de overgang van een zuiver geleide naar een meer marktgerichte economie, economisch sterk gegroeid. Deze aanzienlijke en snelle economische ontwikkeling, met name in een aantal industriele en stedelijke gebieden, is niet vergezeld gegaan met voldoende aandacht voor de schadelijke neveneffecten, in het bijzonder de aantasting van het milieu. Vietnam heeft te lijden onder verschillende soorten van milieuvervuiling, die allen voor het grootste deel een gevolg zijn van de te snelle industriele ontwikkeling. Deze schadelijke neveneffecten worden echter goed onderkend door de centrale en regionale overheden.

De rubber/latex verwerkende industrie (RLP) is, naast meerdere andere industrieen, een van de industrietakken, die door de hoge productie een sterke bijdrage levert aan de vervuiling van het milieu.

Jaarlijks lozen meer dan 29 RLP fabrieken, met een capaciteit van 170.000 ton/jaar (Hoofdstuk 2), ongeveer 4,2-5,1 millioen m^3 afvalwater met een hoge vervuilingsgraad in het milieu. Dit leidt tot een sterke vervuiling van het oppervlaktewater, alsmede het grondwater en de atmosfeer. Het spreekt voor zich dat deze vervuiling een nogal schadelijk effect heeft op de bevolking, die in de buurt van deze bedrijven wonen.

Om een oplossing te bieden aan de watervervuiling veroorzaakt door de lozing van RLP-afvalwater is de afgelopen jaren getracht behandeling met waterzuiveringsinstallaties, zoals conventionele aktiefslibinstallaties en stabilisatievijvers, in te voeren. Deze processen hebben echter ernstige bezwaren, zoals het hoge energieverbruik en de hoge surplus-slibproductie bij het aktiefslibproces en het grote benodigde oppervlak en stankproblemen bij stabilisatievijvers. Met het oog op deze bezwaren kunnen hoog belastbare anaerobe waterzuiveringssystemen, met nam het UASB-proces, een aantrekkelijk alternatief bieden.

Het doel van dit onderzoek is na te gaan of het UASB-proces geschikt is voor de behandeling van RLP-afvalwater onder de omstandigheden, zoals die voorkomen in Zuid Vietnam. Naast anaerobe zuivering is ook aandacht besteed aan de nazuivering van het UASB-effluent, om te kunnen voldoen aan de nationale lozingseisen van Vietnam.

Het onderzoek is uitgevoerd van november 1990 tot mei 1991 en van mei 1993 tot oktober 1993 in Nederland en in de periode van 1991 tot 1995 in Zuid Vietnam.

7.2 DOEL VAN HET PROEFSCHRIFT

Het hoofddoel van dit proefschrift is de toepasbaarheid van het UASB-proces en enkele geschikte nazuiveringsprocessen voor de behandeling van RLP-afvalwater vast te stellen.

Hoofdstuk 1 geeft een beschrijving van anaerobe afvalwaterzuiveringsprocessen en in hoofdstuk 2 wordt een overzicht gegeven van de hoeveelheid en aard van het RLP-afvalwater. Dit overzicht is gebaseerd op metingen en waarnemingen bij 6 RLP-bedrijven. Bovendien wordt in dit hoofdstuk een beschrijving gegeven van het rubber/latex-proces.

In hoofdstuk 3 worden de resultaten gegeven van orienterend onderzoek naar de toepasbaarheid van het anaerobe proces voor de behandeling van RLP-afvalwater. Om dit doel te bereiken werden verschillende series van batch experimenten uitgevoerd voor het vaststellen van 1) de specifieke methanogene aktiviteit van 4 soorten entslib, die beschikbaar zijn in Zuid Vietnam, 2) de anaerobe biologische afbreekbaarheid van het RLP-afvalwater, 3) de anaerobe afbraak van eiwit, 4) het effect van de pH op het anaerobe gistingsproces, 5) het effect van zuurstof en menging op de specifieke methanogene aktiviteitstest (SMA) en 6) het effect van de duur van de bewaarperiode op de SMA van het slib.

In hoofdstuk 4 worden experimentele resultaten gepresenteerd, die zijn verkregen met proeven met een laboratoriumschaal UASB-reactor voor de behandeling van RLP-afvalwater. Ook worden resultaten weergegeven van experimenten met het doel het effect van de pH en effluentrecirculatie op het zuiveringsresultaat vast te stellen.

Hoofdstuk 5 beschrijft het onderzoek naar de nazuivering van anaeroob effluent met stabilisatievijvers met waterplanten, zoals waterhyacinth en algen.

In hoofdstuk 6 worden het ontwerp beschreven van een zuiveringsinstallatie op praktijkschaal voor de Long Thanh fabriek in de provincie Dong Nai en de experimentele gegevens van de eerste 4 maanden, dat deze installatie in bedrijf was.

7.3 EIGENSCHAPPEN VAN HET RUBBER/LATEX AFVALWATER IN VIETNAM

Uit het overzicht van de gegevens, die zijn verkregen van de zes RLP bedrijven blijkt dat RLP-afvalwater vooral vrijkomt bij twee hoofdprocesstappen, en wel de coagulatie stap (serum) en bij het vermalen en versnijden. De meeste gegevens werden verzameld bij de Long Thanh industrie. Dit bedrijf heeft een productiecapaciteit van 10.000 ton blokken rubber per jaar (op basis van drooggewicht).

Het serum-afvalwater heeft een hoge CZV, en wel tot waarden van 5.015-9.962 mg/L, terwijl de pH laag is met waarden in de range van 4,95-5,24. De totale hoeveelheid serumafvalwater bij de Long Thanh fabriek bedraagt 224-300 m^3/d, maar er komen zeer sterke schommelingen voor.

De hoeveelheid afvalwater die wordt gevormd bij het vermalen en versnijden bedraagt 1.500-1.800 m^3/d bij de Long Thanh fabriek, hetgeen een bijdrage betekent tot 80-90% van de totale hoeveelheid afvalwater. Het CZV-gehalte van dit afvalwater is echter laag, te weten 1.800-2.400 mg/L en de pH is hoger met waarden van 6,12-6,43. Gedurende het vermalen en versnijden wordt er 8,64-25,92 m^3/h afvalwater geproduceerd, welke hoeveelheid alleen afhangt van het aantal machines dat in bedrijf is.

Het RLP-afvalwater bevat hoofdzakelijk gemakkelijk afbreekbaar organisch material, zoals vluchtige vetzuren (azijnzuur/mierezuur), suikers, eiwitten en vetten, naast minerale zouten. Als gevolg van de aanwezigheid van deze verbindingen is RLP-afvalwater in principe goed geschikt voor biologische zuivering. Het ruwe afvalwater bevat echter ook niet gecoaguleerde rubberdeeltjes in concentraties tot 350 mg/L. Omdat deze deeltjes het anaerobe biologische proces flink nadelig kunnen beinvloeden, moeten deze ingredienten verwijderd worden, voordat het afvalwater wordt aangeboden aan het zuiveringsproces.

Met het oog op de sterke fluctuaties in zowel de vervuilingsgraad als het debiet is het nodig om een buffertank te installeren voor de afvalwaterzuiveringsinstallatie. Het is mogelijk om de buffertank van een drijflaagruimer te voorzien waarmmee drijvende rubberdeelijes verwijderd kunnen worden.

