Integrated Treatment of
Tapioca Processing Industrial Wastewater

Based on
Environmental Bio-Technology

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CONTENTS

ABBREVIATIONS

ARRPET	:	Asian Regional Research Program on Environmental Technology
AnWT	:	Anaerobic Wastewater Treatment
AeWT	:	Aerobic Wastewater Treatment
BOD	:	Biochemical Oxygen Demand
CDM	:	Clean Development Mechanism
CENTEMA	:	Center for Environmental Technology and Management
COD	:	Chemical Oxygen Demand
DO	:	Dissolved Oxygen
EGSB	:	Expanded Granular Sludge Bed
FB	:	Fluidized Bed
F/M	:	Food-microorganism ratio
GDP	:	Gross Domestic Product
GSL	:	Gas-Solid-Liquid Separator
HRT	:	Hydraulic Retention Time
IC	:	Internal Circulation
IFPRI	:	International Food Policy Research Institute
OLR	:	Organic Loading Rate
PPF	:	Pulverized Polystyrene Foam
PW	:	Pine Wood Pieces
RPF	:	Reticulated Polyurethane Foam
SIDA	:	Swedish International Development Agency
SMA	:	The Specific Methanogenic Activity
SRT	:	Sludge Retention Time
SS	:	Suspended Solids
SSLR	:	Suspended Solids Loading Rate
SVI	:	Sludge Volume Index
TDS	:	Total Dissolved Solids
TS	:	Total Solids
TSS	:	Total Suspended Solids
UAF	:	Upflow Anaerobic Filter
UASB	:	Upflow Anaerobic Sludge Blanket
VFA	:	Volatile Fatty Acid
VSS	:	Volatile Suspended Solid
Vup	:	Upflow Velocity

1

Introduction

1.1 DEVELOPMENT OF THE TAPIOCA PROCESSING INDUSTRY IN VIETNAM

Over the last decade, the Vietnamese economy has been developing rapidly with the industrialization and modernization of the country. The gross industrial export in 1990 was 2-3 billion USD and it had increased to 20 billion UDS by 2004, representing an average growth of 20-25% per year. The forecast is that it would reach 30 billion USD in 2005 (Econet, 22 July, 2005), with the agro-industrial sector playing an important role. According to Goletti et al. (2001), to promote development there is an increasing need for activities that generate and diversify income in rural areas. In this regard, the starch industry in Vietnam provides a good example of rural industrialization whereby low-value agricultural commodities such as cassava and canna are processed into high-value commodities like starch, to be used in a variety of food and non-food industries.

Cassava (*Manihot esculenta Crantz*), known also as tapioca, is one of the major tuber crops grown in more than 80 countries in the humid tropics. In Vietnam, cassava plays an important socio-economic role as a secondary crop after rice (Kim et al., 2003). According to Dieu (2003), cassava cultivation areas in Vietnam can be divided into three regions: (1) the South, concentrated in Tay Ninh, Binh Phuoc, Dong Nai, Binh Thuan, and Dac Lac; (2) the Center, in Gia Lai, Quang Ngai, Binh Dinh, and Quang Nam; (3) the North, in Phu Tho and Ha Tay. The cassava cultivation areas are shown in Fig 1.1. Cultivation of cassava is suited at any of the agronomic conditions prevailing in the production areas, especially in marginal areas. In particular, the plant's excellent drought tolerance allows it to be planted in many types of soil in Vietnam (Bien and Kim, 1990).

A study conducted by Dieu (2003) showed that Vietnam ranked 16 in terms of global cassava production, with production up to 2,050,300 tons per year. In 2002, Vietnam had a cassava cultivation area of 234,900 ha, with an average yield of 8.67 tons/ha/year; it subsequently remained within the range of 200,000 to 300,000 ha (Food Market Exchange, 2003). Nevertheless, cassava yields will increase following the adoption of new cassava varieties and more intensive cultural practices (Bien et al., 2003; Kim et al., 2003). Tapioca producers in Vietnam produced annually approximately 500,000 tons of tapioca starch, equivalent to 1.6 million tons of fresh cassava roots (Vina Econet, 2003).

Prior to 1988, starch processing in Vietnam represented barely 10% of the total use of tapioca starch. Since then, however, an increasing number of participants (more than 62%) in the field of starch processing have been determined, including both household-scale and large-scale factories. In the past few years, in order to increase the value of cassava for exporting, numerous tapioca processing factories have been built and put into operation, especially in the south of Vietnam (see Table 1.1). On average, the export price was approximately 300 USD per ton, compared with less than 200 USD per ton for domestic starch. During 1998, more than 21,000 tons were exported to Singapore, Taiwan, the Philippines, Indonesia, and Malaysia (IFPRI, 1998). Nevertheless, the export prices of starch fluctuated depending on the world market and the importing country; for instance, in March 2005 Vietnam exported tapioca starch to China for 246 USD per ton (People's Daily Online, 04 April, 2005).

According to Vietnam Economic Times News – dated 04 January 2006 – Viet Nam's export turnover of agricultural products, estimated at 5.8 billion USD in 2005, an increase of 29 percent over last year, has proved the effectiveness of agricultural production. Besides, according to the Ministry of Agriculture and Rural Development, the agricultural processing industry registered a production revenue of 5.25 trillion VND (328 million USD) during the first seven months of year 2006, an annual increase of 10 percent. In particular, food processing recorded a revenue of 397 billion VND (24.8 million USD) in July, an annual increase of 11.5 percent.

Fig. 1.1 Map of main cassava cultivation area in Vietnam.

Tapioca starch is also used extensively in various industries such as for monosodium glutamate, in weaving, paper mills, textiles, food, soap, detergents, pharmaceuticals, cosmetics, and so on. An increase in the demand of tapioca starch in domestic and international markets for food processing and other non-food industries has induced a dramatic increase in investments by small and large-scale tapioca production firms (IFPRI, 1998). As starch-using industries develop in Vietnam, it is expected that within the next few years the production of tapioca starch in Vietnam will increase.

Table 1.1 Several typical tapioca companies in South Vietnam until February 2006

Name of companies	Province	Capacity (tons starch/day)
Phuoc Long (VEDAN)	Binh Phuoc	600
KMC (Chon Thanh Dist.)	Binh Phuoc	100
Toan Nang (Dong Phu Dist.)	Binh Phuoc	100
Duc Lieu (Bu Dang Dist.)	Binh Phuoc	100
Wusons	Binh Phuoc	100
Tan Chau-Singapore	Tay Ninh	100
Tay Ninh Tapioca	Tay Ninh	120
Toan Nang	Tay Ninh	100
Truong Thinh	Tay Ninh	100
Nuoc Trong	Tay Ninh	80
Hinh Chang	Tay Ninh	80
Phuoc Hung	Tay Ninh	60
Thanh Binh	Tay Ninh	60
Cam Van	Tay Ninh	60
Viet Ma	Tay Ninh	60
Tan Hoang Minh	Tay Ninh	60
VEDAN	Dong Nai	200
Viet-Thai	Gia Lai	100
Chu Prong	Gia Lai	100
Toan Nang	Dac Lac	80
Dac Lac	Dac Lac	60

1.2 TAPIOCA PROCESSING INDUSTRY: ENVIRONMENTAL PROBLEMS

According to Dieu (2003) the rapid growth of industrialization and urbanization in Vietnam is putting severe stress on natural resources and on the environment, forcing the country to face a number of serious environmental problems, such as water and air pollution, degradation of land resources, soil erosion, over-exploitation of natural resources, and threats to the ecosystem. Important reasons for the rapid increase in environmental pollution are mismanagement and limitations in the prevailing level of technology applied in industrial production processes and in waste treatment (Vietnam News, June 17, 2005).

According to the Worker Newspaper of May 18, 2005, Vietnam’s target GDP growth rate is 7.5% from now on up to 2010, while that set for Hochiminh City is 12%, with revision for a subsequent increase. An analysis, however, shows that when a country’s GDP doubles, its environmental pollution may triple or even increase fourfold. In this regard, the food-processing sector has contributed substantially to Vietnam’s environmental pollution.

Environmental problems in the tapioca processing industry can be divided into specific categories as will be discussed below.

1.2.1 Resource Consumption

Availability of large quantities of water is a requisite in the tapioca processing industry. Observations at tapioca processing factories reveal that there are two kinds of water consumption: (1) from the washing process (due to the harvested roots being contaminated with mud, soil, and dust) and (2) from the extraction process (water is used as the extracting medium). Hence, large quantities of water (mainly surface and ground water) are converted to wastewater that amount up to 15 m^3 per ton of fresh cassava root (details are presented in Chapter 2). This volume must be treated before its release into the environment. According to Sriroth et al. (1998, 2000a, 2000b), the amount of water used to produce 1 ton of starch ranges from 10-30 m^3, and more washing, i.e., more water, improves the starch quality.

After the extraction processes, starch must be dried by hot air to reduce the water content from 35-40% to 11-13%. This process requires a large amount of energy, i.e., coal, petroleum, gas, and electricity. Normally the requirement of electrical and thermal energy for the production of 1 kg of tapioca starch is in the range of 0.320-0.939 MJ and 1.141-2.749 MJ, corresponding to 25% electrical and 75% thermal energy, respectively (Sriroth et al., 2000a)

1.2.2 Wastewater

The growth of the tapioca processing industry resulted in heavy water pollution, as it generates large amounts of wastewater with extremely high concentrations of organic pollutants. Nandy et al. (1995) and Khoa (1998) demonstrated that the washing and extracting processes constitute the main source of tapioca industry wastewater. According to Hien et al. (1999), in order to produce 1 ton of starch, a tapioca processing factory discharges about 12 m^3 of wastewater containing 11,000-13,500 mgO_2/L in terms of COD, 4,200-7,600 mg SS/L and pH 4.5-5.0. Studies by Mai et al. (2001) and Oanh et al. (2001) on large-scale tapioca processing companies give similar tapioca wastewater characteristics, with a total COD in the range of 7,000-41,406 mg/L, a BOD_5 of 6,200-23,077 mg/L, and CN concentrations in the range 19-28 mg/L. These values indicate that the wastewater is highly biodegradable and will result in an excessive environmental damage. Especially in the provinces of Binh Phuoc, Tay Ninh, and Dong Nai, the pollution of wells, springs, and rivers gives the most visible evidence of the devastating environmental side effects of tapioca processing.

A study by Peter et al. (2000) at the villages of Cat Que, Duong Lieu, and Minh Khai (Ha Tay Province), where 6,000 processors support a population of 30,000 residents with starch processing and associated products (such as noodles, maltose, and candy), found that processing 1 ton of cassava roots generates about 10.7 m^3 of wastewater containing high organic matter and suspended solids concentrations, i.e. 6,125 mg/L (COD) and 1,466 mg/L (SS). Residents in tapioca processing villages also agreed that the drinking water was much cleaner during the off-season. Similarly, deterioration of the environmental quality at the village of Tra Co (Dong Nai Province) is another example of adverse environmental impact caused by tapioca wastewater. Characteristics of wastewater from different settling stages measured at several tapioca processing households in Tra Co Village (detailed in Chapter 2) showed that this wastewater is low in pH (3.60-3.79) and has a high organic content (COD 6,244-20,340 mg/L). Thus, this is the best illustration of the surface water pollution status in this area. At present, Dia Spring is polluted heavily due to the discharge of tapioca wastewater. The BOD_5 and COD concentrations of samples at different cross sections of Dia Spring vary in the range of 1,380 - 10,000 mg/L and 2,200 - 11,600 mg/L, respectively. Ammonia (14-101 mg/L), organic nitrogen (42-262 mg/L) and total phosphate (11-46 mg/L) demonstrated high pollution of water resource. During the cassava harvesting season, tapioca production from Tra Co village generates more than 2000 m^3 of wastewater per day causing serious problems for the water quality of local surface resources.

1.2.3 Cyanogens

Cassava is a plant containing cyanoglucosides, which are synthesized in the leaf and stored in all tissues of the cassava plant, including the root. Since cyanide is a well-known metabolic inhibitor, cyanide-containing effluents cannot be discharged without sufficient detoxification. Swiss and German regulations place the limits for discharge in surface water at 0.01 ppm CN^- and in sewers at 0.5 ppm CN^-. For fish, the upper tolerance has been set at 0.1 ppm CN^-. Most micro-organisms lose their biological activity at 0.3 ppm cyanide content (Basheer et al. 1992; Connell and Miller 1984). Arguedas and Cooke (1982) showed that the total cyanide concentration decreased from 400-680 ppm in fresh roots to 1-4 ppm in starch product. Calculation for a factory with a daily capacity of 100 tons of starch (400 tons fresh cassava roots) will release around 16-60 kg cyanide per day, corresponding to 10-40 mg cyanide per litre of wastewater. Fortunately, cyanoglucosides are not stable and are easily degraded under high temperatures or by enzyme activity (Cereda and Mattos, 1996). According to Balagopalan and Rajalakshmy (1998), the ground water sources near cassava and sago starch factories show cyanogen concentrations much higher than the acceptable level, i.e., ranging from 1.2-1.6 mg/L, in comparison with 0.2 mg/L for the drinking water standard. Thus far, there have been no attempts to resolve the cyanide problem resulting from the discharge of wastewater from tapioca/sago starch processing industries.

1.2.4 Solid Waste


Sun drying of fibrous residues

Solid waste from tapioca starch processing comprises root skins and fibrous residues (or cassava pulp). The quantity of each is 2-3% and 15-20%, based on raw cassava root weight, respectively (Hien et al., 1999; Sriroth et al., 2000a; Dieu, 2003). The cassava pulp still contains a high starch (about 50% based on dry weight) and high moisture content (65-75%). Cassava pulp is therefore dried to reduce the moisture and a portion is used as animal fodder because of the high starch concentration. The estimation for a factory with a capacity of 400 tons of fresh cassava roots is a release of around 80 tons of solid waste every day. The generation of noxious odours during the drying and storing phases are related to the occurrence of fermentation in cases when the process is badly managed and exposed to rain, especially during the wet season. A portion of the solid waste is dumped or composted and may become a local source of malignant odours and environmental pollution.

Up until now, mainly the use of fibrous residues for recovering starch and for producing food has been investigated. An extraction of starch from the cassava pulp by enzyme hydrolysis has been reported by Sriroth et al. (2000b), and results of a study by Raupp et al. (2005) showed that the partially hydrolysed cassava solid waste presents digestive function properties that can be used as food for human consumption. Other researchers, Odunfa and Shasore (1987) have tried to solve the problems caused by solid waste generated from the tapioca processing by converting waste peels to reducing sugars and enriching the peels with microbial protein, but the success of the application so far is limited.

1.2.5 Air Pollution

Anaerobic pond release the air pollution

Air pollution mainly originates from the combustion of fuel. An estimation for a factory with a capacity of 100 tons of starch product is that it will consume about 3,500 L of fossil oil (FO) fuel every day, releasing about 71 kg SO_x, 35 kg NO_x, and 9.9 kg dust per day. Hence, the factories have to install an air treatment system for the boiler. In addition, dust from the drying, sieving, and packing processes, and the obnoxious smell from the storage of cassava pulp contribute to the environmental pollution. Another kind of air pollution comes from the greenhouse gases (such as methane and carbon dioxide) released from the degradation of solid waste and the wastewater treatment plant; it also needs to be addressed.

During the past few years, Vietnam received considerable assistance from other countries to support the prevention of environmental pollution. The Green Aid Program, run by Japan's Ministry of Economy, Trade, and Industry, was offered to six Asian countries: Thailand, China, Indonesia, Malaysia, the Philippines, and Vietnam, to provide these countries with the necessary techniques to prevent pollution.

On May 11, 2002, Vietnam and Sweden signed an agreement in Hanoi for bilateral cooperation for improving land and environmental management until 2009. As part of this program, as arranged by the Swedish International Development Agency (SIDA), the Ministry of Natural Resources and Environment, and the Ministry of Industry of Vietnam agreed upon a level of annual financial contributions for programs relating to the safe use of chemicals, to technical assistance, and to environmental impact assessments. It is expected that this program will improve policy-making capacity and law enforcement, as well as human resource development in order to enhance land and environmental management at both central and grassroots levels (TT, VNA, May 12, 2005).

SIDA is also supporting the ARRPET project (Asian Regional Research Program on Environmental Technology) in two phases from 2001 to 2007, supporting research on environmental issues relevant to Asia. The issues covered in these activities include wastewater, solid waste, air pollution, and hazardous waste. In this project, entitled SUSTAINABLE TREATMENT OF TAPIOCA PROCESSING WASTEWATER IN SOUTH VIETNAM in phase 1 and SUSTAINABLE DEVELOPMENT OF TAPIOCA PROCESSING INDUSTRY IN VIETNAM BY INDUSTRIAL ECOLOGY in phase 2, Vietnam (CENTEMA), is responsible for the tapioca starch industry field. Appropriate waste treatment and management methods, which are robust, easy to operate, and suitable for Asian conditions are being developed. Water reuse and recycling form attractive alternatives to meet the growing water demands and would help reducing water scarcity and also lead to an improvement in the quality of the environment.

1.3 TYPICAL ENVIRONMENTAL BIO-TECHNOLOGY APPLICATIONS FOR AGRO-INDUSTRIES WASTEWATER

A large number of studies exist that deal with the use of anaerobic technology for the treatment of agro-industry wastewater on a lab-scale or pilot-scale level. The studies cover many kinds of agro-industry wastewater such as starch, dairy, sugar, coffee, brewery, slaughterhouse, fish, and so on; the typical treatment systems include UASB, Anaerobic Hybrid Reactor, Anaerobic Digestion, Fixed Film Reactor, Anaerobic Fluidized Bed Reactor, and Anaerobic Baffled Reactor (Wiegant and Lettinga, 1985; Nanninga and Gottschal, 1986; Torres-Castillo et al., 1995; Syutsubo et al., 1997; Bello-Mendoza and Castillo-Rivera, 1998; Akunna and Clark, 2000, Rajeshwari et al., 2000; Oliveiraet al., 2001b; Erguder et al., 2001; Palenzuela-Rollon et al., 2002; Torkian et al., 2003; Ramasamy et al., 2004; Barana and Cereda, 2005; Borja et al., 2005; Sanchez et al., 2005). All the studies clearly demonstrated that anaerobic technology is the most suitable option for treating high-strength organic wastewaters such as low energy consumption, less sludge production and high OLR can be applied. Furthermore, also other prominent advantage like energy recovery from biogas of the anaerobic process in comparison to conventional (e.g. aerobic) treatment methods make it a very attractive treatment option for all these types of wastewaters. In practice, however, the reactor design sometimes needs to be modified in order to enable further improvement of the quality of the treated wastewater.

For full-scale applications, some detailed reports presented the treatment of agro-industry wastewater (Butcher, 1989; Zoutberg and Frankin 1996; Zoutberg and Eker, 1999; Ahn et al., 2001; Sharma and Huang, 2004; Rajbhandari and Annachhatre, 2004). These studies reported that application of anaerobic treatment of agro-industry effluent lead to quite reasonable organic pollutions reductions and substantial decreases in the treatment cost. In a study by Frankin (2001) it was reported that the first full scale application of high-rate anaerobic treatment for industrial wastewaters was in the sugar industry in the mid-1970s. Since that time the anaerobic wastewater treatment (AnWT)-technology developed as a standard method of wastewater treatment for a

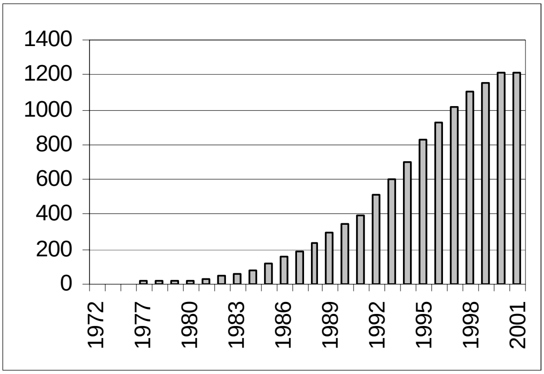


Fig. 1.2 Cumulative number of AnWT-plants for industrial applications (Frankin, 2001).

wide variety of industries. Fig. 1.2 shows the cumulated number of anaerobic treatment plants installed over 65 countries up to 2001 (Frankin's study). The total number of plants at that time was estimated at around 2,000, and the UASB technology was the predominant process, as shown in Table 1.2. This database does not include the thousands of anaerobic lagoons installed in Latin America, China, and India, but these types of treatment systems in fact cannot be designated as a really appropriate solution for environmental protection, e.g. they take up too much land, produce bad smell, too much methane and CO_2 is emitted into the atmosphere, they fill up with solids and have poor removal efficiencies. Frankin demonstrated in his study that the application of anaerobic treatment is highly successful for the treatment of industrial effluents, especially those from the agro-industries. His evaluation shows that the application in the agro-industry sector takes up a large portion: namely, more than 87% in the database (Table 1.3).

Table 1.2 Processes used for industrial wastewater treatment in over 65 countries

No.	**Process**	**Number of treatment plants**	**% average in database**
1.	UASB	682	56
2.	EGSB	198	16
3.	Low rate (lagoon/contact)	187	15
4.	Fixed Film	54	5
5.	Fluidized Bed	16	1
6.	Hybrid	12	1
7.	Undefined/unknown	66	6
	Total in database	**1,215**	**100**

Source*: Frankin, 2001.*

Table 1.3 Industrial applications (in the database) using the anaerobic treatment system

No.	**Process**	**Number of treatment plants**	**% average in database**
1.	Food	389	32
2.	Breweries and beverages	329	27
3.	Distilleries and fermentation	208	17
4.	Pulp and paper	130	11
5.	Chemical	63	5
6.	Landfill leachate	20	2
7.	Undefined/unknown	76	6
	Total in database	**1,215**	**100**

Source*: Frankin, 2001.*

For improving the quality of the treatment plant effluents, many studies recommend the use of a combination of anaerobic with aerobic wastewater treatment, i.e. the use of stabilization ponds or constructed wetland systems as post treatment systems in order to attain the permissible COD, BOD and nutrient concentrations for discharge (El-Awady and Wahaab, 1999;

Rajeshwari et al., 2000; Sousa et al., 2001, Chernicharo et al.; 2001, Nunez and Martinez, 2001; Lacalle et al., 2001; Polito-Braga et al., 2002; Sigge et al., 2002; Huang et al., 2005). The benefits of the combined anaerobic-aerobic treatment sequence and the need to accommodate advantages and disadvantages of each of these processes for a whole system are also presented in Chapter 5.

According to Frankin (2001), the key to achieve high system loading rates is to realize short hydraulic retention times under conditions of maintaining a positive net viable biomass retention. Thus, various reactor designs were developed based on various ways of retaining biomass within the reactor system under high organic and hydraulic loading conditions. In this chapter an overview will be presented of the anaerobic systems in worldwide use for the treatment of industrial wastewater.

Upflow Anaerobic Sludge Blanket (UASB)

The UASB reactor was developed in the Netherlands in the early 1970s (Lettinga et al., 1980). This reactor, as originally proposed by Lettinga, was one of the earliest systems in which development of a granular biomass was observed. As the result of the excellent settling characteristics of this granular biomass and the presence of a specially designed three-phase (biogas, water and biomass) separator device in the upper part of the UASB-reactor, an excellent sludge retention is assured in this reactor system (Frankin, 2001). The major disadvantage of the UASB process comprises, although merely in those cases where proper seed sludge is not available in sufficient quantities, the relatively long start-up period. During the initial phase of the (first) start-up process of a UASB-reactor, inoculated with flocculent seed sludge, a significant washout of sludge generally will manifest and therefore the first reactor start-up would highly benefit from skilled operation (Rajeshwari, 2000).