7.4 TOEPASBAARHEIDSONDERZOEK VAN DE UASB-REACTOR VOOR DE BEHANDELING VAN RUBBER/LATEX AFVALWATER IN VIETNAM

Op grond van de beschikbare informatie over de opstartprocedure van het UASB-proces (Lettinga, 1995) zijn vier soorten potentieel interessante entslibben, die te verkrijgen zijn in Zuid Vietnam, geselecteerd. Dit zijn verse varkensmest (FPM), uitgegiste varkensmest (DPMS), bodemslib van een vervuild kanaal in de stad (CS) en slib uit een septic tank (STS). Voor ieder van deze slibsoorten werd het verloop van de opstart onderzocht in een UASB-reactor op laboratoriumschaal, terwijl voor een entslib eveneens de opstart met een praktijkschaal reactor is gevolgd, om na te gaan hoe de duur van de eerste opstart kan worden beperkt.

Met behulp van de experimentele resultaten kon worden vastgesteld, dat de specifieke methanogene aktiviteiten van DPMS, CS, STS en FPM, respectievelijk 0,13-0,26 g CZV/g VSS.d, 0,12-0,15 g CZV/g VSS.d, 0,11-0,12 g CZV/g VSS.d en verwaarloosbaar waren. In principe kunnen drie van de geselecteerde slibsoorten worden gebruikt als entslib voor het opstarten van een UASB-reactor. DPMS werd echter als het meest geschikte entslib gekozen op grond van de volgende voordelen, die dit slib heeft ten opzichte van de andere:

1. Het is beschikbaar in grote hoeveelheden in Zuid Vietnam,
2. Het heeft een relatief hoge specifieke methanogene aktiviteit,
3. De gezondheidsrisico's zijn laag bij gebruik van dit slib.

Afgezien van het probleem van het vinden van het meest geschikte entslib, is het algemeen bekend dat een ander belangrijke factor, die bepaalt of anaerobe zuivering toepasbaar is, wordt gevormd door de biologische afbreekbaarheid van de organische vervuiling die aanwezig is in het RLP-afvalwater. Het grootste deel van het organische materiaal in RLP-afvalwater, bestaande uit suikers, eiwitten en vetten, wordt eerst omgezet in vluchtige vetzuren, welke vooral bestaan uit acetaat en relatief geringe hoeveelheden propionaat en butyraat. Uit de experimenten bleek dat de biologische afbreekbaarheid van het organische materiaal in RLP-afvalwater 90-95% bedraagt. Sommige eiwitten uit het afvalwater, zoals heveine, bleken echter erg stabiel en slecht afbreekbaar te zijn. De resultaten maakten duidelijk, dat anaerobe zuivering potentieel zeer geschikt is voor de behandeling van RLP-afvalwater.

Met behulp van een SMA-test, die veel eenvoudiger is en daarom meer geschikt voor onderzoek in ontwikkelingslanden als Vietnam, werden aanvullende experimenten uitgevoerd met als doel het effect van de pH, zuurstof en de mengcondities vast te stellen. Bovendien werd het effect van de bewaartijd van slib onderzocht.

7.5 BEHANDELING VAN RUBBER/LATEX AFVALWATER MET LABORATORIUMSCHAAL UASB-REACTOREN

Om ontwerp-parameters voor proefinstallaties en praktijkschaal reactoren voor de behandeling va RLP-afvalwater te kunnen vaststellen, werden op laboratoriumschaal experimenten uitgevoerd met kontinu doorstroomde reactoren.

Uit de resultaten, die met deze experimenten werden verkregen, bleek dat het UASB-proces kan worden toegepast bij organische volumebelastingen tot 28,5 kg CZV/m^3.d., waarbij een CZV-verwijderingsrendement van 79,8-87,9% werd verkregen. De overeenkomstige hydraulische belastingen liepen daarbij op tot 7,3-9,1 m^3/m^3.d bij een hydraulische verblijftijd (HRT) en een opwaartse stroomsnelheid tot 0,4 m/h (9,6 m/d). Bij alle experimenten was, bij de beeindiging van proef, de hoogte van het slibbed in de reactoren 12-15 cm, hetgeen aangeeft dat in feite hogere organische volumebelastingen kunnen worden gehaald door eenvoudig de hoeveelheid slib (hoogte van het slibbed) in de reactor te verhogen, bijvoorbeeld door meer entslib te gebruiken. Door de juiste opstartprocedure te volgen (Hulshoff Pol, 1989; Lettinga, 1995), was het bovendien mogelijk met RLP-afvalwater als substraat, binnen een period van 21-24 dagen, een goede kwaliteit korrelslib te vormen met uitgegiste varkensmest als entslib.

Lage pH-waarden van RLP-afvalwater (tot pH=4,8) gaven een duidelijk nadelig effect op de zuiveringsresultaten van de UASB-reactor te zien. De tijd, die er overheen gaat, voordat het nadelige effect van de lage pH op de resultaten van het UASB-systeem tot uiting komt, hangt behalve van de pH van het influent en de hoeveelheid niet verzuurd organisch materiaal, dat aanwezig is in de voedingsoplossing, vooral ook af van de buffercapaciteit van het slibbed (dat wil zeggen van de opgebouwde hoeveelheid alkaliniteit in het slib) en de toegepaste volumebelasting. Ook werd echter geconstateerd dat het systeem, en dus het slib, zich redelijk goed kan herstellen van een zure schok en soms zelfs in een relatief korte periode. De herstelperiode hangt sterk af van:

+ De samenstelling van het afvalwater,
+ De eigenschappen van het slib,
+ De toegepaste belasting.

In het beschreven experiment herstelde het UASB-systeem volledig binnen 2-3 dagen, wanneer pH-waarden in het influent in het gebied van 6,0-6,2 voorkomen.

De lage influent pH, te weten 4,5-4,8, en de hoge pH-waarde (in de range 8,5-9,4) in het effluent (en dus ook in de rector) die verkregen kan worden, kan bij het bedrijven van een UASB-reactor voor de behandeling van RLP-afvalwater een serieus probleem vormen, in het geval mierezuur wordt gebruikt voor de uitvlokking van de latex. Deze problemen kunnen worden voorkomen door recirculatie van het effluent toe te passen of - indien mogelijk - door de mierezuur-concentratie in het afvalwater binnen de perken te houden.

7.6 SYSTEEM VAN EEN VIJVER MET WATERPLANTEN, NAZUIVERING

Water hyacinth (WH) kan RLP-afvalwater met CZV-concentraties tot 2.480 mg/L, en in sommige gevallen tot 2.900 mg/L goed aan, terwijl de toepasbare concentratie voor algen (ALG) echter lager is dan 2.280 mg/L, welke waarde sterk wordt bepaald door de toegepaste adaptatieperiode.

De belangrijkste bron van vervuiling in RLP-afvalwater, die een snelle afsterving van WH en ALG veroorzaakt, is rubber. Rubber hecht zich als een film op de wortels van WH en het oppervlak van de ALG-cellen, waardoor het transport van water en nutrienten naar de bladeren of de cellen wordt geblokkeerd.

In de vijvers gaat dagelijks een grote hoeveelheid water verloren door evapotranspiratie. Dit kan oplopen tot waarden van 10 m^3/ha.d tot meer dan 100 m^3/ha.d in afhankelijkheid van de omgevingstemperatuur, de luchtvochtigheid, de windsnelheid en de groeisnelheid van WH.

Organische oppervlaktebelastingen (OL) tot 100 en 120 kg CZV/ha.d kunnen toegepast worden voor het ontwerp van respectievelijk WH en ALG vijvers. Bij influent CZV-concentraties onder 300 mg/L worden effluent CZV-concentraties van minder dan 100 mg/L verkregen. Om zuurstof in het effluent te krijgen, moeten bij ALG-vijvers een lage OL worden toegepast.

Als de vijvers in serie worden toegepast, dan moeten WH-vijvers voor en na de ALG-vijver komen. Een barriere van WH in het begin en het eind van de vijver is noodzakelijk voor het verwijderen van rubberdeeltjes van het influent en algen uit het effluent.

7.7 BEHANDELING VAN RLP-AFVALWATER OP PRAKTIJKSCHAAL

De gegevens die werden verkregen uit het laboratoriumonderzoek werden gebruikt voor het ontwerp van een proefinstallatie en een waterzuiveringsinstallatie op praktijkschaal bij de Lai Khe (Binh Duong provincie) en Long Thanh (Dong Nai provincie) rubber latex verwerkingsbedrijven. De praktijkschaal zuiveringsinstallatie in Long Thanh is gedurende 4 maanden gevolgd, vanaf augustus 1995.

De zuivering bestaat uit een schuimverwijdering, een uit 6 compartimenten bestaande UASB-reactor, een vijver met waterplanten en een pompstation om het afvalwater te transporteren van de schuimverwijderingstank naar de UASB-reactor.

Het volume van de schuimverwijderingstank was groot genoeg om de schommelingen in het debiet en samenstelling van het afvalwater te bufferen. Het was echter niet voldoende voor een effectieve verwijdering van de rubberdeeltjes. Deze deeltjes hadden een flink nadelig effect op de zuiveringsresultaten van de UASB-proces. Bij een debiet van ongeveer 1800 m^3/d was de hoeveelheid teruggewonnen rubber 350-400 kg/d.

De zuivering in de UASB-reactor verliep erg goed in de eerste twee weken na de opstart, d.w.z de CVZ_{fil}-concentratie daalde van 2.500-3.000 mg/L naar 800-900 mg/L en het effluent was tamelijk helder met een gehalte aan zwevende stoffen van 94-210 mg/L, terwijl geen enkel schuim verscheen op de oppervlakte van de stabilisatievijvers. Na deze beginperiode liepen de zuiveringsresultaten in de UASB-reactor echter terug, wat vooral een gevolg was van de aanwezigheid van gedispergeerde rubberdeeltjes in het influent, hetgeen tot schuimlaagvorming leidde. Het systeem bleef in bedrijf met het doel een geschikte oplossing voor dit probleem, maar helaas kon vooralsnog onvoldoende aandacht worden besteed aan het elimineren hiervan. Het was in ieder geval duidelijk, dat het anaerobe entslib zich in korte tijd onvoldoende kan aanpassen aan het betreffende rubber afvalwater. Om de zuiveringsresultaten te verbeteren, en nog belangrijker, om goede procescondities te scheppen voor toepassing van UASB-reactoren, is een afdoende methode nodig voor het verwijderen van de rubberdeeltjes. Onder de huidige condities, die aanwezig zijn bij de Long Thanh fabriek, is nazuivering met een stabilisatievijver nog steeds een goede methode, omdat het op zijn minst als een goede buffer dient voor het geval de resultaten in de UASB slecht zijn; het le ert een effluent van goede kwaliteit geschikt om te lozen in het milieu, maar het systeem veroorzaakt dan wel ernstige tank.

7.8 AANBEVELINGEN VOOR VERDER ONDERZOEK

Het is duidelijk dat de zwevende deeltjes, met name de rubberdeeltjes, het UASB-systeem nogal nadelig beinvloeden. Het is daarom essentieel, dat er een effectieve methode wordt ontwikkeld om voldoende zwevende deeltjes te verwijderen, omdat de biologische zuivering met een UASB-reactor dan goed zal verlopen en hoge zuiveringsrendementen kunnen worden verkregen bij hoge belastingen met RLP-afvalwater.

CHƯƠNG 7

TÓM TẮT VÀ THẢO LUẬN

7.1 GIỚI THIỆU

Từ 1990, nhờ chuyển đổi từ nền kinh tế bao cấp sang nền kinh tế thị trường Việt Nam đã có những bước phát triển vượt bậc về mặt kinh tế. Sự phát triển kinh tế nhanh chóng, đặc biệt là việc hình thành nhiều khu công nghiệp và các vùng đô thị, kèm theo việc quan tâm không đầy đủ về các ảnh hưởng có hại đã làm cho chất lượng môi trường ngày càng xấu đi. Việt Nam cũng đã chịu nhiều thiệt hại do vấn đề ô nhiễm môi trường từ việc phát triển công nghiệp quá nhanh. Các vấn đề về ô nhiễm môi trường đã được các cơ quan môi trường của Nhà Nước và địa phương ghi nhận đầy đủ.

Trong công nghiệp, nhà máy chế biến mủ cao su là một trong các nhà máy gây ô nhiễm lớn nhất đến môi trường.

Hàng năm, 29 nhà máy chế biến mủ cao su với công suất 170.000 tấn/năm (Chương 2) xả vào môi trường khoảng 4,2 – 5,1 triệu m^3 nước thải với nồng độ các chất ô nhiễm cao. Nước thải của nhà máy sơ chế mủ cao su đã gây ô nhiễm nặng nề đến môi trường nước mặt, nước ngầm và không khí. Việc ô nhiễm này đã ảnh hưởng nghiêm trọng đến đời sống của nhân dân khu vực xung quanh nhà máy.

Trong những năm gần đây, nhiều hệ thống xử lý nước thải, như quá trình bùn hoạt tính hiếu khí và hồ sinh vật, được xây dựng để xử lý nước thải nhằm giải quyết những vấn đề ô nhiễm môi trường do nước thải của nhà máy sơ chế mủ cao su gây ra. Nhưng các quá trình xử lý này, như quá trình bùn hoạt tính hiếu khí, thường có nhiều nhược điểm, chẳng hạn tiêu thụ nhiều năng lượng, khối lượng bùn sinh ra lớn, hồ sinh vật chiếm nhiều diện tích và tạo nên mùi hôi thối. Trên cơ sở nhược điểm của các quá trình trên, hệ thống xử lý kị khí tốc độ cao, đặt biệt là quá trình UASB (Upflow Anaerobic Sludge Blanket – dòng chảy ngược với lớp bùn kị khí), có thể là phương án thích hợp để xử lý nước thải của nhà máy chế biến mủ cao su.

Nghiên cứu này tập trung vào việc đánh giá tính khả thi của quá trình UASB xử lý nước thải chế biến mủ cao su trong điều kiện của tỉnh phía Nam của Việt Nam. Thêm vào đó, quá trình xử lý triệt để (bậc ba) cũng được nghiên cứu để nước thải sau khi xử lý kị khí đạt tiêu chuẩn chất lượng của Việt Nam trước khi xả vào nguồn.

Nghiên cứu này được thực hiện ở Hà Lan từ tháng 10/1990 đến tháng 5/1991 và tháng 5/1993 đến tháng 10/1993, tại Việt Nam từ năm 1991 đến năm 1995.