Expanded Granular Sludge Bed (EGSB) and Internal Circulation (IC) Systems

The latest generation of AnWT-technology is the development of the EGSB process, it is the logical follow up of the UASB-process, because it relies on the use of granular sludge and in some particular cases it was developed to cope with the huge problems which manifested in a full scale Fluidised Bed (FB) system which was based on the use of carrier materials for biofilm attachment (Frankin, 2001). The EGSB system uses a granular biomass, which is expanded by evolving gas and by hydraulic liquid flow during operation of the system. The IC system is a special, but more complicated, version of the EGSB concept based on an internal liquid circulation system driven by gas lift. The advantage of these EGSB-systems lies in the high applicable organic and hydraulic loading rates and their great potentials for treating very low-strength wastewaters, even at ambient temperatures down to 10 ^{o}C (Lettinga et al., 1998).

Fixed Film or Anaerobic Filter

Immobilization of viable biomass on a fixed carrier represents an alternative method of retaining biomass. A common representative of this principle is the fixed film system operated in either upflow or downflow mode. According to van den Berg et al. (1985) the advantage of the system is that it is well capable to withstand serious toxic shock loads but the disadvantages are the relatively low applicable loading potentials and the high cost of carrier material (Frankin, 2001).

Fluidized Bed (FB)

The FB system, introduced in the early 1980s, is based on the immobilization of biomass in the form of biofilms on fluidized carrier material (sand, basalt, pumice, activated carbon, and so on). The problems encountered in the system were based on excessive growth on the carrier under mild shear conditions (top part of reactor) and no growth on the carrier under high shear conditions (low part of reactor) that were required to fluidize the carrier (Frankin, 2001).

Hybrid System

The hybrid system combines the features of the fixed bed system (in the top of the reactor) and that of the UASB system (particularly the use of granular biomass). Some researchers found that these systems can maintain high treatment efficiencies at high COD-loads. They offer big potentials for very low strength wastewater (Lettinga et al., 1998).

1.4 STATUS OF TAPIOCA WASTEWATER TREATMENT IN THE SOUTH OF VIETNAM

To date, almost all tapioca processing companies in South Vietnam use wastewater treatment systems based on ponds. An ARRPET study (2004, 2005) showed that all wastewater generated from large-scale tapioca production processes in Tay Ninh Province are treated in a pond system. These tapioca companies installed a biological wastewater treatment system based on the use of stabilization ponds, i.e. including anaerobic ponds, facultative ponds, and polishing ponds. Fig. 1.3 shows the general layout of the tapioca wastewater treatment system at the Tan Chau Tapioca Company in Tay Ninh Province. This treatment system with capacity of 1,200 m^3/d consists of eight stabilization ponds, occupying an area of 7.4 ha. Similarly, the Tay Ninh Tapioca Company (also located in Tay Ninh Province) uses a series of twelve stabilization ponds, which cover an area of 15.8 ha and have a capacity of 1,500 m^3/d, is shown in Fig. 1.4.

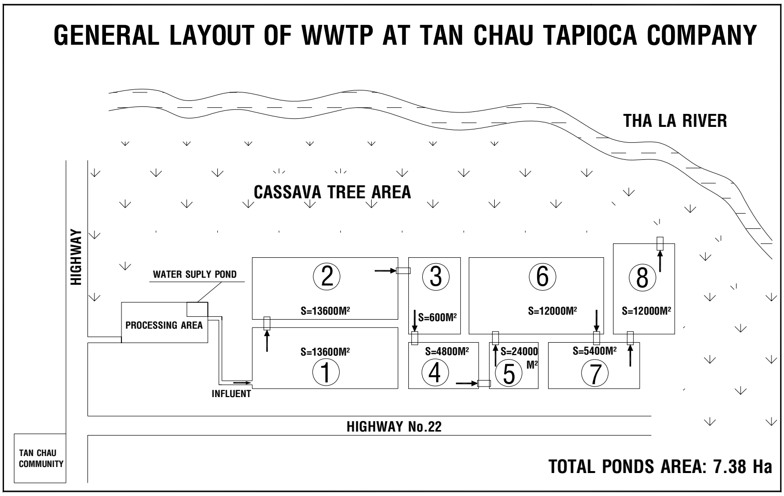


Fig. 1.3 General layout of the Tan Chau Tapioca Company wastewater treatment system.

Although the companies have installed stabilization ponds the effluents of these systems don't meet Vietnamese industrial wastewater discharge standards, which partially can be attributed to the poor design, maintenance and likely also very poor understanding of these systems. Results of an ARRPET study (2005) showed that the effluent of treatment systems using only ponds in Tay Ninh Province is far from stable, the COD and BOD effluent concentrations fluctuate widely, viz. from 88-312 mg/L and 40-174 mg/l for the two ponds systems of the Tan Chau Tapioca Company mentioned above. Moreover, anaerobic ponds fed with a high organic concentration frequently cause offensive odour, mosquito breeding and groundwater pollution.

In the meantime, the Phuoc Long Tapioca Company in Binh Phuoc Province applies a high rate AnWT-technology combined with (micro) aerobic post-treatment, i.e. a system consisting of a combination of the UASB process and a pond system. The effluent from this treatment system is reused for irrigation (to some extent also fertilization) of the company's cassava fields. With this technology the adverse environmental impact is minimal. The flow-diagram of the treatment system is described in Fig. 1.5.

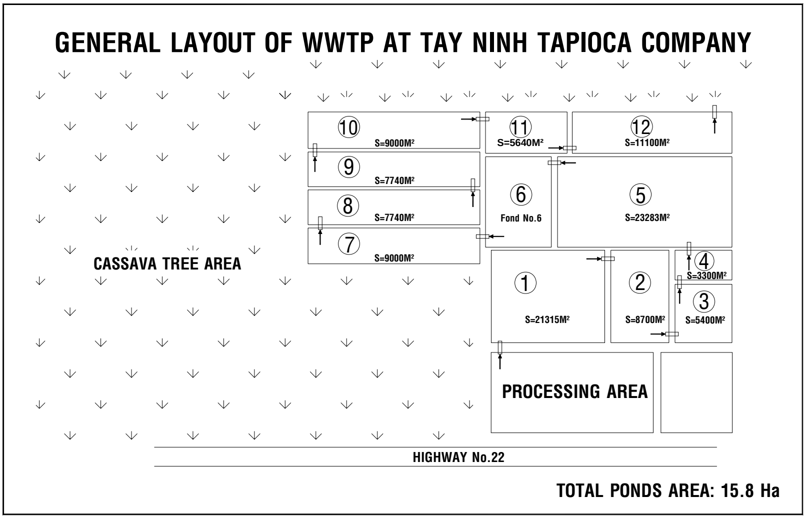


Fig. 1.4 General layout of the Tay Ninh Tapioca Company wastewater treatment system.

In contrast to wastewater originating from large-scale tapioca companies, the wastewater from household-scale tapioca processing units generally still is discharged into existing city sewers (for instance in Ho Chi Minh City and Dong Nai Province) or stored in earth ponds (in Tay Ninh Province). Studies have been carried out to assess the existing state of the tapioca production industry and the type of treatment of their wastewaters in South Vietnam. The results show that almost all household-scale factories located in Dong Nai Province discharge their wastewater to sewers, rivers or lakes and they do this without any pre-treatment. In Ho Chi Minh City, the household-scale factories discharge tapioca wastewater freely into the city's sewage system. In Tay Ninh Province, however, the situation is different. Because of the large space available around households, almost all of the household-scale factories discharge their wastewater there into chain of earth ponds, though ponds without any liner to prevent penetration into the groundwater. Most of them prefer to build a “no discharge” system, with very deep ponds.

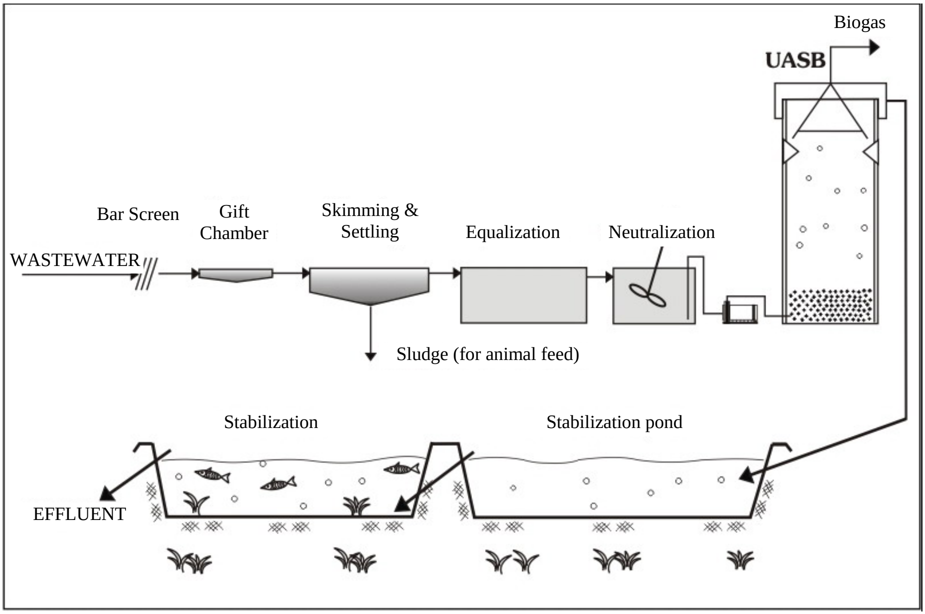


Fig 1.5 Flow-diagram of the Phuoc Long Tapioca Company WW treatment system.

From the above it can be concluded that tapioca processing wastewater in Vietnam still causes a heavy damage to the receiving area due to the large amounts and high pollution strength. Most of the starch companies are located near the banks of rivers or lakes and it has become customary to discharge the wastewater from tapioca factories into these bodies of water. It poses a very serious threat to the environment and quality of life in rural areas. Beginning in 1998, the provincial environmental authority has forced companies to treat their wastewater. Factories then began to discharge wastewater into the chains of artificial ponds because frequently land was available around the companies. However, this treatment technology is unable to provide an effluent meeting the prevailing effluent discharge standards, and therefore the situation of heavy pollution is still continued.

At present, any new tapioca factory in Vietnam has to come up with an environmental impact assessment report and – quite important – they need to install an adequate wastewater treatment system. Consequently, in forthcoming years the situation will improve distinctively.

1.5 RESEARCH OBJECTIVES

This PhD-thesis entitled “INTEGRATED TREATMENT OF TAPIOCA PROCESSING INDUSTRY WASTEWATER – BASED ON ENVIRONMENTAL BIO-TECHNOLOGY” comprises a comprehensive research project aiming on assessment of a proper biological treatment processes for tapioca processing wastewater. The investigations were carried out in the laboratory of CENTEMA, Van Lang University and of the Sub-Department of Environmental Technology, Wageningen University. The main objectives of the study included:

a. Development of an appropriate technology for the treatment of tapioca processing wastewater using high rate AnWT- technology as the core of the system, and with a proper aerobic technology as post-treatment under Vietnamese conditions;

b. Assessment of adequate post-treatment using pond systems in order to meet the prevailing effluent discharge standards;

c. Examination and assessment of the factors that effect the UASB performance, such as in the case of tapioca wastewater: the natural acidification process of wastewater, the temperature, the pH, the presence and availability of nutrients and trace elements, the applicable organic concentration (organic loading rate), and shock loads;

d. Examination and assessment of cyanide toxicity on the hydrolysis and acidification processes of tapioca starch particles and the reduction of cyanide toxicity by ferrous compounds.

1.6 STRUCTURE OF THE DISSERTATION

The dissertation is sub-divided into eight chapters. This chapter, **Chapter 1**, presents an overview of tapioca processing industrial development in Vietnam and its environmental implications. International literature on the tapioca processing industry and its wastewater treatment technologies using biotechnological approaches are described, including an analyses of their strengths and weaknesses. This paragraph outlines the structure of the dissertation and research objectives. **Chapter 2** presents the tapioca production technologies in Vietnam and their wastewater characteristics. Production processes of small- (household-), medium-, and large-scale tapioca processing units are described in detail. The composition and characteristics of tapioca wastewater are presented. Chapters 3 to 6 comprise the experimental part of the study to ascertain appropriate treatment technologies relating to tapioca processing wastewater in Vietnam. **Chapter 3** reports the results of investigations on tapioca wastewater treatment using the Upflow Anaerobic Filter (UAF) process to remove suspended solids prior to treatment in a UASB system. The studies are carried-out on UAF reactors packed with different filter media, viz. reticulated polyurethane foam (RPF), pulverized polystyrene foam (PPF), and sections of pine wood (PW). **Chapter 4** focuses on the start-up of UASB-reactors under conditions of different organic loading rates; the performance of the UASB-reactors was assessed, including the effects of suspended solids. A combination of UAF and UASB reactors to treat tapioca wastewater were investigated. **Chapter 5** deals with the applicability of the activated sludge process for tapioca wastewater, and the feasibility of the pond system for post-treatment. **Chapter 6** describes the factors affecting the anaerobic process for treatment of tapioca wastewater including pH, nutrient and trace elements, OLR, and shock loads. The effect of cyanide and sulfide on the hydrolysis and acidification processes of tapioca starch is discussed in **Chapter 7**, which also deals with the reduction of cyanide toxicity by ferrous compounds. **Chapter 8** moves one step further to develop a suitable technology for environmental friendly tapioca wastewater treatment. Besides, a sustainable development for tapioca processing industry is recommended. As the final chapter, it also comprises the conclusions and recommendations.

2

Tapioca Industry in Vietnam: Processing Technology and Characterization of Wastewater

2.1 GENERAL INTRODUCTION

In Vietnam, starch processing is carried out by large modern factories or in rural households by traditional methods (Dieu, 2003). Household-scale (small-scale) tapioca production has been going on for decades, but in the past few years many large-scale factories have been established, concentrated in South Vietnam, particularly in Tay Ninh Province as described in previous chapter. The 2005 statistical data from DONRE (Department of Natural Resources and Environment) Tay Ninh Province indicates that there are 98 household-scale tapioca units, 11 medium-scale factories, and 16 large-scale factories located in the Tay Ninh area. They consumed an amount of 6,581 tons of fresh cassava roots per day. The large-scale tapioca factories contribute to most of the province's total tapioca production capacity, i.e., 66%, while medium-scale and small-scale units contribute 13 and 21%, respectively.

Despite the benefits of establishing tapioca processing factories, the environmental problem exists and becomes increasingly serious. It is easier for large-scale factories to implement waste prevention and reduction measures, but all the more difficult do so in household-scale enterprises. According to Dieu (2003), the main reasons are the difficulties in making investments for production technology improvement and the lack of environmental awareness and knowledge. Currently, most household-scale production wastewater is discharged untreated into the receiving source, such as Mi Spring and Dia Spring in Dong Nai Province or into the sewage system in Ho Chi Minh City. But in Tay Ninh Province, household-scale production wastewater is stored in earth ponds surrounding the production area, and then discharged into Da Spring, Nho Spring, and Tay Ninh Canal. The pollution of wells and springs in Dong Nai and Tay Ninh Provinces are the direct result of household-scale tapioca processing activities. This should be viewed as a warning for all areas where household-scale tapioca processing units are located. For large-scale factories, wastewater is treated in pond systems, where the effluent does not always meet Vietnamese industrial wastewater effluent discharge standards.

2.2 TAPIOCA PROCESSING INDUSTRY

Depending on the production capacity and technology, tapioca starch processing factories in Vietnam can be classified as household-scale (small-scale), medium-scale, and large-scale. Household-scale refers to a tapioca processing household that uses simple traditional technologies with production capacities of less than 50 tons of fresh cassava roots per day. Medium-scale enterprises have capacities of more than 50-200 tons of fresh cassava roots per day and the production process is more automatic. A large-scale factory applies modern technologies and has an automated production process with capacities of more than 200 tons of fresh cassava roots per day.

2.2.1 Household-Scale Tapioca Production Processes

According to Khoa (1998), the household-scale tapioca processing units are concentrated in eight provinces in Vietnam (Table 2.1). Visits were made to Binh Chieu Village (Ho Chi Minh City), Binh Minh and Tan Binh Villages (Tay Ninh Province) and Tra Co Village (Dong Nai Province). The field observation regarding household-scale production presented below was carried out in Binh Chieu Village, Thu Duc District, and Ho Chi Minh City. The average household-scale production capacity is about 4-5 tons of fresh roots per day, corresponding 1.0-1.4 tons of wet starch per day. The product is wet starch due to limited space.

In this production process manual peeling is applied. The generated wastewater is currently directly discharged into the city's sewage network, and all by-products in solid form are sold.

Table 2.1 Number of districts where household-scale tapioca processing factories are located

No.	City/Province	Number of districts
1	Dong Nai Province	02
2	Ho Chi Minh City	01
3	Tay Ninh Province	02
4	Binh Dinh Province	02
5	Quang Ngai Province	01
6	Quang Nam – Da Nang Province	02
7	Ha Tay Province	02
8	Ha Bac Province	01
	Total	**13**

Source: *Khoa, 1998.*

The household-scale tapioca production units in Thu Duc District (Ho Chi Minh City) are concentrated in Binh Chieu, Tam Hai, and Khiet Tam Villages. Before 1987, Thu Duc District had 84 households that produced tapioca starch. By 2001 it was reduced to 22 households. At the end of 2005, the households for tapioca starch comprised only 12 units, and likely will decrease to 7 households in 2006 due to elimination of the tapioca production households in Tam Hai Village. The reason the number of tapioca production units in Thu Duc District is diminishing is that they cannot compete with large companies with their high quality starch production and the capital costs necessary for a wastewater treatment system.

The tapioca production processes observed at the household scale were very similar, with all households producing wet starch. A diagram of the common production process is described with reference to Dieu (2003) in Fig. 2.1.

The average capacity of small-scale is about 4-5 tons of roots per household per day. The peels of fresh cassava roots are removed manually before the roots are submersed and rinsed in an overflow water tank. This step is necessary to reduce the amount of dirt or sand, as well as to ensure the starch quality. The rinsed roots are subsequently ground before being transferred into an extractor tank. The suspension containing starch and water, called starch milk, is transferred into a series of the first settling tanks. Residual fiber is removed and used for animal feed.

Starch milk left in the first settling tanks for about 7-10 h. The bottom layer consists of wet starch. Then they are mixed thoroughly with water and bleach chemical (10g/ton of fresh cassava root), and left to settle a second time for about 12-14 h (second settling stage). This time the good quality starch is collected. After the release supernatant, dirt starch is moved to another tank and mixed thoroughly with fresh water to settle dirt and unqualified starch (called pulp). The remaining suspension is then transferred from the mixing tank into the third settling tank for further starch recovery. It also takes also about 12-14 h to complete the third settling.

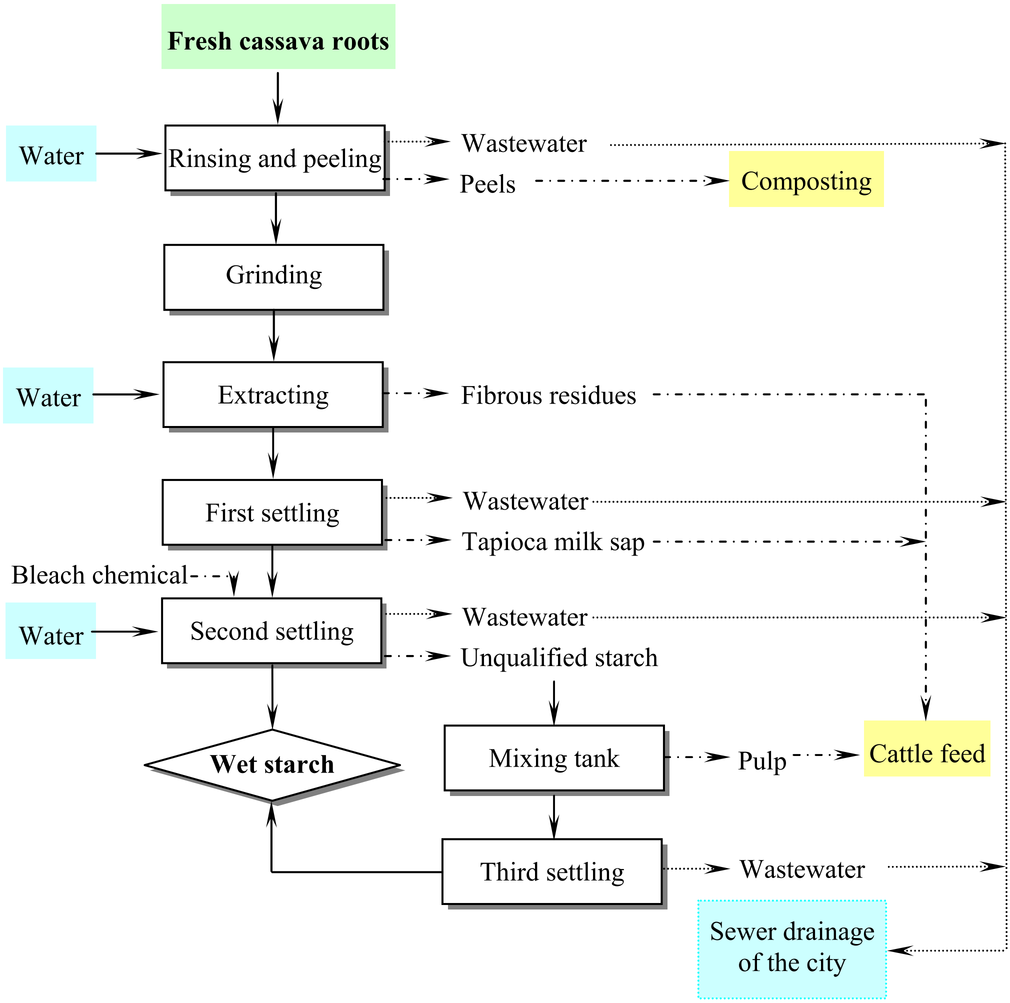


Fig. 2.1 Diagram of the household-scale tapioca production process at Thu Duc Dist, HCMC.

Good quality starch from the second and third settling stages is sold as wet starch. Peels from peeling, fibrous residues from extracting, tapioca milk sap from the first settling, and pulp from the second settling are sold as raw material for animal food production. All production process wastewater is discharged untreated into existing open ditches.

Several medium-scale tapioca factories can be found in Binh Phuoc Province and Tay Ninh Province. Two processes representing medium-scale wet starch and dry starch production are described by Khoa (1998).

Compared to the household scale, the medium-scale tapioca production process has been more automatized and is more up to date. As a result of the greater efficiency of the extracting stage, production efficiency is higher and the generation of by-products is lower than that of household-scale production. However, energy consumption and capital investment in the medium-scale production process is higher.

2.2.2 Large-Scale Tapioca Production Processes

Many of the large-scale tapioca companies are found in the South Vietnam since 1990 aim to satisfy the demands of raw material for monosodium glutamate, textile, paper industries, and so on. Several typical companies to be mentioned here comprise Tay Ninh Tapioca Co., Ltd, Tan Chau Tapioca Co., Ltd. (Tay Ninh Province), KMC Tapioca Co., Ltd., Phuoc Long Tapioca Co., Ltd. (Binh Phuoc Province), and VEDAN Vietnam Company (Dong Nai Province). The following description of a large-scale tapioca production process is based on a field observation made at the Phuoc Long Tapioca Co. In this case, fresh roots placed near the production area are transferred by bulldozer to a material input hopper. After passing through the hopper, fresh roots are dropped onto a conveyor belt, where stones, pieces of iron, and wooden bits of the cassava roots are removed manually by employees before entering a screener. Dirt, sand, and part of the peel are removed by rasping with a screener and by moving along screw transport to rinsing gutter. Wastewater generated in this stage is collected and directed to a sedimentation tank for sand and dirt removal before being discharged to the surface receiving water. Rinsed roots are chopped into small pieces and transferred to grinders. Fine particles from the grinders are transferred into extractors for starch and fiber separation. In this case, extraction is a three-stage process consisting of coarse, fine, and final extracting. In each extractor, SO_2 is applied for bleaching, and starch milk is subsequently dewatered in centrifuges. Wet starch is then dried by hot air. Wastewater generated from the centrifuging stage is discharged and fibrous residues are sold as animal food. The large-scale Phuoc Long Tapioca Company (Binh Phuoc Province) tapioca production process is described in Fig. 2.2.

Compared to household-scale and medium-scale, the production process of a large-scale company obviously is much more modern and has higher production efficiency, but on the other hand, it also needs greater capital investment and the energy consumption is higher. With three-stage extracting, it can be said that almost all the starch in the cassava roots is extracted. Due to bleaching by the application of SO_2, the starch product from this company is always the superior, compared to products from small-scale and medium-scale factories. The wastewater generated, in this case, is treated using biological processes including an UASB (Upflow Anaerobic Sludge Blanket) and pond system. Wastewater from the rinsing and centrifuging stages is treated separately. This is a good solution because the characteristics of these wastewaters vary widely. Rinsing wastewater mainly contains inorganic suspended solids, while centrifuging wastewater contains a high concentration of organic suspended and dissolved solids. Currently, treated rinsing wastewater from a sedimentation tank is not reused for the rinsing stage. However, if a counter current flow is applied, reuse of this treated wastewater in the rinsing stage is applicable and very helpful in reducing the amount of fresh water required.

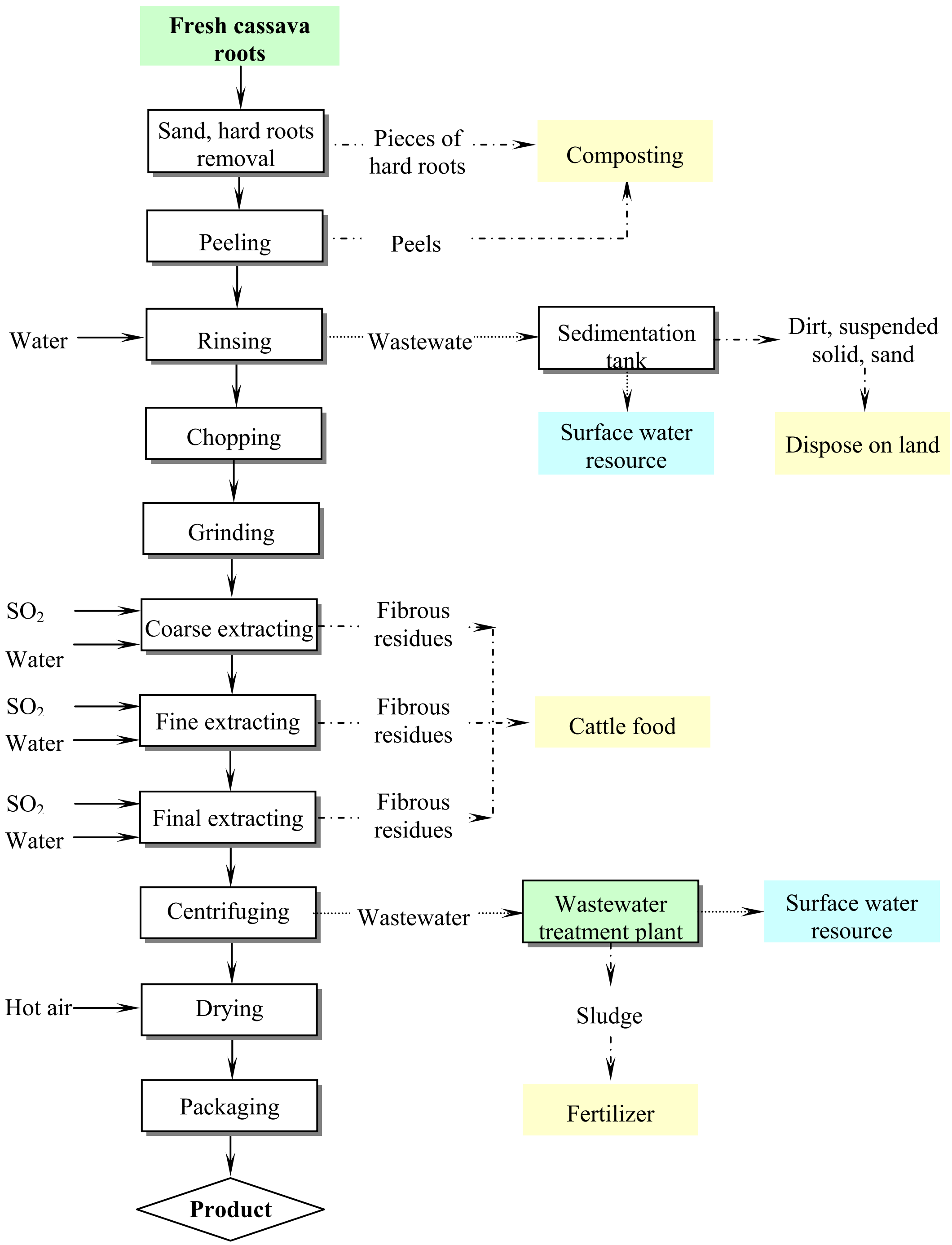


Fig. 2.2 Large-scale tapioca production process at the Phuoc Long Tapioca Co., Ltd.

2.3 COMPOSITION AND FLOW RATE OF TAPIOCA PROCESSING WASTEWATER

2.3.1 Composition of Tapioca Processing Wastewater

The production of tapioca starch creates a huge amount of highly organic matter polluted wastewater. According to Nandy et al. (1995) and Khoa (1998), two main pollution sources from the tapioca production process are wastewater and solid wastes, with wastewater from sedimentation or centrifugation being of great concern. With around 12 m^3 wastewater for 1 ton starch produced, the tapioca starch processing industries obviously can cause extremely heavy pollution to the receiving surface water and to the air in the South Vietnam (Hien et al., 1999).

Large-Scale Industry

Wide variations can be observed in the chemical and physical constituents of primary and secondary settling wastewater obtained from cassava starch factories. In the case of one large-scale tapioca processing factory in Kerala, India, COD concentration of the primary settling wastewater is in the range of 33,600-38,223 mg/L, whereas this value is only 3,800-9,050 mg/L in the case of the secondary settling wastewater (Table 2.2).

Table 2.2 Characteristics of wastewater from a large-scale tapioca processing factory in India

Parameters	Unit	Primary settling wastewater	Secondary settling wastewater
pH	-	4.50 - 4.70	4.50 - 4.70
Total solids	mg/L	35,640 - 42,000	3,200 - 9,600
Total suspended solids	mg/L	33,200 - 37,320	980 - 4,078
COD	mg/L	33,600 - 38,223	3,800 - 9,050
BOD_5	mg/L	13,200 - 14,300	3,600 - 7,050
Free sugar as glucose	mg/L	425 - 1,850	735 - 2,060
Total hydrolysable reducing sugar as glucose	mg/L	22,614 - 29,275	1,120 - 2,761
Total ash	mg/L	1,450 - 1,680	265 – 820
Total nitrogen	mg/L	97 - 182	62 – 86

Source: *Balagopalan et al., 1988.*

Balagopalan et al. (1988) also found that the process to extract starch from cassava tubers requires a large quantity of water, and a significant amount of wastewater therefore is released. As a consequence, most of the starch factories are located near the banks of rivers or lakes and it has become customary to discharge wastewater from tapioca factories into water source, and this poses a serious threat to the environment and quality of life in the rural areas. The extension of these pollution problems in Thailand and India has been well described by a number of researchers.

Studies by Mai et al. (2001), and Oanh et al. (2001) on tapioca wastewater from the large-scale Phuoc Long Tapioca Company (Binh Phuoc Province), and the Vietnam-Thailand Tapioca

Factory (Tay Ninh Province) in Vietnam, respectively, also show that the organic concentration of wastewater from the centrifuging process is as high as up to 23,000 mg/L (BOD_5) and 41,000 mg/L (total COD) (Table 2.3). Results of measurements made by Mai et al. (2001) indicate that rinsing wastewater from the Phuoc Long Tapioca Company contains mainly inorganic matter with a total COD concentration in the range of 320-520 mg/L and suspended solids of 220 to 3,389 mg/L.

Table 2.3 Characteristics of wastewater from large-scale tapioca processing companies in Vietnam

Para-meters	**Unit**	**Phuoc Long* Tapioca Co.**	**Vietnam-Thailand** Tapioca Co.**	**Tây Ninh Tapioca Co.**	**KMC Tapioca Co.**
pH	-	4.90 – 5.70	4.50 - 5.10	4.30 – 4.50	3.78 – 4.53
SS	mg/L	500 - 3,080	3,750 - 4,100	1,588 – 2,650	330 – 4,400
COD_{tt}	mg/L	7,000 - 14,243	14,262 - 41,406	10,701 – 15,560	9,221 – 20,648
COD-VFA	mg/L	-	-	682-930	-
BOD_5	mg/L	6,200 - 13,200	7,125 - 23,077	5,600 – 8,950	6,757 – 15,280
$N\text{-}NH_3$	mg/L	45 - 73	38 – 102	71.4 – 88.1	37.8 – 84.5
N-Org	mg/L	90 - 367	96 – 188	174 -212	220 - 237
$P\text{-}PO_4$	mg/L	10 - 45	15 – 24	53 – 59	47 – 58
SO_4^{2-}	mg/L	26 - 73	13 – 21	10 - 25	21 - 28
CN^-	mg/L	19 - 28	28 - 61	30.0 – 33.6	32.5 – 36.5

***Source:** * Mai et al., 2001; **Oanh et al., 2001.*

Moreover, the presence of the highly toxic cyanide was reported and this compounds generally is fatal to fish at concentration of ± 1 mg/L (Bridgwater & Mumford, 1979). Therefore, with a cyanide concentration up to 96 mg/L (Table 2.3), the water obviously is too polluted for fish to survive. According to Siller and Winter (1998), during the tapioca production process, large amounts of cyanoglycosides are released, these compounds rapidly decayed to cyanide following enzymatic hydrolysis. Depending upon the varying cyanoglycoside content of the cassava varieties, the cyanide concentration in the wastewater can become as high as 200 mg/L.

Household- and Medium-Scale Industry

Previous researches carried out at two medium-scale tapioca factories in Tay Ninh and Binh Dinh Province show that wastewater generated from these companies contains a high organic concentration and a low pH value. The BOD_5 and COD concentrations ranged from 7,400-11,000 mg/L and 13,000-17,700 mg/L, respectively (Table 2.4).

And a survey by Nandy et al. (1995) of wastewater originating from different stages of a small-scale tapioca production process demonstrates that wastewater from the root-rinsing stage is almost neutral (pH of 6.5-7.5), with a total solid content of 550-700 mg/L and BOD_5 and COD concentrations of 40-60 mg/L and 100-150 mg/L, respectively. Wastewater from sedimentation is a slightly acid, with pH values in the range of 4.3-4.5 and a total solid concentration of 4,000-6,000 mg/L. The BOD_5 and COD of this wastewater were in the range of 3,400-6,018 mg/L and

3,870-6,840 mg/L, respectively, with a BOD_5/COD ratio of 0.87 (Table 2.5). It is obviously that it causes heavy pollution to the receiving surface water.

Table 2.4 Characteristics of wastewater from medium-scale tapioca processing companies in Tay Ninh and Binh Dinh Province

No.	Parameters	Unit	Tay Ninh	Binh Dinh
1	pH	-	4.00 - 4.16	5.60
2	TDS	mg/L	1,758 - 2,120	1,587
3	SS	mg/L	1,477 - 2,585	1,197
4	COD	mg/L	14,323 - 17,764	13,068
5	BOD_5	mg/L	8,858 - 11,005	7,381
6	SO_4^{2-}	mg/L	99	79
7	CN^-	mg/L	5.8	3.4

Source: *Khoa, 1998.*

Table 2.5 Characteristics of wastewater from the root-rinsing and sedimentation stages of small-scale tapioca processing enterprises

No.	Parameter	Unit	Root rinsing	Sedimentation 1	Sedimentation 2	Mixture
1	pH	-	6.5 - 7.5	4.5 - 4.7	4.5 - 4.7	4.5 - 5.6
2	TS	mg/L	550 - 700	4,200 - 4,400	4,000 - 6,600	4,000 - 4,300
3	SS	mg/L	400 - 500	680 - 730	1,868 - 2,960	565 - 640
4	TDS	mg/L	150 - 200	3,520 - 3,670	2,132 - 3,640	3,435 - 3,660
5	BOD_5	mg/L	40 – 60	4,800 - 5,700	3,400 - 6,018	4,600 - 5,200
6	COD	mg/L	100 - 150	5,760 - 6,840	3,870 - 6,670	5,631 - 6,409
7	Total nitrogen	mg/L	30 – 38	70 - 75	65 - 74	66 - 72
8	Total phosphate	mg/L	1.0 - 1.4	6.0 - 6.6	5.6 - 6.3	5.8 - 6.4

Source: *Nandy et al., 1995.*

Tapioca production villages at Tra Co Village (Dong Nai Province) and Binh Minh and Tan Binh Villages (Tay Ninh Province) provide excellent evidence. Characteristics of wastewater from different settling stages measured at tapioca processing households are presented in Table 2.6.

Results of chemical examinations of tapioca wastewater generated from different stages of tapioca processing in the Thu Duc District (HCMC, Vietnam) (Table 2.7) once again reveal that tapioca wastewater is a heavy pollution source for any receiving source if proper treatment before discharge is omitted.

Table 2.6 Characteristics of wastewater from the household-scale tapioca processing households surveyed in Tra Co Village

No.	Parameter	Unit	First settling	Second settling	Third settling
1	pH	-	3.60	3.48	3.79
2	TDS	mg/L	1,300	730	400
3	SS	mg/L	1,413	2,050	570
4	VSS	mg/L	1,388	1,900	560
5	BOD_5	mg/L	15,188	9,824	5,000
6	COD	mg/L	20,340	11,353	6,244
7	$N\text{-}NH_3$	mg/L	197	102	24
8	N-Organic	mg/L	470	276	137
9	$P\text{-}PO_4^{3-}$	mg/L	17.0	36.0	19.4

Source: *ARRPET, 2001.*

Table 2.7 Characteristics of wastewater from the root-rinsing and sedimentation stages of household-scale tapioca processing enterprises in the Thu Duc District, HCMC

No.	Parameter	Unit	Root rinsing	Sedimentation 1	Sedimentation 2
1	pH	-	3.5 - 4.8	3.5 – 3.7	3.9 – 4.2
2	SS	mg/L	552 - 1,124	758 - 1,091	215 - 243
3	VSS	mg/L	110 – 125	523 - 764	153 - 165
4	BOD_5	mg/L	532 – 853	13,338 – 16,510	724 - 879
5	COD	mg/L	825 – 1,212	14,577 – 18,243	1,065 – 1,238
6	$N\text{-}NH_3$	mg/L	5.6 - 11.0	81.2 – 92.9	12.2 – 36.8
7	N-Org	mg/L	15.2 – 26.2	25.6 - 275.8	22.5 - 182.0
8	PO_4^{3-}	mg/L	8 – 13	48 - 86	13 - 42

Source: *ARRPET, 2004.*

2.3.2 Flow Rate of Tapioca Processing Wastewater

The flow rate of tapioca wastewater is one of the important parameters for designing of a wastewater treatment plant. The starch content of a fresh cassava root varies from 25-30 percent, and normally four tons of fresh cassava roots yield one ton of dry tapioca starch. As elucidated before a wide variation in the flow-rate of wastewater exists between the household-scale up to large-scale tapioca processing factories. The bulk of the tapioca wastewater in household-scale factories originates from the settling basins, but in large-scale production the major source of wastewater is from the centrifuge stage. A surveying the flow-rate of wastewater from different scales of the tapioca production process by ARRPET (2003, 2005) shows that household-scale flow-rate wastewater ranged from 3.5-5.5 cubic meter per ton of fresh cassava roots, while large scale flow-rate wastewater ranged from 3.0-5.0 cubic meter per ton of fresh cassava roots, depending upon the production technology. The flow-rate of tapioca wastewater is presented in Table 2.8 and Table 2.9.

Table 2.8 Flow-rate of household-scale tapioca processing wastewater

No.	Companies	Flow-rate, (m^3/ton of fresh roots)	Average production capacity (ton of roots/day)	Estimated flow rate, (m^3/day) in area surveyed	Reference
1.	Not identified name	5-10	-	-	Triet, 1993
2.	Not identified name	2.0-2.5	-	-	Dao, 1998
3.	Not identified name	4-5	-	-	Khoa, 1998
4.	Binh Minh Village Tay Ninh Province	8-12	15-80	6,000-8,000	ARRPET, 2003
5.	Tra Co Village Dong Nai Province	4.5-5.5	5-7	2,000-2,500	ARRPET, 2003
6.	Thu Duc District, HCMC	3.5-5.5	4-5	600-800	ARRPET, 2003

Table 2.9 Flow-rate of large-scale tapioca processing wastewater

No.	Companies	Flow-rate, (m^3/ton of fresh roots)	Average production capacity, (ton of roots/day)	Estimated flow rate, (m^3/day) in area surveyed	Reference
1.	S.R.Tapioca Co., Thailand	8-9	-	-	Jesuitas, 1966
2.	Not identified name	10-15	-	-	Triet, 1993
3.	Not identified name	4-5	-	-	Nandy et al., 1995
4.	Not identified name	3	-	-	Hien et al., 1999
5.	Phuoc Long Tapioca Co., Binh Phuoc	3.0-4.0	Aprx. 2,000	6,000-7000	ARRPET, 2003
6.	VEDAN Viet Nam Co., Dong Nai	3.0-5.0	200-240	1000-1,200	ARRPET, 2003
7.	Tay Ninh Tapioca Co., Tay Ninh Province	3.5-5.0	500	1,700-2,500	ARRPET, 2005
8.	Toan Nang Tapioca Co., Tay Ninh	4.0-5.0	400	1,500-2,000	ARRPET, 2005
9.	Tan Chau Tapioca Co., Tay Ninh	4.5-5.0	400	1,500-2,000	ARRPET, 2005
10.	MIWON Tapioca Co., Tay Ninh	4.0-4.8	200-250	800-1,200	ARRPET, 2006
11.	KMC Tapioca Co., Binh Phuoc	4.5-5.5	400-500	2,200-2,300	ARRPET, 2006

2.4 CHARACTERIZATION OF TAPIOCA PROCESSING WASTEWATER

A number of characteristics of wastewater are important for designing of a wastewater treatment facility. One of them comprises the COD concentration, the most relevant measure for the organic pollution strength of a wastewater, although it does not indicate the biodegradability of the organic pollutants. So, for biological treatment processes, aerobic or anaerobic, the biodegradability of organic pollutants obviously is a very important for characterizing the wastewater. Since a high-rate anaerobic biological treatment process is often not sufficient for allowing discharge of the effluent to the receiving water, the COD parameter is also frequently used to assess the remaining organic pollution of the wastewater. In order to determine the appropriate post-treatment processes to complete the treatment of the wastewater, the biodegradable fraction of the COD generally is the relevant parameter. Besides, the change of pH on the flow stream is always quickly due to the conversion of organic matter into VFA. This is a particular property of tapioca processing wastewater.

2.4.1 Anaerobic Biodegradability of Tapioca Processing Wastewater

In practice, the result from an anaerobic biodegradability assay provides a useful indication as to whether biological processes can be applied to treat wastewater. For that purpose the anaerobic batch tests using serum bottles of 1,250 ml are used to assess the anaerobic biodegradability of raw tapioca wastewater. The experiments are described in this section, comprising a very similar procedure as used in the specific methanogenic activity (SMA) tests - by measurement of the substrate depletion rate. An anaerobic sludge originating from a septic tank is used as seed sludge at a concentration of 3 gVSS/L in the assay. After supplying the substrate, nutrients, and trace elements, the bottles are closed and exposed to ambient conditions. The bottles are positioned on the shaker at 50 rpm. Samples are taken daily for pH and COD analyses and COD in the assay are measured in soluble COD form ($COD_{sol.}$). The accumulated gas in the headspace is released daily, but not measured. In these experiments three successive feeds are applied until a steady state is obtained. The biodegradability assessment is calculated based on the results of the third feed.

The goal of this research is to determine the anaerobic biodegradability of the raw tapioca wastewater and the pre-settled tapioca wastewater.

Two series of experiments were performed. In the first run, raw tapioca wastewater was used to assess the anaerobic biodegradability of raw tapioca wastewater. In the second run, a raw tapioca wastewater was used after approximately 2 h settling, consequently that sample contained only fine suspended solids. This experiment was performed to assess the anaerobic biodegradability of pre-settled tapioca wastewater for comparison with the anaerobic biodegradability of raw tapioca wastewater.

The Anaerobic Biodegradability of Raw Tapioca Wastewater

The experimental results of the anaerobic biodegradability of raw tapioca wastewater are presented in Table 2.10.

Table 2.10 The anaerobic biodegradability of raw tapioca wastewater

Item	Unit	Value
First feed		
$COD_{beginning}$	mgO_2/l	2,830
COD_{end}	mgO_2/l	185 - 218
Efficiency	%	92 - 93
Time of experiment	days	46 - 49
Second feed		
$COD_{beginning}$	mgO_2/l	2,754 – 2,765
COD_{end}	mgO_2/l	153 - 185
Efficiency	%	93 - 94
Time of experiment	days	25 - 28
Third feed		
$COD_{beginning}$	mgO_2/l	2,611 – 2,802
COD_{end}	mgO_2/l	169 - 213
Efficiency	%	93 - 94
Time of experiment	days	18 - 22
Anaerobic biodegradability	%	**92.3 – 93.3**

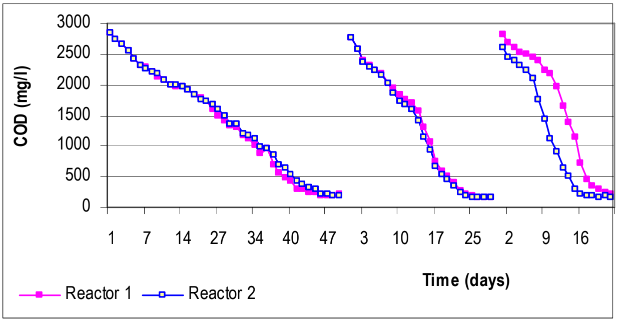


Fig 2.3 Anaerobic biodegradation of raw tapioca wastewater.

As shown in Fig. 2.3 in the first feed, the soluble COD concentration decreased slowly to about 185-218 mg/L, because the sludge was not yet adapted to the tapioca wastewater. In the second feed, the soluble COD concentration dropped faster as a result of already improved adaptation of the sludge to the tapioca wastewater. The soluble COD concentration reached its lowest concentration at $COD_{sol.}$ = 153-185 mg/L after 25-28 days, corresponding to the COD removal efficiency of 93%. In the third feed, the soluble COD concentration decreased relatively slowly during the first 4-5 days and then it dropped rapidly. The soluble COD concentration remained constant at 169-213 mg/L after 18-22 days, corresponding to removal efficiency was 92.3 - 93.3%. The anaerobic biodegradability of raw tapioca wastewater approximated 92.3 -93.3%.

Anaerobic Biodegradability of Pre-Settled Tapioca Wastewater

In this experiment, the two hours pre-settled raw tapioca wastewater was used, consequently the wastewater from which all coarse particles were removed, except the fine suspended solids. The pre-settled wastewater was then diluted with tap water to a suitable COD concentration. The anaerobic biodegradability of pre-settled tapioca wastewater is shown in Table 2.11.