7.2 MỤC ĐÍCH CỦA LUẬN ÁN

Mục đích chính của luận án tiến sĩ này là đánh giá khả năng của quá trình UASB xử lý nước thải chế biến mủ cao su và tính khả thi của các quá trình xử lý bậc ba đối với nước thải sau khi đã xử lý bằng quá trình kị khí.

Chương 1 tổng quan các quá trình kị khí xử lý nước thải và chương 2 trình bày các kết quả khảo sát, nghiên cứu lưu lượng và thành phần nước thải chế biến mủ cao su. Các nghiên cứu này được thực hiện tại sáu nhà máy chế biến mủ cao su. Qui trình công nghệ chế biến mủ cao su từ latex và mủ đất cũng được trình bày trong chương 2.

Chương 3 trình bày các kết quả nghiên cứu ban đầu về tính khả thi của quá trình kị khí xử lý nước thải chế biến mủ cao su. Để đạt được mục đích này các mô hình thí nghiện tĩnh đã được thực hiện bao gồm 1) thí nghiệm xác định hoạt tính methane đặt biệt (SMA) của bốn loại bùn sẵn có ở các tỉnh phía Nam của Việt Nam, 2) khả năng phân hủy sinh học kị khí của nước thải chế biến mủ cao su, 3) khả năng phân hủy sinh học kị khí của protein, 4) ảnh hưởng của pH đến quá trình phân hủy kị khí, 5) ảnh hưởng của oxy và điều kiện khuấy trộn đến thí nghiệm xác định hoạt tính methane đặt biệt của bùn, và 6) ảnh hưởng của thời gian lưu giữ bùn đến hoạt tính methane đặt biệt.

Chương 4 trình bày kết quả thí nghiệm thực hiện trên mô hình UASB trong điều kiện phòng thí nghiệm với nước thải chế biến mủ cao su, các thí nghiệm này cũng bao gồm cả các thí nghiệm về ảnh hưởng của pH đến hoạt động của UASB và ảnh hưởng của việc tuần hoàn nước thải sau khi xử lý.

Chương 5 là các thí nghiệm về các quá trình xử lý triệt để (bậc ba) xử lý nước thải sau quá trình kị khí bằng việc sử dụng hệ thống hồ sinh vật với sự tham gia của các loài thực vật nước như lục bình và tảo.

Chương 6 mô tả thiết kế nhà máy xử lý nước thải tại nhà máy chế biến mủ cao su Long Thành, Đồng Nai và kết quả thí nghiệm của việc vận hành hệ thống xử lý trong 4 tháng.

7.3 TÍNH CHẤT CỦA NƯỚC THẢI CHẾ BIẾN MỦ CAO SU TẠI VIỆT NAM

Kết quả khải sát tại nhà máy chế biến mủ cao su tại các tỉnh phía Nam, Việt Nam đã cho thấy nước thải của quá trình chế biến mủ cao su xả ra từ hai công đoạn chính, đánh đông mủ cao su và cán băm. Nhà máy Long Thành có công suất 10.000 tấn/năm với sản phẩm chính là cao su khối.

Nước thải đánh đông có nồng độ COD cao đến 5.015 – 9.962 mg/L và pH thấp 4,95 - 5,24. Lưu lượng nước thải xả ra từ quá trình đánh đông tại nhà máy chế biến mủ cao su Long Thành khoảng 224 – 300 m^3/ngđ và dao động rất lớn.

Tại nhà máy Long Thành, lưu lượng nước thải xả ra từ quá trình các băm dao động trong khoảng 1.500 – 1.800 m^3/ngđ, chiếm khoảng 80 – 90% tổng lưu lượng nước thải của cả nhà máy, nồng độ COD của nước thải loại này thấp, khoảng 1.800 – 2.400 mg/L và pH cao hơn 6,12 – 6,43. Ở giai đoạn cán, lưu lượng nước thải dao động khoảng 8,64 – 25,92 m^3/h trong thời gian làm việc và phụ thuộc vào số lượng máy cán.

Nước thải chế biến mủ cao su chủ yếu chứa các hợp chất hữu cơ dễ phân hủy sinh học, như các loại acid béo bay hơi (acid acetic/acid formic), các loại đường, đạm, chất béo và một số khoáng chất khác. Trên cơ sở các chất nói trên, nước thải chế biến mủ cao su, về nguyên tắc là thích hợp cho quá trình xử lý sinh học. Nhưng nước thải thô cũng chứa các hạt cao su chưa keo tụ với nồng độ đến 350 mg/L. Vì các hạt cao su này có thể ảnh hưởng xấu đến quá trình xử lý sinh học kị khí, nên chúng cần phải tách khỏi nước thải trước khi đưa vào xử lý sinh học.

Do lưu lượng và thành phần nước thải dao động lớn cần phải xây dựng bể điều hòa trước nhà máy xử lý. Có thể kết hợp bể điều hòa và bể gạn mủ cao su.

7.4 CÁC NGHIÊN CỨU KHẢ THI CỦA THIẾT BỊ UASB XỬ LÝ NƯỚC THẢI CHẾ BIẾN MỦ CAO SU TẠI VIỆT NAM

Trên cơ sở các nghiên cứu về quá trình khởi động UASB (Lettinga, 1995), bốn (4) loại bùn sẵn có ở Việt Nam được lựa chọn để nghiên cứu, phân lợn tươi (FPM), phân lợn đã phân hủy (DPMS), bùn kênh rạch bị ô nhiễm (CS) và bùn của bể tự hoại (STS). Các loại bùn này được nghiên cứu trên các thiết bị UASB trong phòng thí nghiệm về khả năng khởi động ban đầu và sử dụng để vận hành bể UASB của nhà máy xử lý nước thải nhằm làm giảm thời gian khởi động ban đầu. Các kết quả thí nghiệm cho thấy rằng hoạt tính methane đặc biệt của DPMS, CS, STS và FPM tương ứng là 0,13 – 0,26 gCOD/gVSS.ngđ, 0,12 – 0,15 gCOD/gVSS.ngđ, 0,11 – 0,12 gCOD/gVSS.ngđ và không đáng kể. Về nguyên tắc ba loại bùn đầu có thể sử dụng để khởi động bể UASB nhưng bùn DPMS được lựa chọn là loại bùn tốt nhất để đưa vào bể UASB vì các ưu điểm sau so với loại bùn khác:

- Sẵn có tại Việt Nam với khối lượng lớn;
- Hoạt tính methane đặc biệt tương đối cao;
- Ít nguy hại về mặt sinh học (vi trùng gây bệnh).

Ngoài vấn đề tìm kiếm loại bùn thích hợp, nhiều yếu tố quan trọng ảnh hưởng đến tính khả thi của quá trình xử lý kị khí, như khả năng phân hủy của các chất hữu cơ chứa trong nước thải chế biến mủ cao su. Hầu hết các chất hữu cơ chứa trong nước thải, bao gồm các loại đường, đạm và chất béo, trước tiên được chuyển hóa thành VFA, chủ yếu là acid acetic và một lượng nhỏ acid propionic và butyric. Trong thí nghiệm, chúng tôi đã tìm thấy khả năng phân hủy của các chất hữu cơ chứa trong nước thải đạt từ 90 – 95%. Nhưng một vài loại protein, như hevein, là rất bền vững và ít khi bị phân hủy sinh học. Vì những lý do này, rõ ràng là quá trình kị khí có khả năng áp dụng cao trong quá trình xử lý nước thải chế biến mủ cao su.