The results clearly indicate that the conversion of pre-settled tapioca wastewater proceeds – as expected easier than raw wastewater. During the first feed the soluble COD concentration initially relatively slowly, because bacteria needed time to adapt to the tapioca wastewater. The first feed lasted 40 days and at the end the soluble COD concentration ranged from 165-177 mgO_2/l. In the second feed, the lowest soluble COD concentration ranging from 132-162 mg/L was reached after 25 days.

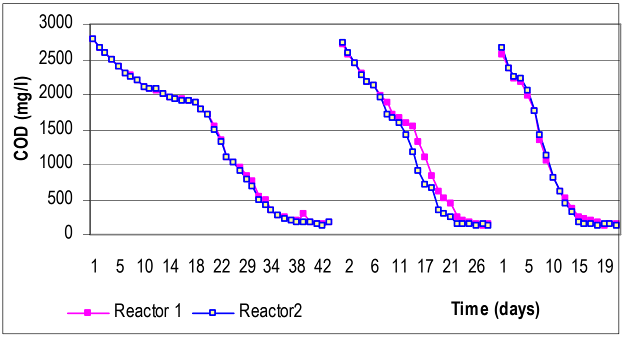


Fig 2.4 Anaerobic biodegradation of pre-settled tapioca wastewater.

Table 2.11 Anaerobic biodegradability of pre-settled tapioca wastewater

Item	Unit	Value
First feed		
$COD_{beginning}$	mgO_2/l	2,776
COD_{end}	mgO_2/l	120 - 177
Efficiency	%	94 - 96
Time of experiment	days	38 - 43
Second feed		
$COD_{beginning}$	mgO_2/l	2,699 – 2,732
COD_{end}	mgO_2/l	132 - 162
Efficiency	%	94 - 95
Time of experiment	days	25 - 28
Third feed		
$COD_{beginning}$	mgO_2/l	2,569 – 2,654
COD_{end}	mgO_2/l	127 - 147
Efficiency	%	94 - 95
Time of experiment	days	17 - 22
Anaerobic biodegradability	%	**94.6 – 94.7**

In the third feed, the COD concentration dropped from 2,569-2,654 mg/L to 127-147 within 17 days, corresponding to a COD removal efficiency was 94,7%. In comparison to the experiment with non-settled wastewater, the degradation proceeds slightly smoother as a result of absence of coarse suspended solids. The fine tapioca suspended solids hydrolyze into dissolved substrate, which then is rapidly converted into the end products. The anaerobic biodegradability of pre-settled tapioca wastewater apparently is slightly higher than that of raw tapioca wastewater, i.e., approximating 94.6- 94.7%.

2.4.2 Aerobic Biodegradability of Tapioca Processing Wastewater

The objective of the present research was to assess the aerobic biodegradability of raw tapioca wastewater and the COD concentrations remaining in the solution after the test run. Parameters such as suitable VSS, HRT, and sludge yield were determined.

The batch experiments are described in this section is very similar to the procedure used in the activated sludge process. The details are described in Chapter 5 - Part A. Septic tank sludge is used as seed sludge, the applied F/M ratios ranged from 0.3 - 0.6. The experimental results were collected during the establishment of steady-state conditions and are presented in Table 2.12.

Table 2.12 Aerobic biodegradability of tapioca processing wastewater

Item	Unit	Period 1	Period 2	Period 3	Period 4
COD influent	mg/L	1,038-1,112	1,439-1,462	2,254-2,278	3,336-3,384
COD effluent					
6 hrs	mg/L	93-95	84-90	270-281	1,251-1,322
12 hrs	mg/L	79-85	51-53	71-79	199-214
24 hrs	mg/L	59-63	53-60	66-71	110-123
48 hrs	mg/L	-	-	-	98-101
Sludge load	gCOD/gVSS.d	0.49-0.51	0.51-0.52	0.55-0.57	0.83-0.86
Yield	gVSS/gCOD.d	0.20-0.22	0.30-0.31	0.17-0.18	0.11
Aerobic biodegradability	%	94.1 - 94.3	96.4 - 96.5	96.9 - 97.1	97.0 - 97.1

The results in Table 2.12 show that at the imposed sludge load of 0.49-0.51 kgCOD/kgVSS.day, the COD concentrations dropped from 1,038-1,112 mg/L to 59-63 mg/L within 24 h of aeration, corresponding to an aerobic biodegradability of 94.1-94.3%. At an imposed sludge load of 0.51-0.52 kgCOD/kgVSS.day, and after 12 h of aeration, the COD concentrations dropped from 1,439-1,462 mg/L to 51-53 mg/L, corresponding to an aerobic biodegradability in the range 96.4-96.5%. If the aeration is stretched, the COD concentration is increased slightly, i.e., from 51-53 to 53-60 mg/L, which can be attributed to the phenomenon of lysis, and nutrients remaining in the dead cells diffuse into the solution also some organic matter (COD). At an imposed sludge load of 0.55-0.57 kgCOD/kgVSS.day, the aerobic biodegradability reached values in the range 96.9-97.1% with lowest COD concentrations of 66-71 mg/L. At a sludge load of 0.83-0.86 kgCOD/kgVSS.day, however, it took 48 h to reach the lowest COD concentrations, because the influent COD concentrations was relatively high, i.e., 3,336-3,384 mg/L, and the effluent COD concentrations were 98-101 mg/L after 48 h. The experimental results reveal a maximum aerobic biodegradability of tapioca processing wastewater of approximated 97%. The assessed sludge yield amounted to 0.17-0.3 kgVSS/kgCOD.day. The settling ability of the sludge was better in the experiments with COD concentrations lower than 2,278 mg/L; the sludge settled faster, and the supernatant was clear.

2.4.3 Change in pH and VFA concentrations during tapioca wastewater storage time at an ambient temperature

The pH of original wastewater is slightly acidic in nature, related to the pH of the water supply, ranging from 5.40-5.90. The quick change in the pH of tapioca wastewater is presented in Fig. 2.5. With **VFA-VN**: VFA concentrations determined by titration method after distillation, analyzed in CENTEMA, according to Anaerobic Lab Work Manual (1995). **VFA-NL**: VFA concentrations determined using GC, carried out in WUR, the Netherlands - the detail in Section 7.2.6).

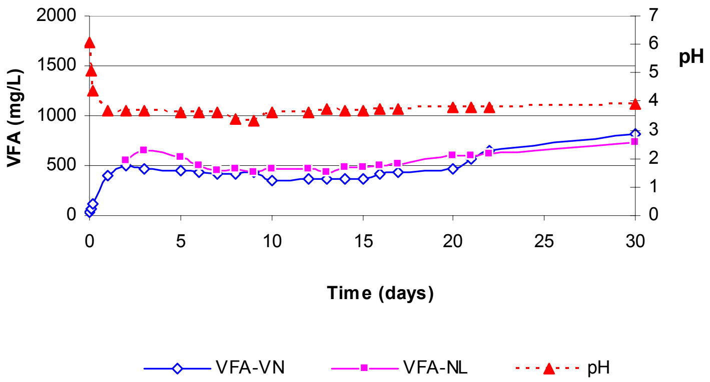


Fig. 2.5 Accumulated VFA in relation to the pH of tapioca wastewater during storage time.

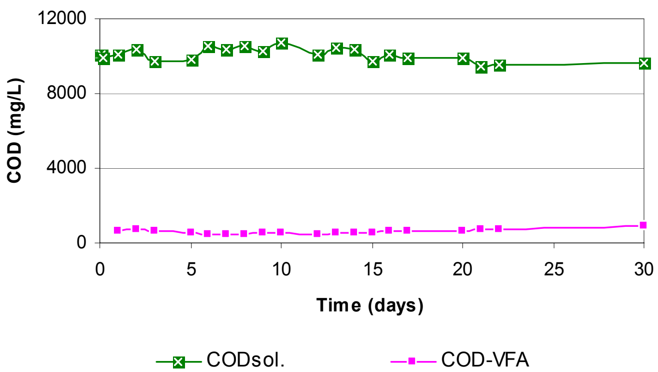


Fig. 2.6 Relationship between soluble COD concentration and COD-VFA of tapioca wastewater (with total COD of 12,200 mg/L) during storage time.

The initial pH after release from the producing process was around 5.90, after which it dropped quickly to pH 5.06 in 2 h and to 4.35 in 4 h. After 1 day, pH reached 3.70 and remained in the range of 3.50-3.70. The VFA concentration of wastewater increased rapidly from 34 to 70 and then to 119 mg/L after 2 h and 4 h, respectively. The VFA concentration reached 500 mg/L after 2 days – in case of VFA-VN, and reached 647 mg/L – in case of VFA-NL. This was due to the acidogenic reactions of glucose, the main products of which are acetate, propionate, butyrate, ethanol, and lactate. (The partial amount of each did not determine). Moreover, in most cases, regardless of whether wastewater originated from a small-scale or a large-scale factory, the ratio of COD-VFA and soluble COD ranged from 5-7%.

2.5 CONCLUSIONS

- The main sources of tapioca processing wastewater originate from the settling or centrifugation stage of the production process;
- The specific wastewater production of household-scale ranges from 3.5-12.0 m^3/ton of fresh cassava roots, while large-scale factories range from 3.0-5.0 m^3/ton of fresh cassava roots;
- Wastewater pollution strength of tapioca processing factories is very high, i.e., CODtt (7,000-41,400 mg/L), BOD (6,200-23,000 mg/L), SS (500-8,600 mg/L), low pH (4.2-5.7), CN^- (19-96 mg/L), besides the ratio of COD-VFA/CODsol. in range of 5-7%;
- The maximum aerobic biodegradability of tapioca wastewater approximated 97%, and the COD concentration in the solution was not lower than 51-53 mg/L;
- The anaerobic biodegradability of raw tapioca wastewater amounts to 92.3-93.3%, and the anaerobic biodegradability of pre-settled tapioca wastewater approximately 94.6-94.7%;
- Almost all wastewater from household-scale factories was discharged untreated into a river or lake, thus causing damage to the environment;
- Almost all large-scale factories treated their wastewater using a series of anaerobic and facultative ponds. However, this technology is not sufficient to satisfy Vietnamese industrial wastewater effluent discharge standards.

3

Remove of Suspended Solids by Applying an Upflow Anaerobic Filter as a Pre-Treatment Step

3.1 GENERAL INTRODUCTION

The Upflow Anaerobic Sludge Blanket (UASB) system has been widely used for the treatment of high-strength wastewater such as that from breweries and beverages, distilleries and fermentations, pulp and paper, and food and so on. Mai et al. (2001) also reported that tapioca processing wastewater containing a high COD concentration can be treated using UASB to reduce COD and to recover energy (methane gas). This wastewater contains a high concentration of SS and colloidal content, with COD-SS and COD-colloidal content ranging from 2,560-4,730 mg/L and 192-360 mg/L, respectively. High concentrations of solids can have a negative affect on the treatment efficiency of UASB reactor. According to Lettinga et al. (1983) the adsorption of finely dispersed SS to sludge granules in the anaerobic treatment of domestic wastewater affects the performance of the process detrimentally. This phenomenon may reduce the sludge-specific activities, through wrapping the active biomass particles with a film of increasingly thick non-biomass matter, which consequently hampers the substrate transport through the active biofilm. Zeeman and Lettinga (1999) reported that the SS and colloidal content in wastewater are primary factors that affect the performance of an anaerobic reactor detrimentally. The Man et al. (1986) observed a dilution of the active biomass in the anaerobic treatment of municipal wastewater in a granular sludge bed UASB-reactor as a result of SS entrapment. Zeeman et al. (1997) reported that the application of UASB systems for the treatment of complex wastewater containing a high amount of SS is usually limited by the accumulation of these compounds in the sludge bed. Likewise, Sayed (1987) found in the treatment of slaughterhouse wastewater in a granular sludge UASB system that at loading rates exceeding 15 $kgCOD/m^3.d$ the accumulation of SS resulted in a serious decrease of the sludge specific methanogenic activity. Depending on its characteristics and concentration, SS present in the wastewater can affect the anaerobic treatment in the following ways (Lettinga and Hulshoff Pol, 1991):

- Reducing the sludge’s specific methanogenic activity due to adsorption and entrapment of poorly or non-biodegradable SS;
- Stimulation of formation of scum layers;
- Counteraction of formation of granular sludge;
- Stimulation of a spontaneous and sudden washout of sludge in the event of prolonged continuous SS entrapment in a granular sludge bed.

Consequently it can be concluded that it is highly recommendable to reduce the SS concentration present in a wastewater prior to subjecting it to treatment in a UASB reactor. Yoda et al. (1985) reported that colloidal particles in the influent are difficult to remove, i.e. they can represent up to 60-70% of the COD content of the effluent of an AFB reactor and this was confirmed by Sayed and Fergala (1995) that the entrapment mechanism for removing suspended solids in a sludge bed was not sufficiently effective in removing colloidal particles. The study of Elmitwalli et al. (2000a) found in the treatment of raw domestic sewage that the presence of an anaerobic biofilm and the removal of suspended solids from the influent increased the removal efficiency of colloidal COD in an anaerobic polyurethane-foam filter, resulted in an average removal efficiency for colloidal COD of 63% at a temperature of 24^oC.

Various experimental studies have been carried out involving a pre-treatment procedure for removing suspended solids from a wastewater using filter media. In these studies it was observed that the presence of anaerobic biofilm on filter media strongly reinforced the removal efficiency of colloidal COD. Using granitic gravel packing as a filter medium, Borja and Banks (1994) investigated a laboratory-scale upflow anaerobic filter for the treatment of palm oil mill wastewater, and found a high substrate removal efficiency of up to 90%. Pozo et al. (2000) studied the anaerobic pre-treatment of slaughterhouse wastewater using fixed-film reactors with non-random support, and found that – the COD removal efficiencies ranging from 85-89% were achieved for organic loading rates of 8 kgCOD/m^3.d, while the highest OLR i.e., at 35 kgCOD/m^3.d - led to a COD efficiencies of 55-75%. Elmitwalli et al. (2002a) demonstrated that the AF reactor system indeed represents an efficient pre-treatment process for removal of suspended COD from domestic sewage. When using such a system as a first step it resulted in a distinct improved removal of colloidal matter and dissolved COD in the second step. The two-step AF + AH system therefore can provide a high removal efficiency for all COD fractions. This was confirmed by results of Halalsheh (2002) who reported that a combined AF with a UASB reactor system operated at 4+8 hrs liquid detention times for treatment of raw sewage gave an average total COD removal efficiency of 70 - 82%.

Factors like the specific surface area, porosity, surface roughness, pore size, and distribution of the packing material were found to play an important role in upflow anaerobic filter performance. Oriented and porous material performed better than random and non-porous material. Reticulated polyurethane foam appeared to be an excellent material for use with an anaerobic filter reactor (Huysman et al., 1983).

The objective of the research presented in this chapter is to assess the appropriateness of an upflow anaerobic filter (UAF) reactor packed with different filter media, viz. reticulated polyurethane foam (RPF), pulverized polystyrene foam (PPF), and sections of pine wood (PW) for the removal of suspended solids from tapioca processing wastewater under conditions prevailing in Vietnam.

3.2 MATERIALS AND METHODS

3.2.1 Overview of Experiments

Three UAF reactors using three types of filtering media, i.e. with: RPF, PPF, and PW were operated using tapioca processing wastewater as influent. The tapioca wastewater used in the experiments was taken from the family-scale factory at Binh Chieu Ward, Thu Duc District, HCMC. The experiments were carried out at room temperature, i.e. 29-35^{0}C in the laboratory at the Center for Environmental Technology and Management (CENTEMA), Van Lang University, Ho Chi Minh City, Vietnam.

3.2.2 Experimental Reactors

In our experiments we selected the UAF reactor system as a pre-treatment process for the removal suspended solids from tapioca wastewater. The diagram in Fig. 3.1 shows the system used in the experiments. The reactor was made of acrylic and had a total volume of 8.550 L; the internal diameter was 100 mm and the height 1,115 mm. The bottom of the reactor was coneshaped in order to attain a uniform feed distribution. In the bottom of the UAF reactor a valve was installed in order to enable the regular discharge of the accumulated sludge. A series of small sampling ports were fitted along the height of the reactor to enable wastewater and sludge sampling. The height of the filter ranged from 650-700 mm. The height from the bottom of the reactor to the filter medium layers was 120 mm. A Gas-Solid-Liquid (GSL) separator was installed at the top of the reactor; the gas was measured by a wet-test gas meter (Meterfabriek Schlummbergen, Dordrecht, The Netherlands). Influent was introduced into the reactor using a peristaltic pump (Watson Marlow 501 U, UK), and the influent tank wastewater was mixed intermittently every 3 min to prevent settling if suspended solids. The treated wastewater left the reactor via the top of the reactor. As mentioned before, the reactor was operated under Vietnamese ambient temperatures in the range 29-35°C throughout the whole experimental period.

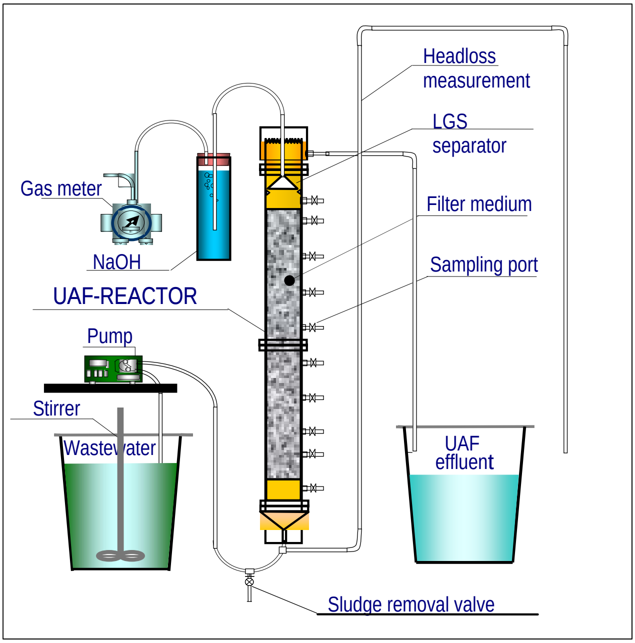


Fig. 3.1 Schematic diagram of the UAF-reactor.

3.2.3 Filtering Medium Materials

The three different types of filtering media selected, viz. - RPF, PPF, PW - were chosen for the experiments:

<u>Reticulated Polyurethane Foam (RPF)</u> This is a porous material with the following characteristics: total sheet thickness: 25 mm, base thickness: 10 mm, nob thickness: 15 mm, density: 19-22 kg/m^3, specific surface area: 500 m^2/m^3, size of pore: 2.5 mm, number of pores: 7-15 pores/inch. The foam was rolled in order to place it at a height of 675 mm in the UAF reactor, corresponding to 67.5 % of the reactor volume.

<u>Pulverized Polystyrene Foam (PPF)</u> This consists of spheres with an average diameter of 2 mm. It was placed in the UAF reactor at up to a height of 670 mm, corresponding to 67.0 % of the reactor volume.

<u>Section of Pine Wood (PW)</u> Its dimension was H*L*W: 20*30*2 mm. It was placed in the UAF reactor up to a height of 650 mm, corresponding to 65.0 % of the reactor volume.

3.2.4 Wastewater Used in The Experiments

The tapioca wastewater used in this experiment was taken from the household-scale (family scale) factory at Go Dua Hamlet, Binh Chieu Ward, Thu Duc District, Ho Chi Minh City. The wastewater was stored under ambient conditions for approximately one week. The composition of this wastewater is presented in Table 3.1.

Table 3.1 Tapioca processing wastewater composition

Composition	Unit	Concentration
pH		3.40-3.72
COD_{total}	mg/L	12,931-15,457
COD_{ss}	mg/L	1,114-2,158
COD_{col}	mg/L	653-710
COD_{sol}	mg/L	10,030-12,644
BOD_5	mg/L	9,783-12,931
SS	mg/L	454-1,850
VSS	mg/L	431-1,830
$N\text{-}NH_3$	mg/L	63-77
$N\text{-}NO_3^-$	mg/L	1.1-7.5
$N\text{-}NO_2^-$	mg/L	0.0-0.2
N-Org	mg/L	196-392
$P\text{-}PO_4$ total	mg/L	39-73
SO_4^{2-}	mg/L	0-27
SVI	mL/gTSS	14.7-33.1

3.2.5 Seed Sludge Used in The Reactors

Septic tank sludge from the Hoa Binh fertilizer factory (HCMC, Vietnam) was used as seed sludge. The raw sludge was screened through a 0.6 mm sieve to remove the sand, fibers, and large pieces of debris before seeding. The seed sludge was 0.20 gVSS per liter of reactor, with the initial sludge characteristics as follows:

- Water content = 89 %
- VSS/(wet sludge) = 6.7 %
- SMA (at ambient temp.) = 0.068 gCOD/gVSS.d

As mentioned above, the presence of bacterial biofilm on the filter media strongly reinforces the removal of colloidal matter and enhances the removal of the total suspended solids content. Hence, the development of a proper bacterial biofilm on the surface filter medium is essential and for this purpose we used a small amount, i.e., about 0.20 gVSS/L, seed sludge during the reactor start-up. The amount of seed sludge should not be low, because the excess of the supplied seed sludge will rinse out of the reactor during its operation.

3.2.6 Procedure

The reactors were filled with tapioca wastewater (with COD around 1,500 mg/L) and the above mentioned amount of seed sludge and then allowed to stand for 3 days to allow initial acclimation of the sludge and some development of bacteria biofilm on the surface of filter bed. The operation of the UAF reactors was started at an influent SS concentration of around 600-800 mg/L and an HRT of 10-12 h, equivalent to an upflow velocity (V_{up}) of about 0.09-0.11 m/h. Once the operation of the reactor reached a 'steady state', or the SS treatment efficiency attained stable values, the HRT was decreased step-by-step from 10-12 h to 6-7 h and to 4-5 h, and the V_{up} increased from 0.09-0.11 to 0.16-0.18 and then 0.25-0.28 m/h. Influent and effluent samples were taken daily to assess the pH, total COD, soluble COD, SS, and VSS. The values of flow rate, biogas production, and headloss were recorded daily at 8 a.m. Once the SS treatment efficiency stabilized, a profile measurement was carried out by taking samples over the height of the reactor to assess the SS removal ability over the height of the filter medium. The stagnant sludge (SS) at the bottom of the reactors was discharged once every 2 days. The settle ability of this sludge was also determined. The cleaning phase of the reactor was carried out once the effluent suspended solid concentration began to increase beyond an acceptable level (SS>200 mg/L), or when a limiting headloss (with RPF 0.10-0.12 m/m, and with PPF 0.53-0.75 m/m) occurred across the filter bed. When either of these two conditions was reached, the operational phase was terminated and the filter was cleaned, viz the accumulated SS in the filter bed was removed, by imposing a downward flow of water through the filter bed and by passing air through the pack bed to enhance the cleaning.

3.2.7 Sampling and Analyses

To assess the treatment processes and efficiency, all parameters were examined daily or every 2 days. The pH was determined immediately after sampling using a pH electrode (never longer than 30 minutes after sampling). The SS, VSS, total COD, and soluble COD were analyzed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1995). The COD soluble was determined using 0.2-micrometer membrane filters.

3.3 RESULTS AND DISCUSSION

3.3.1 UAF Reactor with an RPF Filter Medium

The operational conditions and performance results of the UAF reactor with RPF as a filter medium are summarized in Table 3.2, and a part of the results are depicted in Fig. 3.2. During the start-up period (day 1-34), the imposed HRT varied from 10.8-11.4 h (flow rate of 18-19 L/d and V_{up} around 0.1 m/h). Based on the influent SS concentration of 485-840 mg/L, the suspended solid loading rate (SSLR) was 1.5-1.9 kgSS/m^3.d and based on the influent total COD of 6,771 to 12,833 mg/L, the imposed organic loading rate (OLR) varied from 15.0-28.5 kgCOD/m^3.d. As was expected the SS removal efficiency with values of approximately 15-33% remained relatively low during the first 10 days. During this period the sludge bacteria adapts to the new substrate and the bacterial biofilm on the surface of the filter medium develops. Once this film has developed sufficiently the SS removal efficiency improves significantly to 65-83%, reaching the maximum value at day 24. The SS concentration decreased from 685-840 mg/L in the influent to 140-236 mg/L in the effluent, but – as could be expected in view of the high COD load and the small amount of retained active biomass in the filter the COD treatment efficiency remained very low, i.e. the total COD concentration of influent decreased from 6,771-12,833 mg/L to 5,185-9,275 mg/L, corresponding to the COD treatment efficiency of 16.3-27.7% and the soluble COD concentration dropped from 5,743-11,468 mg/L to 5,074-8,786 mg/L, corresponding to the soluble COD treatment efficiency of 11.6-23.4%.

The total volume of sludge discharged once every two days amounted to approximately 600-800 mL each time. The sludge characteristics were determined to find out the appropriate method for treating this kind of sludge. The assessed settling ability of the sludge is depicted in Figure 3.5. The ratio volume of solids per total volume of mixture discharged amounted to 30-40% after 6-8 h of settling. Total solids ranged from 23.8-24.8 g/L and the ratio of VSS/TS ranged from 81.3-99.4%, with a typical range from 90.6-98.5%.

Table 3.2 Operational conditions and UAF reactor results with an RPF filter medium

Parameters	Units	Period 1	Period 2	Period 3
SS inf.	mg/L	485-840	500-1,300	725-1,267
SS eff.	mg/L	140-236	213-420	180-332
COD tt, inf	mg/L	6,771-12,833	11,844-16,457	6,746-8,624
COD tt, eff	mg/L	5,185-9,275	10,715-14,476	6,925-7,729
COD sol, inf	mg/L	5,743-11,468	10,971-15,177	5,384-7,365
COD sol, eff	mg/L	5,074-8,786	10,281-13,749	6,853-7,300
HRT	hours	10.8-11.4	6.0-6.8	4.6-4.7
Q	L/d	18-19	30-34	44-45
$\mathbf{V_{up}}$	m/h	0.1	0.16-0.18	0.25-0.26
SSLR	kgSS/m^3.d	1.5-1.9	1.9-5.0	3.7-6.7
OLR	kgCOD/m^3.d	15.0-28.5	45.7-63.5	34.7-45.4
Headloss	m/m	0.00-0.10	0.00-0.10	0.00-0.12
Exp. Time*	days (total)	34	127 (161)	79 (240)
$\mathbf{E_{SS}}$	%	65.5-83.3	57.4-72.5	68.6-85.8
$\mathbf{E_{COD\ tt}}$	%	16.3-27.7	3.2-12.0	0-19.7
$\mathbf{E_{COD\ sol.}}$	%	11.6-23.4	0.6-9.4	0-8.5

** The total experimental day is in the brackets*

In the next period (day 35-161), the imposed HRT varied from 6.0-6.8 h (a flow rate of 30-34 L/d) and V_{up} around 0.16-0.18 m/h. Based on the influent wastewater SS concentration of 500-1,300 mg/L the imposed suspended solids loading rate was 1.9-5.0 kgSS/m^3.d, and based on the influent total COD concentration of 11,844 to 16,457 mg/L the imposed organic loading rate amounted to 45.7-63.5 kgCOD/m^3.d. At the end of this period, the SS concentration dropped from 500-1,300 mg/L to 213-420 mg/L, but once again the COD removal efficiency obviously remained very low. Due to the extremely short HRT, the low active sludge content in the reactor just a minor fraction of the biodegradable matter can be converted, i.e. the total COD concentration dropped from 11,844-16,457 mg/L to 10,751-14,476 mg/L, consequently the COD treatment efficiency amounted to only 3.2-12.0 %. Obviously the same is true for soluble COD reduction, it amounted to 0.6-9.4 %. During this period, the cleaning phase was done after 15-20 days.

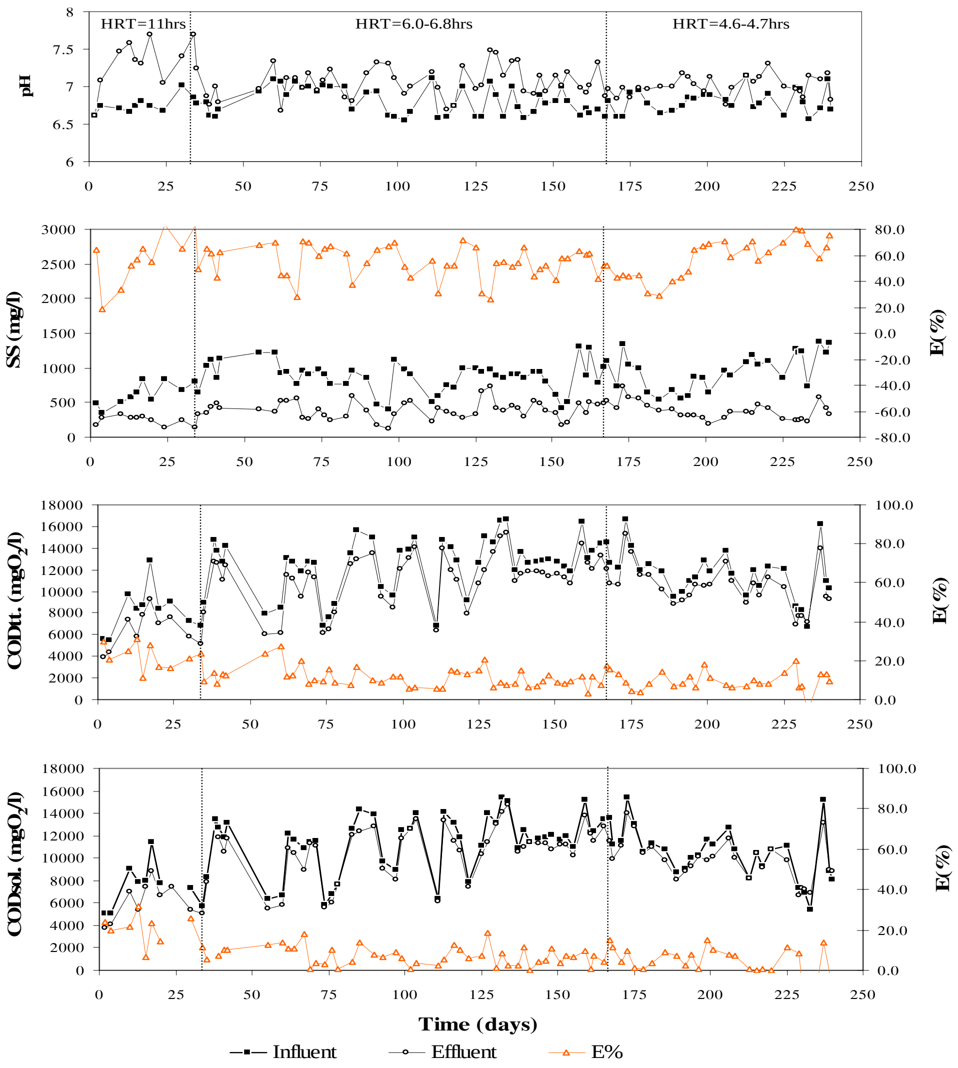


Fig. 3.2 Experimental results obtained with the UAF reactor packed with RPF filter medium. The HRT was decreased stepwise from 11 to 6 then to 4 h. and the V_{up} increased from 0.10 to 0.17 then to 0.26 m/h.

In the third period (day 162-240) the HRT varied from 4.6-4.7 h, corresponding to a flow rate of 44-45 L/d and V_{up} around 0.25-0.26 m/h. Based on the influent SS concentration of 725-1,267 mg/L the corresponding SSLR varied from 3.7-6.7 kgSS/m^3.d, and the OLR varied from 34.7-45.4 kgCOD/m^3.d (based on the influent total COD concentration of 6,746-8,624 mg/L). Also during this period the SS removal efficiency remained relatively stable with values in the range 68.6-85.8%, and obviously the COD removal efficiency during this period was very low. The experimental results clearly show that the SS removal mechanism in the UAF reactor mainly can be attributed to a combined process of coagulation, sedimentation and filtration.

3.3.2 UAF Reactor with a PPF Filter Medium

Operational conditions and performance results of a PPF-packed UAF reactor are summarized in Table 3.3 and the results are depicted in the experimental curves shown in Fig. 3.3. During the start-up period (day 1-66) the HRT varied from 10.7-11.4 h (flow rate of 18-19 L/d and V_{up} around 0.09-0.10 m/h), which gave with the SS concentration of influent wastewater ranged from 900-983 mg/L, a suspended solid loading rate (SSLR) varying from 1.9-2.1 kgSS/m^3.d. The imposed COD loading rate (OLR) was 14.3-26.9 kgCOD/m^3.d. During the start-up period the SS removal efficiency was far from stable i.e. at ranged from 39.7-80.3 %, the influent SS decreased from 515-1,225 mg/L to 192-530 mg/L. However, from day 58 onwards the SS removal efficiency became quite stable with values in the range 72.2-74.1 %, the influent SS decreased from 900-983 mg/L to 235-268 mg/L. And as expected the system was unable to remove a substantial amount of COD, i.e. the efficiency remained below 11%.

Table 3.3 Operational conditions and results involving UAF reactor with a PPF filter medium

Parameters	Units	Period 1	Period 2
SS inf.	mg/L	900-983	992-1166
SS eff.	mg/L	235-268	253-352
COD tt, inf.	mg/L	6,787-12-779	9,140-12,617
COD tt, eff.	mg/L	6,015-11,595	7,913-10,660
COD sol, inf.	mg/L	5,809-11,408	7,913-11,093
COD sol, eff.	mg/L	5,651-11,221	7,361-10278
HRT	h	11.4	6.2-6.4
Q	L/d	18	32-33
$\mathbf{V_{up}}$	m/h	0.09-0.10	0.17-0.18
SSLR	kgSS/m^3.d	1.9-2.1	3.7-4.5
OLR	kgCOD/m^3.d	14.3-26.9	34.2-48.9
Headloss	m/m	0.00-0.75	0.00-0.75
Exp. Time*	days (total)	66	98 (164)
$\mathbf{E_{SS}}$	%	72.2-74.1	64.8-74.5
$\mathbf{E_{COD\ tt}}$	%	9.3-11.6	13.4-17.3
$\mathbf{E_{COD\ sol.}}$	%	1.6-11.4	7.0-14.2

** The total experimental day is in the brackets*

The operation of PPF-packed UAF reactors suffered from clogging problems, which likely mainly can be attributed to the fact that the density of PPF is distinctly lower than water. As a result in an aqueous solution the packing beads will float upward and the beads will press against each other. In particular once the bacterial biofilm has developed, the structure of the filter bed becomes quite dense and then clogging easily happens, especially at increased upflow velocities. The experiment with the PPF filter medium was terminated at an HRT of 6.2-6.4 h.

The accumulating suspended solids at the bottom of reactors were discharged daily; the total volume for sludge mixture discharged was around 600-700 mL each time. The ratio volume of solid parts per total volume of mixture amounted to 30-35% after 6-8 h of settling.

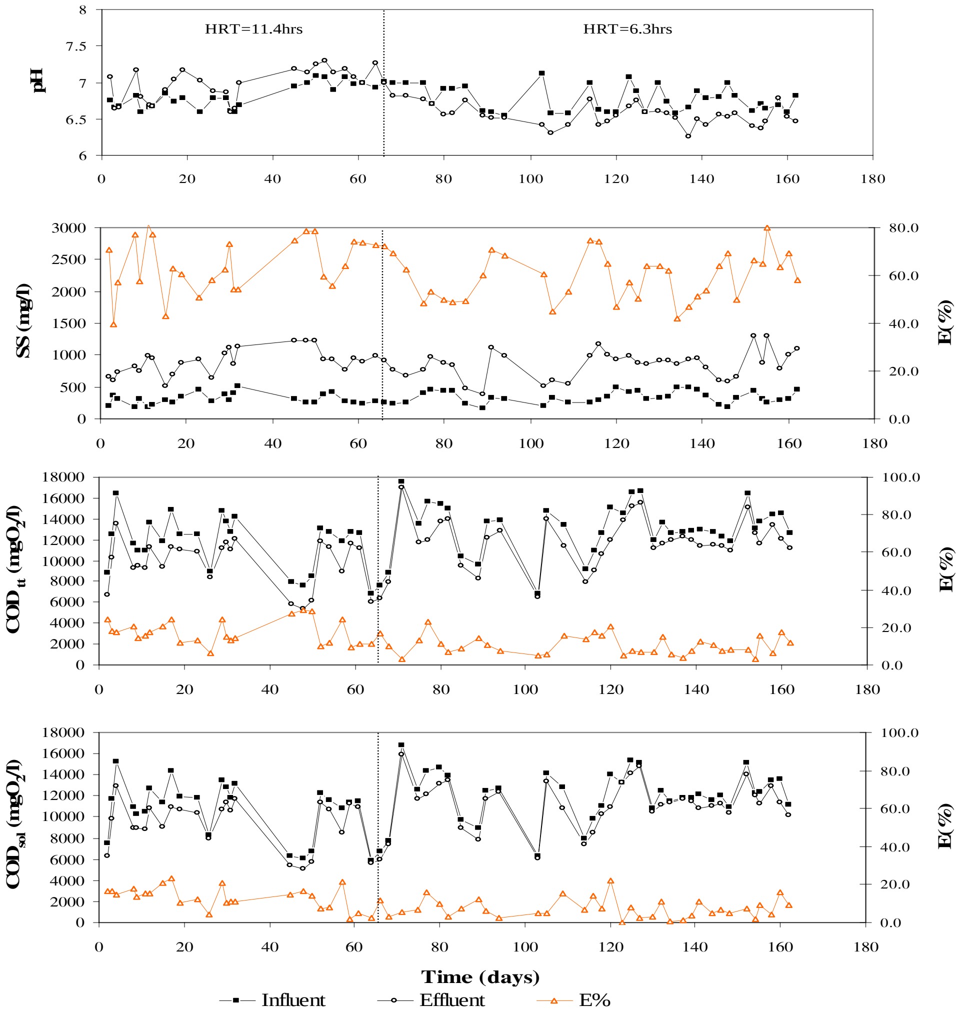


Fig. 3.3 Experimental results obtained with UAF reactor packed with a PPF filter medium. The HRT decreased from 11 to 6 h. And the V_{up} increased gradually from 0.10 to 0.17 m/h.

The cleaning procedure was conducted once the headloss exceeded a value of 0.53-0.75 m/m. Normally the cleaning procedure was completed after 10-13 days of filter phase for UAF with PPF-filter medium.

3.3.3 UAF Reactor with PW as a Filter Medium

The operational conditions and performance results of PW-packed UAF reactor are summarized in Table 3.4 and the results are depicted in the experimental graphs in Fig. 3.4. During the start-up period (day 1-56) the conditions were similar as in the two previous experiments (HRT was 11.4 h, flow rate of 18 L/d, V_{up} around 0.1 m/h). Based on the influent SS-concentration of 755-962 mg/L the suspended solid loading rate (SSLR) varied from 1.9-2.0 kgSS/m^3.d. The total COD concentration of influent wastewater ranged from 13,546-15,411 mg/L.

Table 3.4 Operational conditions and results involving UAF reactor with a PW filter medium

Parameters	Units	Period 1	Period 2	Period 3
SS inf,	mg/L	755-962	992-1,166	731-1,183
SS eff,	mg/L	162-288	212-300	148-290
COD tt, inf,	mg/L	13,546-15,411	9,140-12,617	9,632-13,760
COD tt, eff,	mg/L	11,755-13,478	7,852-10,418	8,596-12,288
COD sol, inf,	mg/L	12,604-14,641	7,913-11,093	8,229-12,728
COD sol, eff,	mg/L	11,559-13,097	7,361-10,175	8,229-12,032
HRT	h	11.4	6.2-6.4	4.6-4.7
Q	L/d	18	32-33	44-45
$\mathbf{V_{up}}$	m/h	0.09-0.10	0.17-0.18	0.24
SSLR	kgSS/m^3.d	1.9-2.0	3.8-4.5	3.8-6.2
OLR	kgCOD/m^3.d	28.5-32.4	35.3-48.7	50.7-72.4
Headloss	m/m	0.00	0.00	0.00
Exp. Time*	days (total)	56	101 (157)	88 (245)
$\mathbf{E_{SS}}$	%	70.1-79.1	72.0-78.6	75.5-82.8
$\mathbf{E_{COD\ tt}}$	%	10.0-23.2	14.1-20.7	7.3-10.8
$\mathbf{E_{COD\ sol,}}$	%	5.7-19.3	7.0-17.3	0-5.5

** The total experimental day is in the brackets*

The results show a low SS removal efficiency during the start-up time, i.e., ranging from 50.7-61.3 %, but the efficiency improved to 70.1-79.1% from during period 30-55, the SS concentration dropped from 755-962 mg/L to 162-288 mg/L. Similarly as in the other experiments the system was unable to provide a good COD treatment efficiency it remained below 23%. The pH increased from 6.60-7.09 to 7.03-7.76.

The accumulating suspended solids at the bottom of reactors were discharged once every 2 days; the total sludge volume discharged amounted to about 600-700 mL each time. The sludge settleability is shown in Figure 3.5. The ratio volume of solids per total volume of mixture discharged amounted to 30-40% after 6-8 h of settling. Sludge mixture characteristics were total solids in the range 2.6-3.1%, the VSS/TS ratio in the range 83.4-98.2%, with typical values from 90.1-93.6%.

In the second period, from day 57 to day 157 the imposed HRT amounted to 6.2-6.4 h (flow rate 29-32 L/d and V_{up} 0.17-0.18 m/h). Based on the influent SS concentration (range 992-1,166 mg/L) the suspended solid loading rate amounted to 3.8-4.5 kgSS/m^3.d. At the end of this period the SS removal efficiency reached a value in the range 72.0-78.6% (effluent SS concentration of 212-300 mg/L). During this period, the cleaning procedure was carried out after 20-22 days of filter operation at an HRT of 6.2-6.4 h.

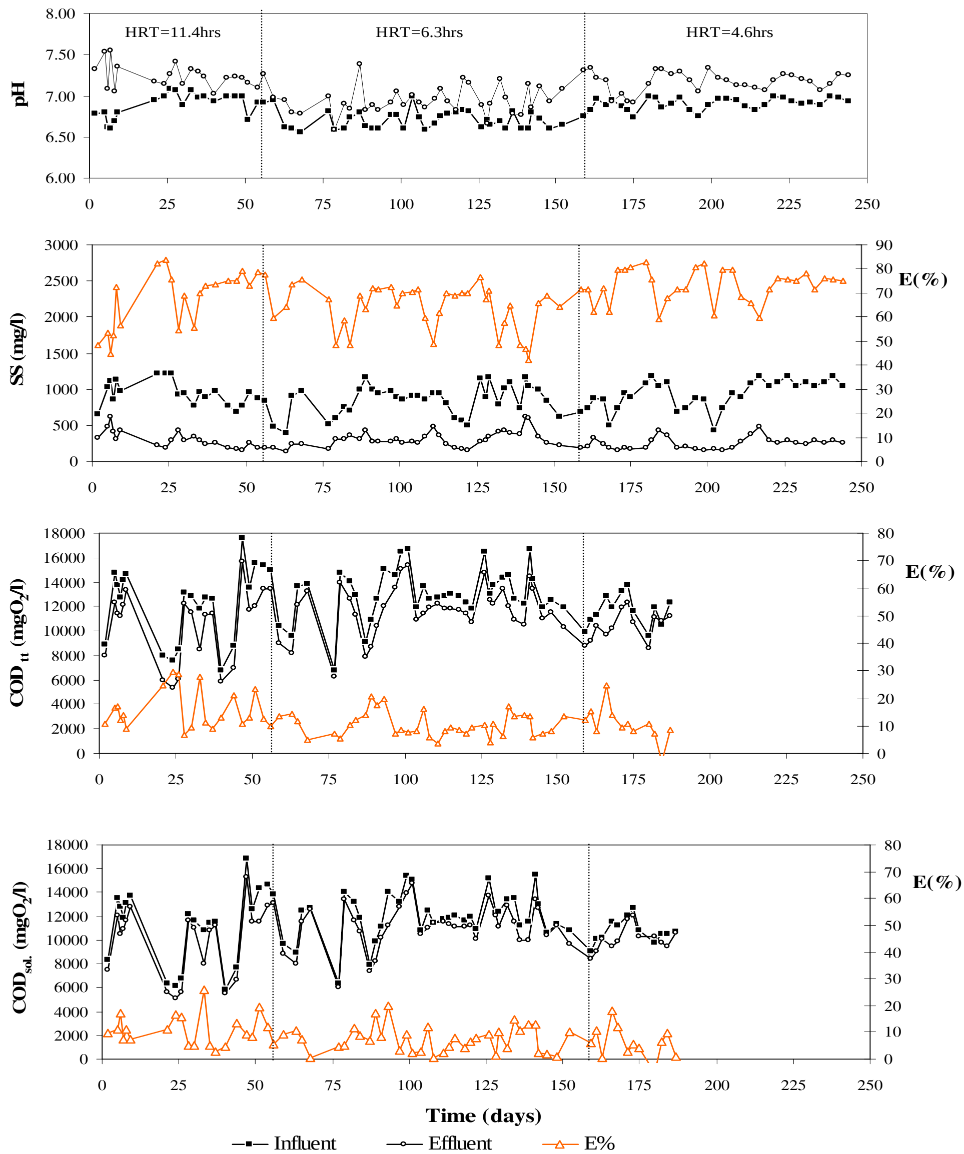


Fig. 3.4 Experimental results involving UAF reactor with a PW filter medium. The HRT decreased from 11 to 6 then to 4 h. The V_{up} increased gradually from 0.10 0.17, to 0.24 m/h.

In the third period (day 158-245) at an imposed HRT from 4.6-4.7 h (flow rate of 44-45 L/d and V_{up} around 0.24 m/h) the imposed SSLR varied from 3.8-6.2 kgSS/m^3.d at influent SS concentrations in the range 731-1,183 mg/L. During this period the SS removal remained relatively high and stable with values in the range 76-83%, i.e. the SS concentration decreased from 731-1,183 to 148-290 mg/L.

3.3.4 Characteristics of Waste Sludge from UAF Reactors

The results of the settling experiments of the discharged sludge are shown in Fig. 3.5. These results indicate that the sludge deposit after 3 h of settling reached values in the range 20-40% of the total volume of the discharged sludge mixture. The results clearly demonstrate the good settling/thickening characteristics of the sludge. However, the sludge clearly is far from sufficiently stabilized and therefore further stabilization in a separate digester is necessary; and with that then benefit should be taken from the recovery of the produced biogas.

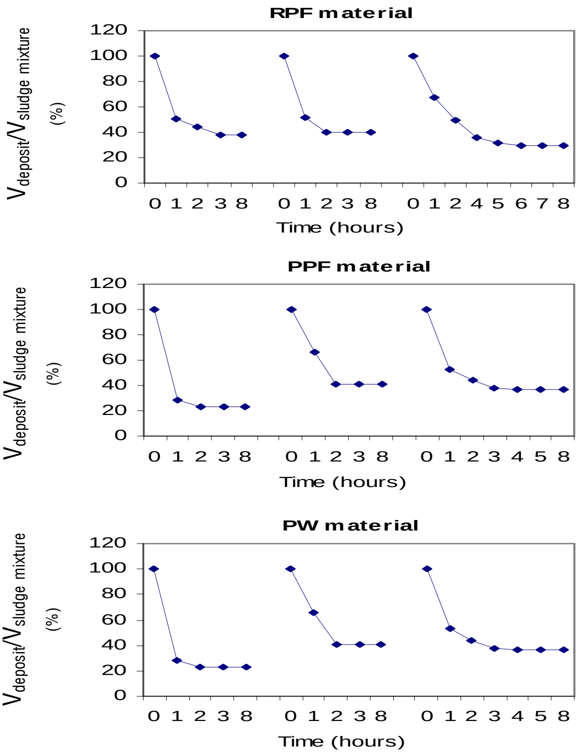


Fig. 3.5 The ratio volume of deposit per total volume of sludge mixture discharged after settling versus the time for the different filter media.