Việc sử dụng thí nghiệm hoạt tính methane đặc biệt của bùn là đơn giản và đủ chính xác để áp dụng ở các nước đang phát triển như Việt Nam và thí nghiệm này được thực hiện để đánh giá ảnh hưởng của pH, oxy và điều kiện khuấy trộn. Thêm vào đó, ảnh hưởng của thời gian lưu giữ bùn cũng được nghiên cứu.

7.5 XỬ LÝ NƯỚC THẢI CHẾ BIẾN MỦ CAO SU TRÊN MÔ HÌNH PHÒNG THÍ NGHIỆM UASB TẠI VIỆT NAM

Các thí nghiệm trên mô hình phòng thí nghiệm có dòng chảy liên tục và được thực hiện để xác định các thông số thiết kế cho trạm pilot và nhà máy xử lý nước thải chế biến mủ cao su.

Từ kết quả thu được trong các thí nghiệm, rõ ràng là quá trình UASB có thể áp dụng để xử lý nước thải chế biến mủ cao su với tải trọng hữu cơ đến 28,5 kgCOD/m^3.ngđ, hiệu quả xử lý đạt 79,8 – 87,9%, tương ứng với tải trọng thủy lực đến 7,3 – 9,1 m^3/m^3. Thời gian lưu nước là HRT là 3,3 – 2,6 h và vận tốc nước đi lên là 0,4 m/h (9,6 m/ngđ). Trong tất cả các thí nghiệm, chiều cao lớp bùn trong thiết bị UASB là 12 – 15 cm vào cuối giai đoạn nghiên cứu, điều này nói lên rằng tải trọng chất hữu cơ có thể tăng lên khi tăng khối lượng bùn. Thêm vào đó, bằng việc áp dụng qui trình vận hành hợp lý (Hulshoff Pol, 1989, Lettinga, 1995) quá trình tạo hạt từ bùn phân lợn đã phân hủy xuất hiện trong vòng 21 – 24 ngày đối với nước thải chế biến mủ cao su.

Giá trị pH thấp (pH = 4,8) của nước thải chế biến mủ cao su đã ảnh hưởng xấu đến quá trình hoạt động của UASB. Thời gian của bùn trước khi chịu ảnh hưởng xấu do pH thấp phụ thuộc vào một phần pH của nước thải và lượng các chất hữu cơ không bị acid hóa của nước thải thô, đặc biệt phụ thuộc vào khả năng đệm của bùn (như độ kiềm tích tụ trong bùn) và tải trọng chất hữu cơ. Nhưng các thí nghiệm cũng tìm thấy rằng, toàn bộ hệ thống, trong đó có bùn, có thể hồi phục tương đối tốt trong thời gian ngắn sau khi bị ảnh hưởng do pH thấp. Thời gian hồi phục phụ thuộc vào:

- Tính chất của nước thải;
- Tính chất của bùn;
- Tải trọng hữu cơ.

Trong các thí nghiệm đã được thực hiện, thời gian hồi phục hoàn toàn của hệ thống UASB là 2 - 3 ngày sau khi sử dụng nước thải có pH 6,0 – 6,2.

Với pH đầu vào thấp 4,5 – 4,8 , pH của nước thải sau khi xử lý có thể rất cao (từ 8,5 tới 9,4) đã thực sự là vấn đề khó khăn khi vận hành bể UASB xử lý nước thải chế biến mủ cao su sử dụng acid formic trong khâu đánh đông. Vấn đề này có thể khắc phục bằng việc tuần hoàn nước thải sau khi xử lý, hoặc – có thể – giới hạn nồng độ acid formic trong nước thải.

7.6 HỆ THỐNG HỒ SINH VẬT, XỬ LÝ TRIỆT ĐỂ (BẬC BA)

Lục bình (WH) có thể chịu dựng ở nồng độ COD trong nước thải chế biến mủ cao su đến 2.480 mg/l và trong một vài trường hợp có thể đến 2.900 mg/l, còn đối với tảo (ALG) thì thấp hơn, khoảng 2.280 mg/l, phụ thuộc vào quá trình thích nghi.

Chất ô nhiễm chính trong nước thải chế biến mủ cao su gây chết hàng loạt và nhanh chóng lục bình và tảo là cao su. Các hạt cao su dính bám và tạo thành màng trên bộ rễ của lục bình và bề mặt tảo đã ngăn cản việc vận chuyển nước và chất dinh dưỡng đến lá hoặc tế bào.

Trong các hồ sinh vật, một khối lượng lớn nước mất đi do bay hơi, từ 10 m^3/ha.ngđ đến hơn 100 m^3/ha.ngđ phụ thuộc vào nhiệt độ và độ ẩm của khí quyển, tốc độ gió và sự tăng trưởng của lục bình.

Tải trọng bề mặt (OL) đến 100 và 120 kgCOD/ha.ngđ có thể áp dụng để thiết kế hồ sinh vật có tảo và lục bình. Với nồng độ COD của nước thải đầu vào dưới 300 mg/L, sau khi xử lý nồng độ COD sẽ dưới 100 mg/L. Để oxy có mặt trong nước, hồ sinh vật với sự tham gia của tảo phải có tải trọng thủy lực thấp.

Khi vận hành nối tiếp nhau, hồ sinh vật với sự tham gia của lục bình phải đứng trước và sau hồ tảo. Hàng rào lục bình trước và sau hồ sinh vật sẽ xử lý các hạt cao su ở trước hồ và tảo ở sau hồ.

7.7 NHÀ MÁY XỬ LÝ NƯỚC THẢI CHẾ BIẾN MỦ CAO SU

Số liệu trong phòng thí nghiệm được sử dụng để thiết kế cho trạm xử lý dạng pilot tại nhà máy chế biến cao su ở Lai Khê (Bình Dương) và nhà máy xử lý nước thải tại nhà máy chế biến mủ cao su Long Thành (Đồng Nai). Nhà máy xử lý nước thải tại Long Thành được vận hành trong 4 tháng, từ tháng 8 năm 1995.

Nhà máy xử lý nước thải bao gồm bể tách mủ cao su, bể UASB 6 ngăn, hệ thống hồ sinh vật 2 bậc và trạm bơm đưa nước từ bể gạn mủ cao su vào bể UASB.

Thể tích của bể gạn mủ cao su đủ để điều hòa sự dao động của lưu lượng và thành phần nước thải. Nhưng không có hiệu quả trong việc tách các hạt cao su. Các hạt cao su này ảnh hưởng xấu đến sự hoạt động của bể UASB. Với lưu lượng nước thải 1.800 m^3/ngđ, khoảng 350 – 400 kg mủ cao su được thu hồi mỗi ngày.