On the other hand, instead of exposing the sludge to an anaerobic digestion process, it also could be recycled for agricultural use as a soil conditioner (but obviously this also applies for the digested residues) or for animal feed. The analyses of the TSS and VSS of the sludge shows a TSS range from 20,630-26,120 mg/L and a VSS/TSS range from 90.6-95.8%, i.e. a fairly concentrated sludge can be produced with an exceptionally high organic matter content and with a high biodegradability (regarding the characteristics of the tapioca wastewater).

In addition, also the collected waste sludge from cleaning procedure of the filter medium was analyzed for TSS and VSS concentration. Its TSS-content range from 3,767-5,720 mg/L and also for this sludge obviously the VSS/TSS ratio was very high with values in the range 93.4-95.7%. The SVI of sludge after 30 min settling ranged from 65-68 mL/gTSS. The total volume of waste sludge resulting from the cleaning process was up to 14-17 L each time, which makes up a total excess sludge production about 1.7-2.1 L per liter of reactor.

Final Discussion

Until now the most popular pre-treatment process for complex types of wastewaters like for instance tapioca wastewater is applying primary settling. However with this traditional method just a moderate removal of COD and SS can be accomplished, i.e. according to our findings in this study a 2 h sedimentation period of raw tapioca wastewater the TSS-content only can be reduced from 678-1,560 mg/L to 522-1,138 mg/L the, which is far too low in case the next treatment step would be a high rate AnWT-system. Therefore, it is important to find other - more effective – means to remove solids from the raw wastewater prior to subjecting it to the AnWT-step and – based on literature data we selected the UAF reactor system.

Elmitwalli et al. (2000) demonstrated that an AF-filter packed with clean RPF sheets is well capable of removing most of the COD_{ss} (>75%) from raw sewage by a mechanism of physical entrapment and filtration, though at low HRT values of 0.5 h this system was found to be inefficient to remove colloidal COD. However, the presence of an anaerobic attached biofilm substantially improved the removal efficiency of colloidal COD.

Table 3.5 Tapioca wastewater compositions before and after UAF reactor

Composition	Unit	Raw WW	Influent UAF	Effluent UAF
pH		3.40-3.72	6.48-6.80	6.48-7.61
COD_{total}	mg/L	12,931-16,457	6,746-16,457	5,585-14,476
COD_{ss}	mg/L	1,114-2,158	985-1,110	323-412
COD_{col}	mg/L	653-710	325-398	211-429
COD_{sol}	mg/L	10,030-12,644	5,384-15,177	5,074-13,749
SS	mg/L	454-1,850	900-1,183	180-352
VSS	mg/L	421-1.830	835-1,030	139-330
$N-NH_3$	mg/L	63-77	-	186-231
$N-NO_3^-$	mg/L	1.1-7.5	-	0.0-0.2
$N-NO_2^-$	mg/L	0-0.2	-	Trace
N-Org	mg/L	196-392	-	10-102
$P-PO_4$ total	mg/L	39-73	-	29-70

Effluent characteristics are shown in Table 3.5, with the SS concentration ranging from 189-352 mg/L and the VSS concentration ranging from 139-330 mg/L, i.e., the ratio of VSS/SS up to 93-97%.

The results of the UAF experiments conducted in this study with three different filter media also clearly show the potential of this upflow filter system as pre-treatment step for tapioca processing wastewater, i.e. prior to subjecting the wastewater to a high-rate anaerobic treatment step. With all three filter materials - RPF, PPF, and PW, after a satisfactory bacterial biofilm on the material surface had developed - a relatively high SS removal efficiency was found with values up to 75-85%. The results suggest that the media-specific surface area does not play a crucial role in the ultimate reactor performance. The high entrapment capacity of the filter media and the regular discharge of accumulated SS on the bottom of the reactor are the main mechanisms for the high removal efficiency of solids, provided the sludge accumulating at the bottom of reactors is discharged periodically, e.g. once every day or at least every 2 days, the performance remains satisfactory. Halalsheh (2002) reported that a combined process of AF and UASB reactor operated at 4+8 h for sewage gave an average total COD removal efficiency of 70-82%. Elmitwalli et al. (2002a) recommended the application of an AF reactor operated at an HRT of 4 h for the pre-treatment of domestic sewage at low temperature. The application of the combined AF+AH system operated at an HRT of 4+8 h results in a high removal efficiency of up to 71% for all COD fractions.

The results of our present study demonstrate that a UAF reactor operated at an HRT below 11 h only provides – and in fact only can provide - a very low total COD removal efficiency, i.e. below 27%, at an OLR of 15-60 kgCOD/m^3.d. Consequently from these results it can be concluded that a UAF reactor as a pre-treatment step and when applied at short HRT only can provide an effective removal of suspended solids (COD_{ss} and COD_{col}) but not of soluble COD, because the retained amount of viable (active) sludge still remain too low for that.

Our experiments reveal that the main drawback of UAF reactor packed with PPF as filter material is clogging of the filter media. The density of the PPF material is lower than water and consequently it will float in an aqueous medium and then the beads will be pressed against each other. In particular, once the bacteria biofilm has been developed, the surface filter bed will get a dense structure, which will result in a frequent clogging problem. This phenomenon becomes more serious at higher upflow velocities. Any serious clogging problem did not happen in the PW packed filters and it occurred only occasionally in the RPF packed filters.

The results of our investigations also show that the filtration process becomes less satisfactory once a large amount of SS has accumulated within the filter media. Due to the presence of dead zones and channeling, especially in the lower part of the PPF and RPF filter media the system starts suffering from channel formation, and then the required good contact between incoming SS and the biofilm seriously declines, and with that the removal mechanism of the TSS removal deteriorates and as a result the SS content in the effluent will increase and the headloss across the filter bed will increase (headloss never happened for the PW filter bed). At this stage, the filter needs be cleaned, viz the excess of accumulated SS within the filter bed needs to be removed.

Table 3.6 The characteristic of sludge discharged from UAF reactors

Source of sludge	Period	Volume of sludge	Characteristics
From the bottom of reactors	Every day (PPF)	0.5-1.0 L or 0.06-0.13 L/L reactor	TSS = 20.6-26.1 g/L VSS/TSS = 90.6-95.8% Sludge after 3h settling: 20-40% of total volume
	Each 2 days (RPF&PW)	0.6-1.3 L or 0.08-0.16 L/L reactor	
From cleaning phase	10-13 days (PPF)	12-15 L or 1.5-1.9 L/L reactor	TSS = 3.8-5.7 g/L VSS/TSS = 93.4-95.7% SVI = 65-68 mL/gTSS
	20-25 days (RPF&PW)	14-17 L or 1.7-2.1 L/L reactor	

After cleaning, the SS removal efficiency then will improve again and become stable for a certain period of time, i.e. until a new cleaning procedure has to be conducted. By applying this cleaning procedure regularly the SS effluent concentration of UAF reactors can be maintained at a satisfactorily low value. The PPF filter medium needs to be cleaned every 10-13 days, and the RPF and PW filter media every 20-25 days.

On the basis of our findings, we consider PW packing to be the most suitable for Vietnamese conditions. Its price is low, it is easy to purchase and its use results in a simple operation involving the UAF process. Although the PPF material is low in price, it is problematic in operation due to clogging. The RPF material is too expensive, while it also needs to be imported.

3.4 CONCLUSIONS

- The main mechanism of SS removal in the UAF-reactor is a combined process of agglomeration, coagulation, sedimentation, sorption and filtration through the biofilm developed on the filter medium;
- UAF-reactors packed with RPF, PPF, and PW filter materials give high SS removal efficiency, i.e., 68-85%, 64-74%, 75-83%, respectively, lowering the SS content from 900-1,183 mg/L in the influent to 180-352 mg/L in the effluent;
- UAF-reactors can be applied as pre-treatment step prior to high rate processes such as UASB to overcome the SS problems in these high rate reactors;
- The PW filter material is selected for application in Vietnam in view of its low price, ease of purchase, and ease of operation. The PPF material is difficult to operate due to clogging problems and the RPF material is too expensive;
- Sludge (SS) accumulating at the bottom of reactors can be discharged every day or two days and then can be recycled for agricultural purposes;
- In order to get a stable SS effluent, filter media needs to be periodically cleaned, normally after 10-13 days of filter phase for PPF filter medium, and 20-25 days for RPF and PW filter media.

4

UASB Treatment of Tapioca Processing Wastewater

4.1 GENERAL INTRODUCTION

The success of anaerobic high-rate systems is due to their abilities to apply relatively high loading rates while maintaining long SRT at relatively short HRT. As a result these systems have excellent sludge immobilization characteristics. In these treatment systems, wastewater flows through an anaerobic sludge bed where purification takes place by means of complex bio-physical-chemical interrelated processes. Organic matter is converted into sludge and biogas, mainly methane, comprising a useful end product, plus carbon dioxide.

Tapioca processing wastewater contains a high concentration of organic matter, suspended solids, and organic nitrogen. The ratio of BOD/COD is extremely high, ranged from 0.76 to 0.89, especially some samples, this ratio reached 0.91. Therefore, application of the anaerobic process for treating tapioca processing wastewater appears to be the most logical and feasible option. This technology is now functional in over 65 countries and the total number of installed anaerobic treatment plants is estimated at around 2,000, with UASB technology being the most predominant process (Frankin, 2001)

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 and Hulshoff Pol, 1991). The most important feature of the UASB system is the sludge granulation phenomenon. Sludge aggregates will be dispersed under the influence of up-flowing biogas and wastewater. This mixing brought about by the biogas is important for achieving the desired contact. The dispersed sludge aggregates generally can be retained sufficiently well in the reactor by separating the biogas at an early stage, which is accomplished by using a gas-solid-liquid separator device (GSL separator) 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 inbuilt 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 GSL separator constitutes an essential UASB-reactor accessory.

The UASB system selected for this research offers several advantages, as indicated below (Lettinga, 1998):

- Very low investment costs;
- Very low operation costs; i.e., a very low energy consumption;
- Instead of consuming energy, useful energy can be recovered from produced biogas;
- It can be applied practically anywhere and on any scale;
- Very high OLR can be applied, and thus less land is required to construct the system;
- The amount of excess sludge produced is relatively low and well stabilized, and the dewatering capacity of the sludge is high;
- Methanogenic organisms can be preserved unfed for long periods (more than one year) with no serious deterioration in their activity or important characteristics.

One more serious drawback of the anaerobic treatment system of high rate AnWT systems like the UASB-reactor implies the long start-up period in the event that a sufficient amount of adapted seed sludge is not available. In that case 2-8 months are often required for the development of a sufficient amount of well-adapted anaerobic granular sludge (Liu et al, 2002). However since increasing amounts of high quality seed sludge come available, the drawback at due time belongs to the past. The UASB-reactor 'first' start-up (i.e. when adapted sludge is hardly available) is highly governed by the development of an easily settleable, preferentially granulated type, of sludge. In the "granulation" process, a dispersed viable biomass agglomerates and is growing within discrete well-defined granules. It comprises a complex process that generally starts with extremely small viable bacterial matter aggregates or with small (seed sludge) carrier materials to which viable bacterial matter has been attached. This process of microbial granulation is very complex, it involves a variety of trophic bacterial groups (depending on the composition of the wastewater) with their own physico-chemical and microbiological interactions (Schmidt, 1996). The high specific methanogenic activities of granular sludge and their high settle abilities generally allow application of high volumetric loading rates, i.e., over 50 kg COD/m^3.d under mesophilic conditions (Hulshoff Pol et al, 2004). However, a high concentration of suspended matter in wastewater, such as is the case for tapioca wastewater, is detrimental to the development of granular sludge (Lettinga et al, 1980).

Considerable attention has been paid to the use of UASB-reactors for treating various kinds of industrial wastewaters such as that from palm oil mills, slaughterhouses, breweries, and dairies. Little attention has been given so far, however, to a USAB-reactor's capacity to treat tapioca wastewater, viz. with respect to the applicable OLR and the optimal conditions (e.g. COD concentration range) to be applied during the start-up period. The present experiments were therefore conducted to examine the effect of the OLR during the initial start-up and the subsequent UASB-reactor performance. Regarding the specific characteristics of tapioca wastewater special attention has been afforded to the effect of suspended solids on the performance of the anaerobic treatment process and the granulation process particularly. For this purpose UASB-reactors were fed with tapioca processing wastewater in Vietnamese conditions.

Experiments were performed in 2.l liter UASB-reactors in an experimental room at CENTEMA at ambient temperature conditions ranging from 27 to 34^{0}C. Continuous experiments were carried out in each of the investigations presented in this paper. The UASB-reactors were inoculated with septic tank sludge up to 13.2gVSS/L of the reactor. In other words, 410g raw sludge equivalent to 26.8g VSS was supplied into the 2.10 L reactor. The starting organic loading rate was 3 kg COD/m^3.d, corresponding to an influent COD of approximately 1500 mgO_2/l. The imposed organic loading rate (OLR) was increased stepwise each

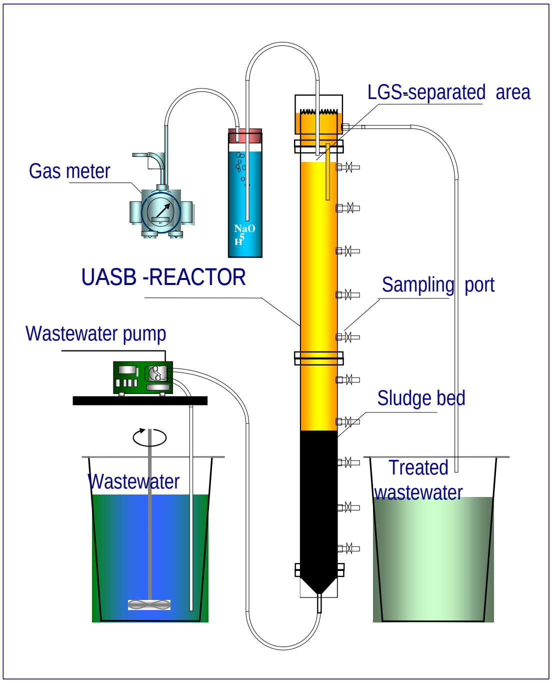


Fig. 4.1 Schematic diagram of a lab-scale UASB.

time once at least 80% of biodegradable COD was removed. The organic loading rates were 3 kg COD/m^3.d, 6 kg COD/m^3.d, 10 kg COD/m^3.d, 15 kg COD/m^3.d, and 20 kg COD/m^3.d, up to 42 kg COD/m^3.d. The OLR was elevated by increasing the influent COD concentration during the initial phases of the experiment and later by reducing the HRT. At the beginning of the experiment the reactors were operated at a flow rate of 4.5 - 6.0 L/d; later the flow rate was increased to 8.0 L/d (corresponding to an HRT of 8.4 -11.2 h) and even to 6.3 h. The pH, SS, alkalinity, and COD of influent and effluent, methane, flow rate, and temperature were recorded daily.

4.2 MATERIALS AND METHODS

4.2.1 Experimental Reactors

All experiments were performed using acrylic laboratory-size UASB-reactors. Figure 4.1 shows the schematic diagram of the reactor set-up. The reactor consisted of an acrylic pipe with a total volume of 2.10 L, the internal diameter was 50 mm and the height 1000 mm. The height of the digestion region was 300 mm, its volume 600 ml; the height of the settling region was 700 mm and its volume 1,400 ml. The bottom of the reactor was conically shaped in order to achieve an even feed distribution; its height was 50 mm and volume 100 ml. A series of small (10 mm) ports were fitted at intervals of 100 mm along the height of the reactor for wastewater and sludge sampling. A galvanized steel gas - solid - liquid (GSL) separator with a diameter of 10 mm was installed at the top of the reactor. A silicone tube was used to connect the gas collector to an alkaline liquid (10% NaOH) displacement system, where the CO_2 is removed from the gas. The methane production was measured by a wet-test gas-meter (Meterfabriek Schlummbergen, Dordrecht, the Netherlands). The influent was introduced in the reactor bottom using a peristaltic pump (Watson Marlow 501 U, UK). The treated liquid left the reactor via a notch weir placed at the top of the settler compartment. The reactors were operated at ambient temperatures of 27 to 34^{o}C throughout the experimental period. All calculations with respect to process performance were based on a volume of 2.1 L. The reactors were covered with dark paper to prevent the growth of algae on the interior wall surface.

4.2.2 Wastewater for Experiments

The raw tapioca wastewater used in the experiments was taken from household factories in Binh Chieu, Thu Duc district (used in Section 4.3.1 and 4.3.2), or taken from large-scale factory - Phuoc Long Tapioca Company, Binh Phuoc district (used in Section 4.3.3). The compositions of original wastewater are presented in Table 4.2 and Table 4.9. Either the diluted or the original tapioca wastewater was used as feed solution. Wastewater was stored under ambient conditions for approximately one week.

4.2.3 Biomass

In each of the experiments, septic tank sludge (taken from the Hoa Binh fertilizer factory, HCMC, Vietnam) was used as seed sludge. Before seeding the reactor, the raw septic tank sludge was screened through a 0.6 mm sieve to remove larger debris, sand, and fibers. The reactors were inoculated with approximately 400 g of septic tank sludge based on wet weight, for 2.1L reactor. The seed sludge filled the reactor up to a height 35-40 cm (35-40% total volume of each reactor). The initial characteristics of the seed sludge are indicated in Table 4.1

Table 4.1 The characteristics of seed sludge in the experiments

Parameters	**Units**	**The seed sludge used in experiments:**		
		Section 4.3.1	Section 4.3.2	Section 4.3.3
Water content	%	89.3	86.9	90.3
VSS/wet sludge	%	6.7	8.2	6.2
SMA	gCOD/gVSS.d	0.067	0.135	0.149
Amount of VSS seeded	$gVSS/L_{reacror}$	12.8	13.0	10.5

4.2.4 Nutrient and Trace Element Solutions

For the batch methanogenic activity experiments a basal media was used containing the following nutrients (in mg/l): NH_4Cl: 280, K_2HPO_4: 250, $MgSO_4.7H_2O$: 100, $CaCl_2.2H_2O$: 10, $NaHCO_3$: 400, Yeast: 100 and trace elements (in mg/l): $FeCl_2.4H_2O$: 2.00, H_3BO_3: 0.05, $ZnCl_2$: 0,05, $CuCl_2.2H_2O$: 0.038, $MnCl_2.4H_2O$: 0.50, $(NH_4)_6Mo_7O_{24}.4H_2O$: 0.05, $AlCl_3.6H_2O$: 0.09, $CoCl_2.6H_2O$: 2.00, $NiCl_2.6H_2O$: 0.092, Na_2SeO_3. $5H_2O$: 0.164, $C_{10}H_{16}N_2O_8$: 1.00, Resazurine: 0.20, HCl: 0.001 ml. The nutrient and trace elements were prepared as a concentrated stock solution and diluted when supplied.

The basal media used for the anaerobic reactor experiment contained the following nutrients (in mg/l): NH_4Cl: 1,040, KH_2PO_4: 169.8, $(NH_4)_2SO_4$.: 169.8, $MgCl_2.6H_2O$: 150, KCl: 270, Yeast: 19.8

Trace elements (in 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, $C_{10}H_{16}N_2O_8$: 1.0, Resazurine: 0.02, HCl: 0.0001 ml. The nutrients and trace elements were prepared as a concentrated stock solution and diluted when supplied.

4.2.5 Sampling and Analyses

To assess the performance of the UASB reactors all relevant parameters were examined daily. The pH was determined with a pH electrode immediately after sampling. The wastewater flow rate of influent was recorded every day at 8 am. A wet-test gas meter measured the amount of gas produced after it passed through the alkaline solution. This gas amount was recorded daily at 8 am. The concentrations of SS, VSS, total COD, and alkalinity were analyzed according to the Standard Methods for the examination of water and wastewater (APHA, 1995). The COD of suspended solids, COD colloidal, and COD soluble were determined using Whatman filter paper No. 40 and a 0.2-micrometer membrane filter, and were calculated as described in Chapter 7.

The specific methanogenic activity (SMA) of sludge samples was assessed using a 500ml serum bottle at ambient temperatures (28-34^{o}C). Based on the laboratory conditions in Vietnam the course of soluble COD was followed to assess the SMA of the sludge (Viet, 1999). A mixture of acetate, propionate, and butyrate with an initial concentration of 600 mg/l (C_2:C_3:C_4 = 1:1:1 – equivalent to a total COD of 2.64 g/l) was used as substrate. All experiments were performed in triplicate using 2gVSS/L in the assay. After supply of substrate, nutrients, and trace elements the bottles were closed and then exposed to ambient conditions under shaking at 50 rpm. Samples were taken daily by syringe for pH and soluble COD analyses. The accumulated gas in the headspace was released daily, but not measured since the ambient temperature varied too much. In these experiments three successive feeds were applied. After the termination of each feed the concentrated standard VFA solution was injected by syringe and needle into the serum bottles.

4.3 RESULTS AND DISCUSSIONS

4.3.1 UASB-Reactor Start-up at Different Organic Loading Rates and Influent Concentrations with Raw Tapioca Wastewater

As mentioned before all four UASB reactors were seeded with 12.8gVSS per liter of reactor of septic tank sludge (410 g of wet sludge, corresponding to 26.8g of VSS for the 2.1 L reactor). During the start-up of a UASB-reactor, the COD concentration of the influent is an important factor. In order to reinforce the selection pressure of the system, i.e. to stimulate the granulation process a concentrated feed solution, e.g. like tapioca processing wastewater in our experiments needs to be diluted to a value in the range of 1,500 - 3,000 mg/L. However, since in practice fresh water for dilution sometimes is not available in sufficient amounts we decided to conduct this study in order to assess the (optimal) suitable COD concentration range of tapioca wastewater for the proper start-up of USAB-reactors.

Table 4.2 The compositions of wastewater in the experiments

Composition	Units	Original wastewater (from household-scale)
pH	-	3.58-3.95
COD_{total}	mg/L	12,785-27,071
BOD_5	mg/L	9,775-23,540
SS	mg/L	459-10,875 (typical 700-2,200)
VSS	mg/L	437-10,750
$N\text{-}NH_3$	mg/L	67-80
$N\text{-}NO_3^-$	mg/L	1,1-7,5
$N\text{-}NO_2^-$	mg/L	0-0,2
N-Org	mg/L	196-214
Total phosphorus	mg/L	65-77
SO_4^{2-}	mg/L	0-27
CN^-	mg/L	30.5-40.8
Acidity	$mgCaCO_3/L$	1,200-3,140

The experimental results in the four UASB-reactor start-ups obtained with different concentrations of tapioca wastewater are summarized in Table 4.2, 4.3, 4.4, and 4.5 and in more detail presented in graphical form in Fig. 4.2, 4.3, 4.4 and 4.5. The efficiencies mentioned in Table 4.3, 4.4, 4.5 and 4.6 represents the COD removal efficiency at the steady-state period, as the COD removal efficiency remained relatively stable.
The UASB-reactor started up at a COD feed concentration of 1,400-1,500 mg/L and an initial HRT of 8.1-9.7 h. already after 20-22 days of operation gave an excellent COD treatment efficiency of 93-96%. This primary start-up period lasted 37 days, and in the next period the influent COD concentrations were increased to 3,000-4,600 mg/L. This second period lasted only 12 days. At day 40 a small amount of granular sludge with a diameter of around 1.0-1.5 mm clearly manifested at the bottom of the reactor.

Table 4.3 UASB-reactor start-up at an influent COD concentration of 1,400-1,500 mg/L

Parameters	**Units**	**Organic loading rate (kgCOD/m³.d)**			
		3.1 – 3.6	**6.4 – 7.1**	**10.1 – 13.0**	**13.9 – 18.4**
$COD_{total,in}$	mgO_2/L	1,489 – 1,512	3,037 – 4,648	3,952 – 5,692	5,827 – 7,683
HRT	h	8.1 – 9.7	8.1 – 11.5	7.8 – 11.2	10.0 – 10.9
Flow-rate	L/d	4.8 - 5.2	4.4 - 5.1	4.1 - 6.0	4.6 - 5.0
Exp. time	days	1 - 37	38 - 50	51 - 121	122 - 150
		Experimental results during the steady-state			
$COD_{total,in}$	mgO_2/L	1,489 – 1,512	3,037 – 3,109	5,000 – 5,098	5,827 – 6,801
$COD_{total,eff}$	mgO_2/L	52 – 82	277 – 366	403 – 537	3,086 – 3,161
$COD_{sol,in}$	mgO_2/L	1,320 – 1,466	2,780 – 2,890	4,784 – 4,932	4,322 – 5,942
$COD_{soll,eff}$	mgO_2/L	41 – 56	113 – 171	305 – 529	2,781 – 3,010
E_{CODtt}	%	95 – 97	88 – 91	89 – 92	46 – 55
E_{CODsol}	%	96 – 97	94 – 97	89 – 96	48 – 53

The height of the sludge bed at the beginning of the reactor start-up was 34 cm, by day 88 of the operation it reached a height of 38 cm and by day 120 it reached 39 cm, while at that time the height of the granular sludge bed already amounted to 25 cm. The diameter of the granular sludge was estimated at 1.2-2.2 mm and the estimated amount of total VSS in the reactor by day 120 was 22.1 g. The assessed SMA amounted to a quite satisfactory value of 0.77-0.82 gCOD/gVSS.d.

During the 150 days operation of this UASB reactor the OLR was increased three times, with as highest value 18.4 kgCOD/m^3.d, but then the treatment efficiency dropped to moderate values of 46-55 for TSS and 48-53 % for COD_{sol}. The average measured methane gas (at ambient temperature - after removal of hydrogen sulfide and carbon dioxide by alkaline solution – NaOH 10%) production was in the range 290-350 liters per 1 kilogram of COD removed.

The SS influent concentration ranged from 180-270 mg/L and in the effluent 108-191 mg/L at the OLR of 13.9-18.4 kgCOD/m^3.d. The ratio of VSS/SS in the effluent ranged from 93-96%.

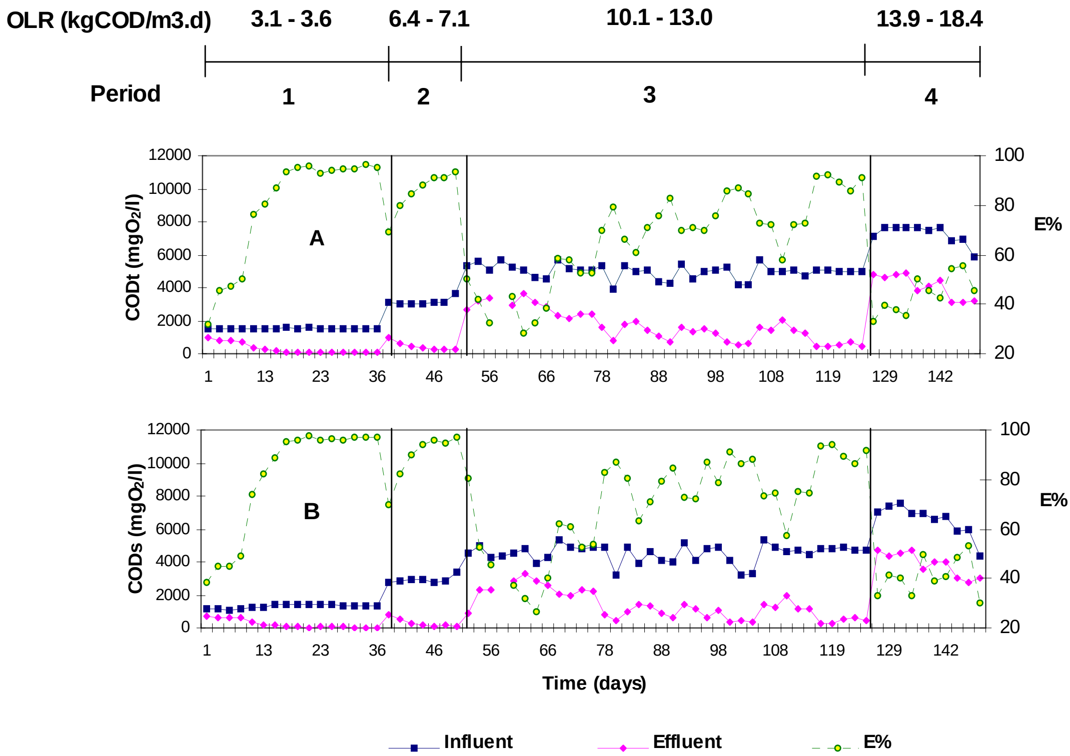


Fig. 4.2 Operational OLR and performance of the first UASB-reactor start-up at an influent COD of 1,400-1,500 mg/L.

Table 4.4 UASB-reactor start-up at an influent COD concentration of 2,500-3,800 mg/L

Parameters	Units	Organic loading rate (kgCOD/m^3.d)	
		6.8-8.3	**11.0-12.3**
$COD_{total,in}$	mgO_2/l	2,509 - 3,886	5,061 - 5,636
HRT	h	7.7 - 11.2	10.0 - 12.1
Flow-rate	L/d	4.5 - 6.5	4.1 - 5.1
Exp. time	days	1 – 121	122 – 145
		Experimental results during the steady-state	
$COD_{total,in}$	mgO_2/L	2,797 – 2,902	5,061 – 5,784
$COD_{total,eff}$	mgO_2/L	312 – 526	1,931 – 3,085
$COD_{sol,in}$	mgO_2/L	2,686 – 2,738	4,332 – 4,730
$COD_{soll,eff}$	mgO_2/L	186 – 516	1,590 – 2,147
E_{CODtt}	%	81 – 89	54 – 62
E_{CODsol}	%	81 – 93	55 – 63

Table 4.3 and Fig. 4.3 present the performance results of the second UASB-reactor started up at 6.8-8.3 kgCOD/m^3.d. Here the COD removal efficiency fluctuated significantly during the primary start-up period, i.e., ranging from 35-65%. This period lasted 121 days, and the maximum total COD removal efficiency reached 81-89%, consequently lower than found in the first UASB reactor started up at 3.1-3.6 kgCOD/m^3.d.

In this second UASB reactor, the total sludge bed height at the start was 34 cm, but by day 88 and 120 it was only 18.5 and 19 cm respectively. Obviously a significant washout of sludge occurred from the reactor. Nevertheless by day 55 the first, although still very small, amount of granular sludge was observed at the bottom of the reactor. The granular size was 0.5-1.0 mm. After day 120 of the operation, the diameters and total amount of granular sludge in the reactor did not increase further. The estimated total amount of VSS in the reactor by day 120 was 9.0 g, and the assessed SMA amounted to 0.38-0.39 gCOD/gVSS.d, distinctly lower than found in the first reactor system.

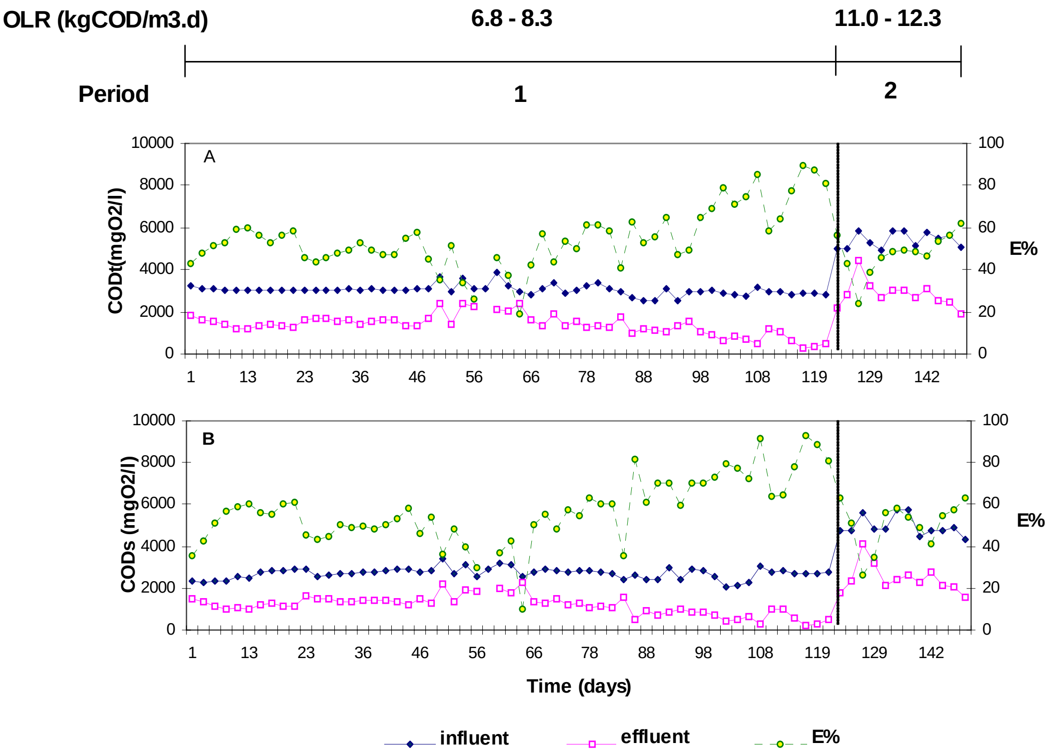


Fig. 4.3 Operational OLR and performance of the second UASB-reactor, with a start-up COD influent concentration of 2,500-3,800 mg/L.

Moreover also the specific methane gas production remained significantly behind that found in the first reactor, i.e. it was in the range 0.10-0.18 liter per one gram of total COD removal, indicating that part of the removed COD had not been converted.

The OLR of this second UASB reactor started up at 6.8-8.3 kgCOD/m^3.d, was increased to 11.0-12.3 kgCOD/m^3.d from day 122. But in view of the disappointing COD treatment efficiency the operation of the system was terminated at day 145. The SS influent ranged from 68-618 mg/L and that of the effluent from 64-450 mg/L. The ratio of VSS/SS in the effluent ranged from 93-95%.

Table 4.5 UASB reactor start-up at an influent COD concentration of 5,200-6,900 mg/L

Parameters	Units	Organic loading rate (kgCOD/m^3.d)	
		14.8-15.5	None
HRT	h	8.4-11.2	
Flow-rate	L/d	4.5-6.0	
Exp. time	days	1-114	
$COD_{total,in}$	mgO_2/L	5,240 - 6,943	
$COD_{total,eff}$	mgO_2/L	3,942 – 4,016	
$COD_{sol,in}$	mgO_2/L	4,960 – 6,434	
$COD_{soll,eff}$	mgO_2/L	3,444 – 3,830	
E_{CODtt}	%	15 – 44	
E_{CODsol}	%	22 – 49	

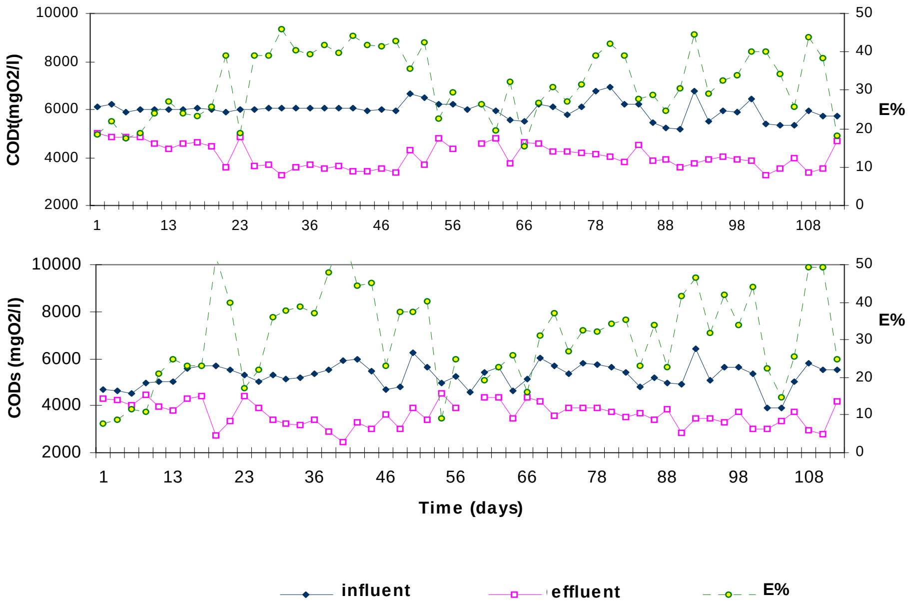


Fig. 4.4 Operational OLR and performance of the third UASB-reactor, with start-up at a influentCOD concentration of 5,200-6,900 mg/L.

In the third UASB reactor the total COD removal efficiency at a start-up at 6.8-8.3 kgCOD/m^3.d remained quite poor with values in the range 15-44%, consequently much lower than those found in the second UASB-reactor. Moreover the values also fluctuated significantly during the primary start-up period.

The height of the total sludge bed at the start-up period was 34 cm and by day 88 and 120 it had dropped to 24.5 and 26 cm respectively, once again due to washout of sludge. Granular sludge manifested at the bottom of the reactor by day 55, though the bead diameter was very small with values in the range 0.5-1.0 mm, and the total mount was marginal. After 120 days of operation the diameter of the granular sludge had not further increased, but the height of the granular sludge bed then reached 10 cm. We observed that (influent) suspended solids had accumulated in the sludge bed; it consisted of well-settling flocculent sludge aggregates. The estimated amount of total VSS in the reactor by day 120 was 22.0 g, and its SMA amounted to 0.37-0.39 gCOD/gVSS.d. The calculated specific gas production, however, was significantly lower than was found in the first reactor, i.e., it ranged from 0.12-0.19 liter per one gram of total COD removal. Regarding the low COD treatment efficiency we decided not to increase further the OLR of the reactor; the experiment was terminated at day 114. The SS influent of the reactor ranged from 172-1,260 mg/L, and of effluent from 152-780 mg/L at the imposed OLR of 13.9-18.4 kgCOD/m^3.d. The ratio of VSS/SS in the effluent ranged from 0.92-0.95.

Table 4.6 UASB-reactor start-up at an influent COD concentration of 8,500 – 13,800 mg/L

Parameters	**Units**	**Organic loading rate (kgCOD/m^3.d)**	
		16.8-26.1	**6.4-8.0**
HRT	h	8.4 - 12.6	10.0 - 12.1
Flow-rate	L/d	4.0 - 6.1	4.5 - 6.0
Exp. time	days	1 – 110	111 - 120
$COD_{total,in}$	mgO_2/L	8,528 - 13,886	2,797 - 2,970
$COD_{total,eff}$	mgO_2/L	6,089 - 12,302	2,625 - 2,825
$COD_{sol,in}$	mgO_2/L	6,566 – 12,120	2,686 – 2,738
$COD_{soll,eff}$	mgO_2/L	5,343 – 11,094	2,424 – 2,512
E_{CODtt}	%	15 – 42	15 – 20
E_{CODsol}	%	25 – 55	21 – 25

In the fourth UASB-reactor we obtained very similar results as in reactor three;, the total COD removal efficiency remained very low with values of 15-42%. The height of the total sludge bed at the start-up period was 34 cm, and by day 88 and day 120 it reached a value of 38 cm. By day 40 granular sludge with a small diameter of around 0.5-1.0 mm manifested at the bottom of the reactor, but the amount were minimal. After 120 days of operation the diameters of the granular sludge were still similar, but the height of the granular sludge bed reached 20 cm. We again observed accumulation of a substantial amount of suspended flocculent solids in the sludge bed, especially also at the bottom of the reactor. The estimated total amount of VSS in the reactor by day 120 was 27.3 g, and its SMA amounted to 0.37-0.38 gCOD/gVSS.d.

In order to assess the system's performance we decided on day 111 to reduce the OLR of the reactor from 16-26 to 6.4-8.0 kgCO/m^3.d. However, during the next 10 days of operation the COD treatment efficiency failed to improve and therefore the experiment was terminated on day 120 (see Fig. 4.5). The SS influent ranged from 773-2,320 mg/L, and the SS effluent from 515-1,200 mg/L during the operation. The ratio of VSS/SS of the effluent ranged from 0.89-0.94.

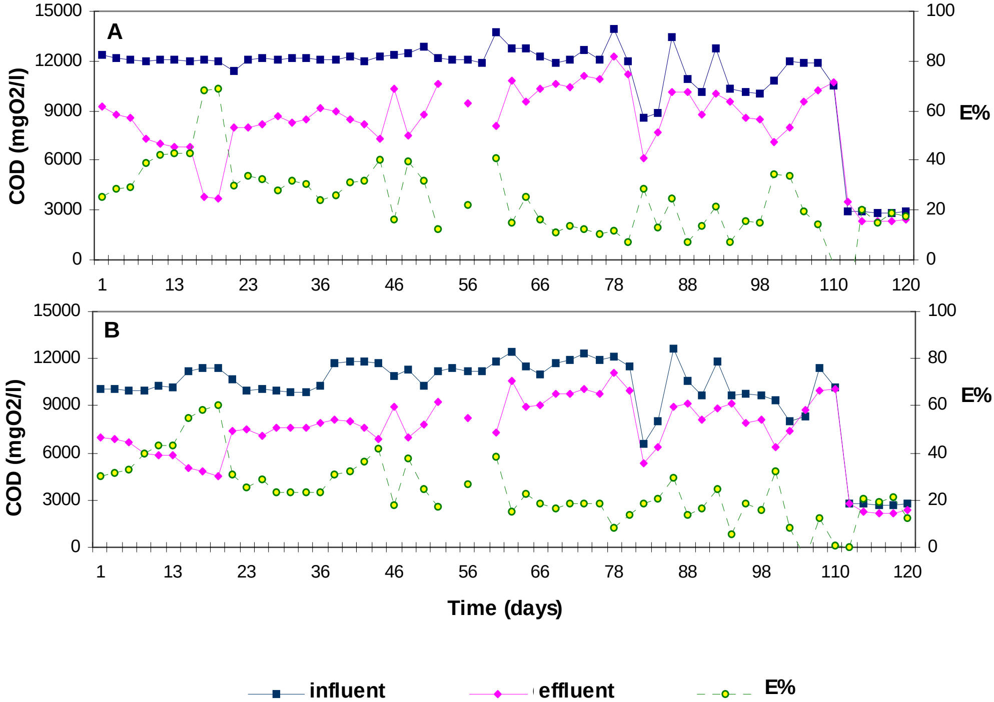


Fig. 4.5 Operational OLR and performance of the fourth UASB-reactor, with start-up at an influent COD concentration of 8,500-13,800 mg/L.

Summarizing the above experimental results obtained with UASB-reactor start-up with raw tapioca wastewater we can conclude the following:

- At COD influent concentrations around 1,500mg/L and imposed HRT 8-10 h a high COD treatment efficiency can be achieved within a period of only 37 days, i.e. about 95-97%, while within a relatively short period of time a maximum OLR (i.e., influent COD around 5,800-7,600 mg/L) of 10-13 kg COD/m^3.d at high treatment efficiency can be applied.
- Start-up at a COD influent concentration exceeding 1,500mg/L, i.e., 2,500-3,800 mg/L and HRT 8-10 h and OLR up to 11-12.3 kgCOD/m^3.d resulted in a distinctly poorer COD

treatment efficiency, i.e. between 53 and 89% and approximately 60-70 days were needed to reach steady-state treatment efficiency.

- Start-up at a COD influent concentration of 5,200-6,900 mg/L and 8,500-13,700 mg/L at HRT 8-11 h and OLR up to 15.5 kgCOD/m^3.d gave very low COD treatment efficiency in the range 15-44% during 114 days of operation.
- Granular sludge manifested at the bottom of the reactors in all the experiments by day 40-55 of operation, but diameters of granules and the total amount of granular sludge differed greatly.
- The SMA assessed at ambient temperature of the seed sludge in all four reactors improved distinctly, viz from 0.133-0.137 gCOD/gVSS.d to **0.77-0.82** gCOD/gVSS.d in the first reactor and to values between 0.37-0.39 gCOD/gVSS.d after 120 days for the other reactors.

The results clearly show that the start-up of UASB-reactors with raw tapioca wastewater proceeds much better at lower influent COD concentrations of around 1,500 mg/L and imposed OLR's around 3kgCOD/m^3.d or at the maximum 3,000 mg/L at imposed OLR's around 6 kgCOD/m^3.d. Under these conditions after the start-up maximum OLR's are possible up to 12 kgCOD/m^3.d.

4.3.2 Performance of UASB Treatment of Tapioca Processing Wastewater after SS Removal in a Pre-Treatment Step

As mentioned in Chapter 3, a number of previous studies demonstrated that application of UASB systems for the treatment of complex wastewater containing a high amount of SS can become problematic due to the accumulation of SS in sludge beds. This will generally result in a decrease (or at least not in a satisfactory increase) in the sludge's specific methanogenic activity when high loading rates are applied. The SS present in the influent can affect the anaerobic process particularly also detrimentally because it impairs the development of granular sludge. We therefore decided to conduct some complementary experiments to examine the effects of lowering the SS-content of the wastewater on the anaerobic treatment performance of the UASB-reactor and the granulation process particularly by using pre-treated tapioca processing wastewater as under Vietnamese conditions. The results of operation UAF-reactors are presented in previous chapter, and the effluent of UAF-reactor is used in this experiment. The characteristics of pre-treated tapioca processing wastewater are presented in Table 4.7. Like in the experiments discussed in the proceeding paragraph a septic tank sludge was used as seed sludge. The UASB-reactor was inoculated with 13gVSS/liter$_{reactor}$. The assessed SMA of seed sludge amounted to 0.135 gCOD/gVSS.d.

The reactor start-up was done at a COD concentration of 1,300-1,800 mg/L and at an HRT of around 9-11 h. and the wastewater used in the experiment concerned the effluent of UAF-reactor which was fed with the wastewater of a household-scale tapioca factory (see Chapter 3). The experimental results at steady-state are presented in Table 4.8 and the details are shown in Fig. 4.6.