Trong hai tuần đầu sau khi khởi động, bể UASB hoạt động rất tốt, nồng độ COD_{loc} giảm từ 2.500 – 3.000 mg/L còn 800 - 900 mg/Ll, nước thải sau khi xử lý khá trong với nồng độ SS khoảng 94 – 210 mg/L và không đóng váng trên mặt hồ sinh vật. Nhưng sau đó hiệu quả xử lý của bể UASB giảm xuống vì các hạt cặn cao su trong nước thải và tạo thành lớp màng tích tụ trên bề mặt. Việc vận hành được tiếp tục thực hiện để tìm cách giải quyết thích hợp. Nhưng thật không may mắn là điều kiện không cho phép. Dù sao đi nữa thì một điều rõ ràng là bùn kị khí trong có khả năng thích nghi trong thời gian ngắn. Để cải thiện hiệu quả xử lý cần phải tạo điều kiện môi trường tốt cho việc áp dụng bể UASB và các phương pháp đầy đủ để xử lý cặn lơ lửng là điều cần thiết. Trong điều kiện hiện nay ở nhà máy chế biến mủ cao su Long Thành, hệ thống hồ sinh vật vẫn là quá trình xử lý triệt để (bậc ba), vì ít ra hệ thống hồ này hoạt động như quá trình dự phòng khi hiệu quả xử lý của bể UASB thấp, nước thải sau hồ sinh vật có chất lượng tốt trước khi xả vào nguồn nước nhưng chúng lại sinh ra mùi hôi thối.

7.8 ĐỀ NGHỊ CÁC NGHIÊN CỨU TRONG TƯƠNG LAI

Rỏ ràng là nồng độ cặn lơ lửng có nguồn gốc từ các hạt cao su không keo tụ đã ảnh hưởng xấu đến sự hoạt động của hệ thống UASB. Vì vậy cần phải nghiên cứu và áp dụng các biện pháp đầy đủ để xử lý chúng, vì như vậy quá trình xử lý sinh học của bể UASB sẽ diễn ra ổn định và có hiệu quả ở tải trọng cao.

SUSTAINABLE TREATMENT OF RUBBER LATEX PROCESSING WASTEWATER
The UASB – System Combined with Aerobic Post – Treatmet

Nguyễn Trung Việt

REFERENCES

APHA., (1989). Standard Methods for the examination of water and wastewater.

Barker, H. A. (1961). Fermentation of nitrogenous organic compounds. *In: Gunsalus, I. C. and Stanier, R. Y. (eds.). The bacteria.* Vol. 2. Academic Press, New York.

Battersby, N. S. and Wilson, V. (1988). Evaluation of a serum bottle technique for assessing the anaerobic biodegradability of organic chemicals under methanogenic conditions. *Chemosphere,* 17, 2441-2460.

Beaubien, A., Baty, M., Harduin, H., Manem, J., Mechinot, A. and Ehlinger, F. (1994). Treatment of distillery condensates with anaerobic membrane bioreactor. *In: Seventh International Symposium on Anaerobic Digestion, 23-27 January 1994, Cape Town, South Africa, Poster Paper,* pp 260-263.

Bhaskaran Nair, V. K. (1980). Handbook of natural rubber production in India. The Rubber Research Institute of India. pp 337-477.

Birch, R. R., Biver, C., Campagna, R., Gladhill, W. E., Pagga, U., Staber, J., Raust, H. and Botinck, W. J. (1989). Screening of chemcals for anaerobic biodegradability. *Chemosphere,* **19**, 1527-1550.

Bobilioff, W., (1923). Anatomy and physiology of Hevea Brasiliensis. *Part one: Anatomy of Hevea Brasiliensis.*

Breure, A. M., van Andel, J. G., (1984). Hydrolysis and acidogenic fermentation of a protein, gelatin, in an anaerobic continuous culture. *App. Microbiol. Biotechnol.* **20**, 40-45

Cadi, Z., Moletta, R., Beaubien, A. and Huyard, A. (1994). Performance of a memberane-equipped methanogenic reactor in a two-phase anaerobic digestion system. *In: Seventh International Symposium on Anaerobic Digestion, 23-27 January 1994, Cape Town, South Africa, Poster Paper,* pp 256-259.

Cardon, B. P. and Barker, H. A. (1947). Amino acid fermentation by *Clostridium propionicum* and *Diplococus glycinophilus. Arch. Biochem.* **12**: 165-180.

Chan, D. B and Pearson, E. A., (1970). Comprehensive studies of solid waste management - Hydrolysis rate of cellulose in anaerobic fermentation. SERL report No. 70-3, University of California, Berkeley.

De Zeeuw, W., (1984). Acclimatization of anaerobic sludge for UASB-reactor start-up. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Dolfing, J. (1985). Kinetic of methane formation by granular sludge at low substrate concentration. *Applied Microbiology and Biotechnology,* **22**: 77-81.

Edgar, A. T., 1958. Manual of rubber planting (Malaya). Published by The Incorporated Society of Planter, Kuala Lumpur, Federation of Malaya, pp 356-519.

Florencio, L., Jenicek, P., Field, J. A. and Lettinga, G. (1993). Effect of cobalt on the anaerobic degradation of methanol. *J. Ferment. Bioeng.* **75**: pp. 368-374.

Florencio, L., Field, J. A. and Lettinga, G. (1994a). The importance of cobalt for individual trophic groups in an anaerobic methanol degrading consortium. *Appl. Environ. Microbiol.* **60**: pp. 227-234.

Florencio, L., (1994b). The fate of methanol in anaerobic bioreactors. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Grobicki, A. and Stuckey, D. C. (1989). The role of formate in the anaerobic beffled reactor. Research note. *Wat. Res.* Vol. **12**, pp. 1599-1602.

Guier, W. and Zehner, A. J. B., 1983. Conversion process in anaerobic digestion. Water Sci. Technol., **15** (8-9), pp. 127-167.

Hien, P. M., Oanh, L. T. K., Viet, N. T. and Lettinga, G., (1998). Closed wastewater system in the tapioca industry in Vietnam. International WIMEK congress, Wageningen, The Netherlands.

Hughes, D. E. (1979). What is anaerobic digestion? An overview. *In: Anaerobic digestion. Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* pp. 1-14. Applied science publishers Ltd., London.

Hulshoff Pol L. W., (1989). The phenomenon of granulation of anaerobic sludge. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Huser, B. A., Wuhrmann, K. and Zehnder, A. J. B., (1982). *Methanothrix soehngenii* gen. nov. sp. nov., a new acetotrophic non-hydrogen-oxidizing methane bacterium. *Arch. Microbiol.,* **132:** pp. 1-9.

Iza, J., Colleran, E., Paris, J. M. and Wu, W. M., (1991). International workshop on anaerobic treatment technology for municipal and industrial wastewaters: Summary paper. *In: Anaerobic treatment technology for municipal and industrial wastewaters. Proceeding of the IAWPRC Specialised Workshop held in Valladolid, Spain, 24-26 September 1990. Wat. Sci. Tech.* Vol. 24, No. 8, pp. 1-16.

Iza, J., (1991). Fluidized bed reactors for anaerobic wastewater treatment. *In: Anaerobic treatment technology for municipal and industrial wastewaters. Proceeding of the IAWPRC Specialised Workshop held in Valladolid, Spain, 24-26 September 1990. Wat. Sci. Tech.* Vol. 24, No. 8, pp. 109-132.

James, A., Chernicharo, C. A. L., Campos, C. M. M., (1990). The development of a new methodology for the assessment of specific activity. *Wat. Res. Vol.* **24**, No. 7, pp. 813-825

Jetten M. S. M., (1991). Acetate metabolism in *Methanothrix soehngenii*. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Kato M. T., (1994). The anaerobic treatment of low strength soluble wastewaters. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Kennedy, K. J. and Droste, R. L., (1991). Anaerobic treatment in downflow stationary fixed film reactors. *In: Anaerobic treatment technology for municipal and industrial wastewaters. Proceeding of the IAWPRC Specialised Workshop held in Valladolid, Spain, 24-26 September 1990. Wat. Sci. Tech.* Vol. 24, No. 8, pp. 157-177.

Kiener A. and Leisinger, T. (1983). Oxygen sensitivity of methanogenic bacteria. *Appl. Microbiol.* **4**: 305-312.

Koster I. W., (1989). Toxicity in anaerobic digestion with emphasis on the effect of ammonia, sulfide and long-chain fatty acids on methanogenesis. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Kush, A., (1994). Isoprenoid biosynthesis: the *Hevea* factory! *Plant Physiol. Biochem.*, **32**, 761-767.

Lettinga, G., van Velsen, L., de Zeeuw, W. and Hobma, S. W., (1979). The application of anaerobic digestion to industrial pollution treatment. *In: Anaerobic digestion. Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* pp. 167-186. Applied science publishers Ltd., London.

Lettinga, G., Hobma, S. W., Klapwijk, A., van Velsen, A. F. M. and de Zeeuw, W., (1980). Use of the Upflow Sludge Blanket (USB) reactor concept for biological wastewater treatment. *Biotechnol. Bioengin.* **22**: pp. 699-734.

Lettinga, G., Grin, P., Hobma, S. W., Hulshoff Pol, L. W., Roersma, R., Sayed, S., van Velsen, A. F. M., Wiegant, W. and De Zeeuw, W., (1983a). Upflow Blanket Processes. *In: Proceeding Third International Symposium on Anaerobic Digestion, 14-19 August 1983, Boston, USA.* pp. 139-158.

Lettinga, G., Grin, P., Hobma, S. W., Hulshoff Pol, L. W., De Jong, P., Roersma, R. and De Zeeuw, W., (1983b). Design, operation and economy of anaerobic treatment. *Wat. Sci. Technol.* **15**: pp. 177-195.

Lettinga, G., de Zeeuw, W. J., Hulshoff Pol, L., Wiegant, W., Rinzema, A., (1985). Anaerobic wastewater treatment based on biomass retention with emphasis on the UASB-process. *In: Anaerobic digestion 1985. Proceedings of the Fourth International Symposium on Anaerobic Digestion, 11-15 November 1985, Guangzhou, China.* pp. 279-301.

Lettinga, G. and Hulshoff Pol, L. W., (1991). UASB process design for various types of wastewaters. *In: Anaerobic treatment technology for municipal and industrial wastewaters. Proceeding of the IAWPRC Specialised Workshop held in Valladolid, Spain, 24-26 September 1990. Wat. Sci. Tech.* Vol. 24, No. 8, pp. 87-107.

Lettinga G., (1995). Anaerobic digetion and wastewater treatment systems. *Antonie van Leeuwenhoek* **67**: pp. 3-28.

Lindner, P. and Shomer, I. (1984). Interference of azide in assays of carbohydrates. *Food Chemistry* **14**, 1-13.

Lohani, B. N. (1984). Environmental quality management. South Asian Publishers, New Delhi.

Loren, G. P., (1962). Rubber, botany, production, and utilization. London, Leonard Hill [Books] Limited. Interscience Publishers, INC., New York. pp 1-207.

McCarty, P. L., (1964). Anaerobic waste treatment fundamentals-part one, chemistry and microbiology. *Public Works,* **95**: pp. 107-112. Anaerobic waste treatment fundamentals - part two, environmental requirements and control. *Public Works,* **95**: pp. 123-126.

McInerney, M. J. and Bryant, M. P., (1979). Metabolic stages and energetics of microbial anaerobic digestion. *In: Anaerobic digestion. Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* pp. 61-89. Applied science publishers Ltd., London.

McInerney, M. J. (1988). Anaerobic hydrolysis and fermentation of fats and proteins. *In: Biology of anaerobic microorganism.* John Wiley & Sons. 373-415.

Moir, G. F. J. (1959). Ultracentrifugation and staining of *Hevea* latex. *Nature,* **184**, pp. 1626-1628.

Moosbrugger, RE., Loewenthal, RE., Marais, GvR., (1990). Pelletisation in a UASB system with protein (casein) as substrate. *Water SA Vol. 16* No. **3**, 171-178.

Nachaiyasit, S. and Stuckey, D. C. (1994). The anaerobic baffled reactor: influence of process parameters on system performance. *In: Seventh International Symposium on Anaerobic Digestion, 23-27 January 1994, Cape Town, South Africa, Poster Paper,* pp 271-274.

Nagarwala, N., Ranade, D. R., Dudhbhate, J. A. and Godbole, S. H. (1985). Effect of disinfectants, phenolic compounds and detergents on anaerobic digestion of cattle dung. *In: Anaerobic digestion 1985. Proceedings of the Fourth International Symposium on Anaerobic Digestion, 11-15 November 1985, Guangzhou, China.* pp. 426.

Nahle, C. (1991). The contact process for the anaerobic treatment of wastewater: Technology, design and experiences. *In: Anaerobic treatment technology for municipal and industrial wastewaters. Proceeding of the IAWPRC Specialised Workshop held in Valladolid, Spain, 24-26 September 1990. Wat. Sci. Tech.* Vol. 24, No. 8, pp. 179-191.

National Academy of Sciences, (1977). Guayule : An alternative source of naturalrubber. Washington DC, D.C.

Nishio, N., Kakizono, T., Nagai, S., Silveira, R. G. and Takemoto, S. (1992). Nutrient control by the gas evolution in methanogenesis of methanol by *Methanosarcina barkeri. J. Ferment. Technol.* **73:** pp. 481-485.

Nyns, E. J., Naveau, H. P., Chome, R. and Bertrand, Y., (1979). Digesters - A worldwide review. *In: Anaerobic digestion. Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* pp. 37-59. Applied science publishers Ltd., London

Oleszkiewicz, J. A. and Romanek, A. (1989). Granulation in anaerobic sludge bed reactors treating food indystry waste. *Biological Wastes* **27**, 217-235.

Pavlostathis, S. G. and Giraldo-Gomez, E., (1991). Kinetics of anaerobic treatment. *Wat. Sci. Tech.* Vol. 24, No. 8, pp. 35-59.

Pfeffer, J. T., (1974). Temperature effects on anaerobic fermentation of domestic refuse. *Bioeng. and Biotechnol.,* **16**: 771.

Pfeffer, J. T., (1979). Anaerobic digestion processes. *In: Anaerobic digestion. Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* pp. 15-35. Applied science publishers Ltd., London.

Polhamus, L. G. (1962). Rubber - Botany, Production and Utilization. London Leonard Hill [Books] Limited, Interscience Publishers, Inc. New York. pp 201-207.

Sayed, S. K. I., van Campen, L., Lettinga, G., (1987). Anaerobic treatment of slaughterhouse waste using a granular sludge UASB reactor. *Biological Waste,* **21**, 11-28.

Sayed, S. K. I., (1987). Anaerobic treatment of slaughterhouse wastewater using the UASB process. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Scherer, P and Sahm, H. (1981). The effect of trace elements and vitamins on the growth of *Methanosarcina barkeri. Acta Biotechnol.* **1,** 57-65.

Scherer, P., Lippert, H. and Wolff, G. (1983). Composition of the major elements and trace elements of 10 methanogenic bacteria determined by inductively coupled plasma emission spectrometry. *Biol. Trace Element Res.* **5,** pp. 149-163.

Scherer, P. (1989). Vanadium and molybdenum requirement for the fixation of molecular nitrogen by two *Methanosarcina* strains. *Arch. Microbiol.* **151,** pp. 44-48.

Schulze, D., Menkhaus, M., Fiebig, R., and Dellweg, H., (1988). Anaerobic treatment of protein-containing waste waters: correlation between coenzyme F_{420} and methane production. *Appl. Microbiol. Biotechnol.* **29**: pp 506-510

Shelton, D. R and Tiedje, J. M. (1984). General method for determining anaerobic biodegradation potential. *Appl. Environ. Microbiol.*, **47**, 850-857.

Smith, M. R. and Mah, R. A., (1978). Growth and methanogenesis by *Methanosarcina* strain 227 on acetate and methanol. *Appl. Environ. Microbiol.*, **36:** pp. 870-879.

Soedjanaatmadja, U. M. S., Subroto, T. and Beintema, J. J. (1995). The effluent of natural rubber factories is enriched in the antifungal protein hevein. *Bioresource Technology* **53,** pp. 39-41.

Son, M. (1983). Natural rubber in Vietnam (*in Vietnamese).* Vietnam rubber research institute.

Son, M. (1994). Annual report (*in Vietnamese).* Vietnam rubber research institute.

Stafford, D. A., Wheatley, B. I. and Hughes, D. E., (1979). Anaerobic digestion. *Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* Applied science publishers Ltd., London.

Standing Committee of Analysts, UK. Dept. of the Environment. (1988). The assessment of biodegradability in anaerobic digesting sludge: Method for the examination of waters and associated materials. Her Majesty's Stationery Office (HMSO), London.

Stronach, S. M., Rudd, T. and Lester, J. N., (1986). Anaerobic digestion processes in industrial wastewater treatment. Springer-Verlag. 166-167.

Tata, S. J., (1980). Studies on the lysozyme and components of microhelices of *Hevea brasiliensis* latex. PhD thesis, University of Malaya, Kuala Lumpur.

Tilche, A. and Vieira, S. M. M., (1991). Discussion report on reactor design of anaerobic filters and sludge bed reactors. *In: Anaerobic treatment technology for municipal and industrial wastewaters. Proceeding of the IAWPRC Specialised Workshop held in Valladolid, Spain, 24-26 September 1990. Wat. Sci. Tech.* Vol. 24, No. 8, pp 193-206

Tchobanoglous, G. and Burton, F. L., (1991). Wastewater engineering. Treatment, disposal & reuse. Third edition. Metcalf & Eddy, Inc. McGraw-Hill, Inc. pp. 1002-1013.

van Haandel, A. C. and Lettinga, G., (1994). Anaerobic sewage treatment. A practical guide for regionals with a hot climate. John Wiley & Sons.

van Lier, J. B., (1995). Thermophilic anaerobic wastewater treatment; Temperature aspects and process stability. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

van Velsen, A. F. M. and Lettinga, G., (1979). Effect of feed composition on digester performance. *In: Anaerobic digestion. Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* pp. 113-130. Applied science publishers Ltd., London

Viet, N. T., (1987). Waterhyacinth treatment of vegetable oil wastewater. Msc Thesis. Asian Institute of Technology (AIT). Bangkok, Thailand.

Wang, K. (1994). Integrated anaerobic and aerobic treatment of sewage. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Wang, S. C., Tseng, I. C. and Wang, L. C., (1986). The characteristics of *Methanosarcina* and *Methanothrix* in an anaerobic digester. *In: Water Treatment Conference, 15-19 September 1986, RAI Halls, Amsterdam, The Netherland.* pp. 29-38.

Webster, C. C. and Baulkwill, W. J. (1989). Rubber. Tropical agriculture series. John Wiley & Sons, Inc., New York, pp 35-62.

Webster, C. C. and Paardekooper, E. C. (1990). The rubber tree, *Hevea brassiliensis. Tropical Agriculture Series,* G Wrigley, AICTA.

Wessel, M., (1990). Rubber (unpublished). Wageningen Agricultural University, The Netherlands.

Widdel, F., (1986). Growth of methanogenic bacteria in pure culture with 2-propanol and other alcohol as hydrogen donor. *Appl. Environ. Microbiol.,* **51:** pp. 1056-1062.

Young, J. C. (1991). Factors affecting the design and performance of upflow anaerobic filter.

Zeeman G. (1991). Mesophilic and psychrophylic digestion of liquid manure. PhD. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Zehnder, A. J. B., (1988). Biology of anaerobic microorganisms. John Wiley & Sons.

Zeikus, J. G., (1979). Microbial populations digester. *In: Anaerobic digestion. Proceedings of the First International Symposium on Anaerobic Digestion, held at University of College, Cardiff, Wales, September 1979.* pp. 61-89. Applied science publishers Ltd., London

Zinder, S. H., (1988). Conversion of acetate to methane by thermophiles. *In: Anaerobic digestion. 5th International Symposium on Anaerobic Digestion, help in Bologna, Italia, 22-26 May, 1988.* pp. 1-12.

CURRICULUM VITAE

The author of this dissertation was born in Ha Noi Capital, Vietnam. He obtained his bacherlor degree at the Ha Noi University of Civil Engineering in the field of Environmental Engineering. His master of science degree was awarded from the Asian Institute of Technology (AIT), Bangkok - Thailand, Environmental Engineering division. The title of the master thesis is "Waterhyacinth treatment of vegetable oil wastewater". Since 1980 he worked as lecturer in the Ho Chi Minh Polytechnic University at Department of Environmental Engineering. In 1995 he had moved to the Department of Environmental Technology and Bio-Technology, Van Lang University. In November, 1990 he started his Ph.D. studies in "sandwich" program at both the Department of Environmental Technology, Wageningen Agricultural University, Wageningen - The Netherlands, and the Department of Environmental Engineering, the Polytechnic University, Ho Chi Minh City - Vietnam. Since 1995 based on the studies of UASB process in South Vietnam, he and his colleges have designed, constructed, installed and operated several industrial wastewater treatment plants using UASB process, such as tapioca processing wastewater (3,000 m^3 UASB-reactors), rubber latex processing wastewater (432 m^3 UASB-reactors), sea food processing wastewater (162 m^3 UASB-reactors), soya milk wastewater (48 m^3 UASB-reactors), soft-drink wastewater (36 m^3 UASB-reactors), fermented sticky rice wine wastewater (24 m^3 UASB-reactor). He believes that the anaerobic processes can be applied widely to treat wastewater in Vietnam, especially in industries. His address is:

Department of Environmental Technology and Bio-technology
Van Lang University
45 Nguyen Khac Nhu, District 1
Ho Chi Minh City, Vietnam

Tel: 84.8.8365317

or,

Center for Environmental Technology and Management (CENTEMA)
Van Lang University
C4/5-6 Dinh Bo Linh, P. 26, Binh Thanh District
Ho Chi Minh City, Vietnam

Tel: 84.8.8981501-4
Fax: 84.8.8981605

E-mail: Centema1@hcm.vnn.vn