Table 4.7 The characteristics of pre-treated tapioca wastewater

Parameters	**Units**	**Effluent UAF**
pH	-	6.48-7.61
COD_{total}	mg/L	5,585-14,476
COD_{ss}	mg/L	323-412
COD_{col}	mg/L	211-429
COD_{sol}	mg/L	5,074-13,749
SS	mg/L	180-352
VSS	mg/L	139-330
$N\text{-}NH_3$	mg/L	186-231
$N\text{-}NO_3^-$	mg/L	0.0-0.2
$N\text{-}NO_2^-$	mg/L	Trace
N-Org	mg/L	10-102
$P\text{-}PO_4$ total	mg/L	29-70

The UASB reactor was started up at a COD concentration of 1,300-1,800 mg/L and an HRT of 9-11 h. During the start-up period the imposed organic loading rate (OLR) amounted to 2.9-4.8 kgCOD/m^3.d. During the first three days the performance of the appearance of the UASB-reactor was quiet, the gas produced amounted only to 0.1-0.2 l/day, and the COD removal efficiency to approximately 29-48%. During this period the bacteria adapted to the new substrate. From day 11 onwards the treatment efficiency rose to 72-89% and reached 90-92% at the end of this period, corresponding to a COD effluent concentration of 126-142 mg/L. The pH increased from 7.1-7.4 to 7.8-8.0. This primary start-up period lasted 27 days; then the OLR was increased stepwise from 2.9-4.8 kgCOD/m^3.d to 29-43 kgCOD/m^3.d. And during this process the treatment efficiency remained quite high with values in the range of 84.3-90.3%. The COD concentration decreased from 10,498-14,330 mg/L to 1.082-2.178 mg/L. Already by day 20 a granular sludge with a diameter of about 1.2-1.5 mm clearly manifested at the bottom of the reactor, i.e. with a granular sludge bed height around 6 cm and from then onwards the height of the granular sludge bed increased gradually, i.e. by day 69 it reached 20 cm and the diameter of the granular sludge then was 1.5- 2.0 mm.

From day 117-131, the operation of the UASB-reactor was temporarily interrupted for a period of 14 days (Tet holidays in Vietnam). After resuming the reactor operation at the same OLR, tentatively a substantially lower treatment efficiency was found, even less than 10%, but the performance then improved gradually to 70-72% after 20 days, and recovered completely after 30 days with values in the range of 90-92%. On day 166 we increased the influent COD concentration from 6,590 to 14,330 mg/L (see Fig. 4.6). This shock load led to a drop in the treatment efficiency for a few days, but already after 10 days the efficiency reached values of 84-90 %, corresponding to a reduction in the influent COD concentration from 11,237-14,080 to 1,515-1,838 mg/L. On day 229 the influent COD suddenly dropped from 10,498 mg/L to 4,615 mg/L, consequently (a kind of ‘pit’ shock load. The results show a decline in the treatment efficiency for some days; this at least can be partially attributed to the time gap (residence time) between incoming wastewater and effluent leaving the system.

Table 4.8 UASB-reactor operational conditions and treatment efficiency in treating UAF-reactor effluent (see Table 4.7)

Parameter	Units	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6
OLR	$kgCOD/m^3.d$	2.9-4.8	5.3-9.2	10.7-13.7	14.1-21.6	23.7-42.4	28.6-42.7
$COD_{tt, inf.}$	mg/L	1,426-1,817	2,384-3,389	4,748-5,751	6,590-7,654	11,200-12,400	9,211-9,500
$COD_{tt, eff.}$	mg/L	142-422	220-320	245-588	601-880	710-2,051	743-1,070
$COD_{sol, inf}$	mg/L	1,350-1,729	2,243-3,226	3,961-5,521	6,273-6,422	6,644-8,257	6,988-8,264
$COD_{sol, eff}$	mg/L	60-88	114-240	87-108	441-610	348-1,585	544-1240
HRT	h	9.0-11.0	9.0-12.6	10.1-11.2	9.4-12.0	8.3-8.4	6.2-6.3
V_{up}	m/h	0.09-0.11	0.08-0.11	0.09-0.10	0.08-0.12	0.12	0.18
Q	L/d	4.6-5.5	4.0-5.5	4.5-5.0	4.2-6.0	6.0-6.2	8.0-8.2
Exp. Time	days (total)	27	39 (66)	27 (93)	72 (165)	105 (270)	24 (294)
E_{CODtt}	%	90.1-93.4	91.7-92.8	87.6-95.7	88.5-90.9	81.7-93.8	88.4-91.9
E_{CODsol}	%	93.5-96.5	93.3-96.2	97.3-98.4	90.5-93.0	83.8-94.8	85.2-92.2
Biogas	L/d	2.4-2.7	4.8-6.2	6.5-6.8	9.2-10.7	19.1-27.3	22.6-26.1

In another parallel UASB-reactor experiment, two shock loads were imposed during the steady operation of the system at a HRT of 7.8-8.1 h. In the first shock load, the influent COD concentration was elevated from 5,250 mg/L to 13,055 mg/L in a 24 h stretch and then returned to 5,091 mg/L. In the second imposed shock load, the influent COD concentration was increased from 4,916 mg/L to 14,822 mg/L in a 24 h stretch and then it was returned to 5,779 mg/L. Details of the experimental results will be presented in Chapter 6.

The SMA of the reactor sludge assessed at an ambient temperature after 120 days, 160 days and after 312 days of operation amounted to 0.77-0.82 gCOD/gVSS.d, 0.79-0.88 gCOD/gVSS.d and 0.92-1.06 gCOD/gVSS.d, respectively. The biogas (mainly methane) produced ranged from 320-440 liters per kilogram of converted COD based on measurements from a wet-test gas-meter (after the biogas passed through the alkaline solution to remove the CO_2 and H_2S, but not the water content). The exact composition of the gas could not be analyzed.

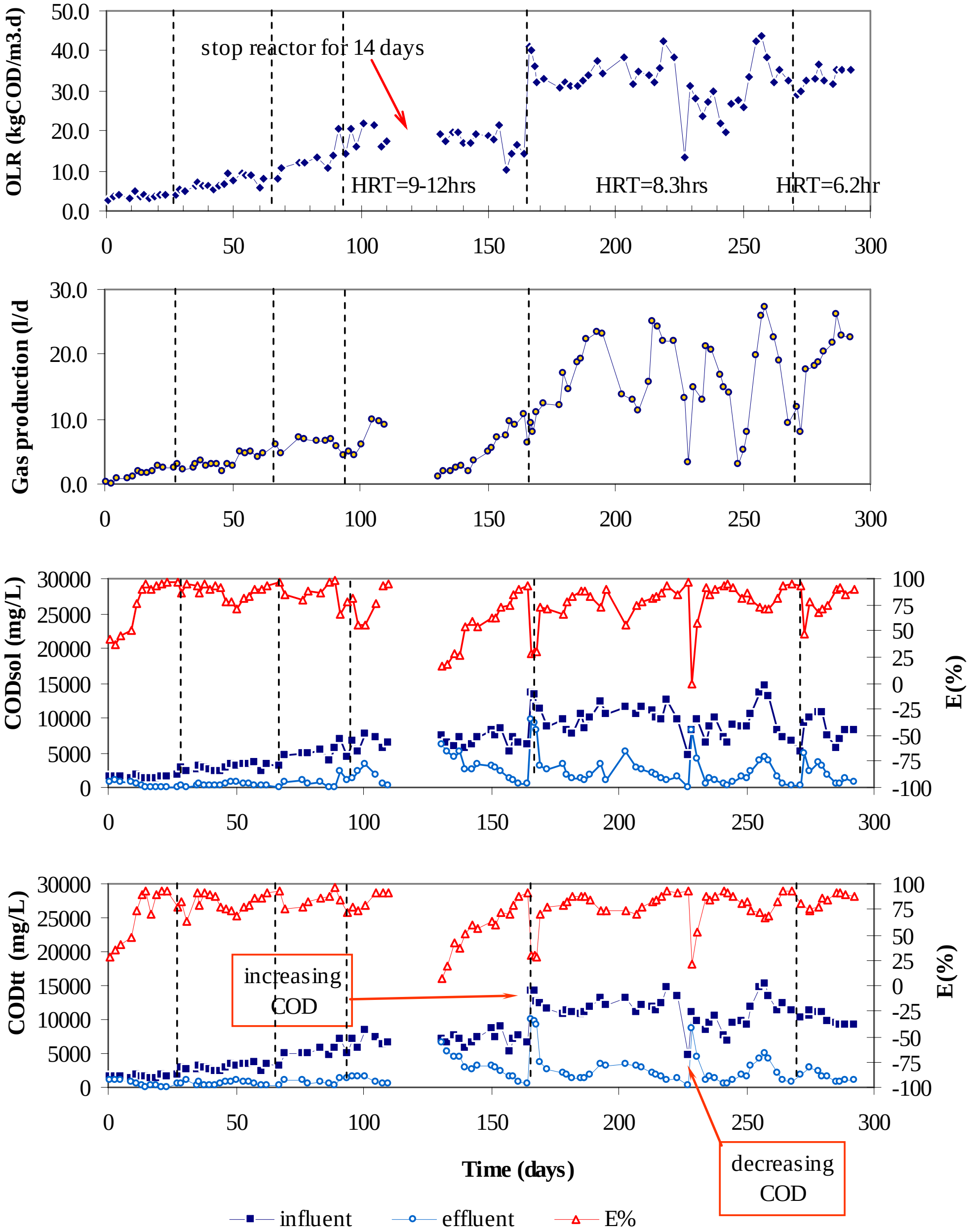


Fig. 4.6 Operational parameters and performance of the UASB-reactor during the experiment, with SS removal as a pre-treatment step.

4.3.3 UASB-Reactor Treatment of Raw (Without SS Removal) Tapioca Processing Wastewater from a Large Scale Plant

The experiments were conducted with septic tank sludge as seed sludge supplied in an amount of 10.5 gVSS per liter of reactor. We conducted another similar experiment but the influent wastewater consisted of diluted original wastewater from a large-scale tapioca factory (without the SS removal step). The experimental results obtained at the steady-state periods are presented in Table 4.9 and the details are shown in Fig. 4.7. The characteristics of original tapioca processing wastewater used in the experiment are presented in Table 4.8.

During the primary start-up period, the imposed organic loading rate amounted to 2.1-4.1 $kgCOD/m^3.d$, and the HRT varied from 11.7-13.2 h and the wastewater used originated from a household-scale factory and it was diluted with tap water. After 5 to 6 h of operation, the gas production in the reactor had already commenced. The COD removal efficiency remained relatively low during the first few days, i.e., approximately 25-45%, but during this period the bacteria could adapt to the new substrate. After day 5 the treatment efficiency rose to 75-80% and reached 83-86% at the end of this period (day 11), corresponding to an effluent COD concentration of 240-280 mg/L. The pH increased from 6.8-7.0 to 8.1-8.4. The experimental data clearly show, like those in the previous paragraph, that the fresh septic tank seed sludge had a sufficiently high specific activity and adapted rapidly to the new substrate.

Table 4.9 The characteristics of wastewater in the experiment

Parameters	Units	Original wastewater (from large-scale factory)
pH	-	4.5-5.9
COD_{total}	mg/L	7,850-12,244
COD_{sol}	mg/L	6,120-9,050
BOD_5	mg/L	6,420-10,010
SS	mg/L	560-2,980
$N\text{-}NH_3$	mg/L	47-88
$N\text{-}NO_2^-$	mg/L	Trace
$N\text{-}NO_3^-$	mg/L	Trace
N-Org	mg/L	109-335
$P\text{-}PO_4$	mg/L	10-51

In the second period, the OLR was increased to values ranging from 3.5 to 8.8 $kgCOD/m^3.d$, while the flow rate and HRT were kept in the range of 3.7-5.1 L/d and 9.9-13.6 h, respectively. The COD removal efficiency rapidly improved from 79% at the first day to 92-94% in the next two days and ultimately it even reached values of 94-95% at the end of this period, corresponding to the COD reduction of 1,757-4,550 to 96-102 mg/L in the effluent. As a result of the high treatment efficiency the pH increased from 6.7-7.0 to 8.3-8.6. The SS influent ranged from 43-230 mg/L, but SS effluent usually higher, ranged from 45-1,053 mg/L due to the SS washout. At this imposed loading rate, the first granules manifested after 26 days of operation and at an OLR of 6 $kgCOD/m^3.d$. The diameter of the particles amounted to 0.5-1.5 mm. From day 15 to day 22, the amount of washed-out sludge increased significantly, up to

2,020 mg/L (Fig. 4.8). This can be attributed mainly to the high biogas production, i.e., amounting to values of 0.9-1.3 up to 2.4-2.5 L/d. Following day 23 the sludge washout suddenly dropped (See Fig. 4.8), and granular sludge was clearly visible by day 26. The total height of the sludge bed in the reactor was 31cm and the height of granular sludge bed about 5-6 cm. Since the total influent COD fluctuated significantly, this also was the case for imposed OLR and therefore the treatment efficiency took a longer time to stabilize, i.e., about 17 days.

Table 4.10 Operational conditions and treatment efficiency of the UASB-reactor, using diluted original wastewater from a large-scale factory

Parameters	Units	Period 1	Period 2	Period 3	Period 4	Period 5
OLR	$kgCOD/m^3.d$	2.1-4.1	3.5-8.8	6.5-11.0	9.8-15.7	13-25
$COD_{tt,\ inf.}$	mg/L	1,628-2,053	2,906-3,419	3,484-4,761	6,929-7,830	9,007-10,602
$COD_{tt,\ eff.}$	mg/L	247-544	189-412	271-465	331-391	656-894
$COD_{sol,\ inf.}$	mg/L	1,405-1,571	1,846-1,942	2,603-3,432	5,535-6,276	6,941-8,130
$COD_{sol,\ eff.}$	mg/L	149-205	102-123	114-232	234-248	311-391
HRT	h	11.7-13.2	9.9-13.6	12.0-13.2	11.0-13.2	11.0-14.4
Q	L/d	3.8-4.3	3.7-5.1	3.8-4.2	3.8-4.6	3.5-4.6
Exp. Time	days	11	17 (28)	14 (42)	26 (68)	48 (116)
E_{CODtt}	%	73.5-85.6	87.9-93.5	86.7-92.3	94.7-95.8	90.8-93.8
E_{CODsol}	%	85.4-90.2	93.6-94.7	93.2-96.1	95.8-96.3	93.1-96.2
Biogas	L/d	0.9-1.3	2.5-3.0	4.8-5.2	8.1-10.4	8.2-13.1

Parameters	Units	Period 6	Period 7	Period 8	Period 9	Period 10
OLR	$kgCOD/m^3.d$	23-38	34-42	38-56	56-101	36-108
$COD_{tt,\ inf.}$	mg/L	10,236-11,671	9,194-9,954	7,893-9,023	7,200-9,091	4,286-9,105
$COD_{tt,\ eff.}$	mg/L	889-1,127	846-1,175	789-1,022	1,745-2,123	1,351-3,200
$COD_{sol,\ inf.}$	mg/L	8,000-8,927	6,252-8,498	5,760-7,449	5,566-6,075	3,417-8,158
$COD_{sol,\ eff.}$	mg/L	289-509	402-532	294-395	1,098-1,354	755-2,750
HRT	h	6.8-8.3	5.2-6.8	4.3-3.7	1.8-2.0	1.8-2.0
Q	L/d	5.8-7.1	7.1-9.3	9.0-12.9	24-26	24-26
Exp. Time	days	32 (148)	22 (170)	21 (191)	18 (209)	30 (239)
E_{CODtt}	%	90.0-92.2	89.0-91.1	88.3-91.0	73.4-78.4	56.9-68.5
E_{CODsol}	%	94.4-96.6	94.3-95.3	94.8-95.6	75.7-81.9	52.4-77.9
Biogas	L/d	18.1-19.4	25.3-27.4	23.9-31.1	60.5-62.0	-

In the sixth period, when we used original wastewater – from large-scale factory to increase OLR to 23-38 $kgCOD/m^3.d$, the HRT was reduced from 11-13 h to 7-8 h. The treatment efficiency was satisfactory with values of 87-95%. In the next period, the HRT was reduced to 5-7 h, then to 3-4 h, corresponding to the OLR of 34-42 $kgCOD/m^3.d$ and 38-56 $kgCOD/m^3.d$, respectively. The results show only a slight decrease in treatment efficiency, i.e., 88-92%. During this period, the SS removal is much improved the influent SS decreased from 623-2,305 mg/L to 187-307 mg/L in the effluent.

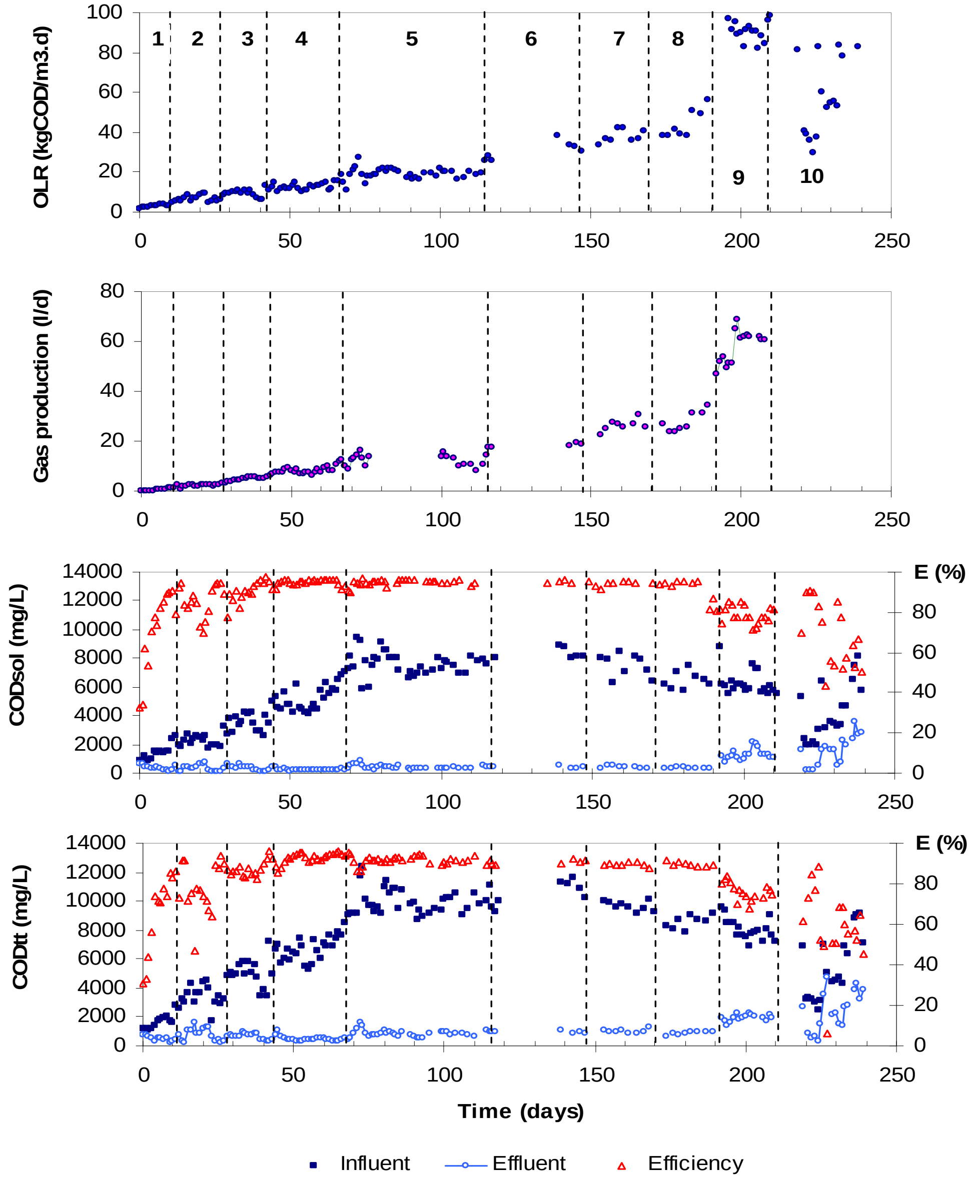


Fig 4.7 Operational parameters and UASB-reactor performance during the experiment, without SS removal as a pre-treatment step.

In the ninth period, when the HRT was reduced to 1.8-2.0 h and the OLR reached the very high values of 83-100 kgCOD/m^3.d, the treatment efficiency indeed dropped significantly, i.e., to values in the range of 68-84%. The gas production (mainly methane) fluctuated relatively high, viz. equivalent 0.37 – 0.54 L methane gas for 1 gram COD converted.

4.3.4 General Discussion

The results obtained in these investigations clearly show that UASB-reactor performance tends to decrease at increased imposed COD concentrations during the primary start-up period; this in fact is not surprising. The SMA of the septic tank sludge is low and therefore then insufficient capacity is available in the system to digest the large amount of organic matter supplied to the system. The start-up at a lower COD concentration demonstrates a much better performance in terms of COD removal efficiency. During the reactor operation under these conditions, the methanogenic activity of sludge increased steadily along with the higher imposed OLR. In the experiment at a start-up load of 3 kgCOD, granular sludge manifested at the bottom of the reactor at day 40 of the operation. When conducting the primary start-up at a higher OLR, considerably more time was needed for the granulation process, i.e., up to 50-55 days.

During 240 days of operation, there was no significant difference in the COD removal efficiency between UASB-reactors operated with a pre-treated or non pre-treated (for SS removal) feed, provided the primary start-up was made in the proper way. But the performance of UASB-reactors operated with wastewater from a large-scale factory (without SS removal step) was better than with the household type of wastewater as a result of its more stable wastewater composition. Even when the SS content of the wastewater was relatively high, with values up to 1,100-1,800 mg/L, the overall UASB performance remained almost unaffected and a minimal detrimental effect on the granulation during the experimental period (about 300 days) was observed.

According to Quarmby and Forster (1995); Batstone and Keller (2001) the presence of carbohydrates, as in tapioca wastewater, promotes the production of extracellular polysaccharides, which enhance bacterial agglomeration and hence are believed to be essential to the formation of granules necessary for the success of UASB reactors. In our case, after 20-26 days of operation a small amount of granular sludge with a diameter of 0.8-1.2 mm had already become visible at the bottom of the reactors, and from then onwards this amount increased gradually. After 60-70 days of operation the size of the granular sludge amounted to about 1.5-2.0 mm. The rapid granulation can be attributed mainly to the relatively high microbial growth prevailing under the imposed relatively high OLR, i.e., 5-6 kgCOD/m^3.d. After prolonged operation the granular sludge growth rate stabilized. Although we clearly observed sludge granulation, we also observed that granules removed from the reactor were reduced to small fragments due to the friction with the outlet pipe.

Since the performance of a UASB-reactor depends on the sludge retention and the specific activity of the retained sludge, we regularly monitored the total amount of sludge present in the reactors, and used sludge samples from the reactor to assess the SMA. Because of the inferior settling ability of a flocculent sludge, the height of the total sludge bed was measured after 1 h when we interrupted the feeding of the reactor. The accumulated sludge biomass in the reactors increased along with the operation of the reactors. When pre-treated wastewater (for SS removal) was treated, the height of the total sludge bed changed from 35 cm at the start-up period to 31, 36, 37, 36, and 38 cm at day 30, 85, 120, 160, and 312 during the operation. The amount of sludge did not significantly increase, due to sludge washout and the low sludge yield of anaerobic process, but - significantly - the SMA of sludge in the reactor improved substantially. The SMA (assessed at ambient temperature) improved from 0.135 at the beginning then to 0.80, 0.84, and 1.00 gCOD/gVSS.d. after 120, 160, and 312 days of operation. When the UASB-reactor was operated with raw tapioca wastewater, the height of the total sludge bed changed from 40 cm at the start to 35, 38, 37, 36 cm at day 49, 145, 180, 240 respectively. The sludge SMA improved from 0.149 at the beginning to 1.12 and 1.05 gCOD/gVSS.d after 180 and 240 days of operation.

During the start-up period, heavy SS washout frequently occurred, but once granular sludge was present the effluent SS concentration significantly decreased and it continued to decline. The average ratio of VSS/SS in the effluent ranged from 0.92-0.96. The results in Fig 4.8 show the SS washout during the primary start-up of a UASB-reactor running on raw tapioca wastewater (Section 4.3.3). In particular during the period from day 15-17 the temporary washout was significant, due to the imposed higher OLR, i.e., it increased from 2-4 to 3-9 kg COD/m^3.d. Once a major part of the poorly settling sludge had been rinsed out from the system and the first granules had manifested on day 26 at the bottom of the reactors, the sludge washout decreased.

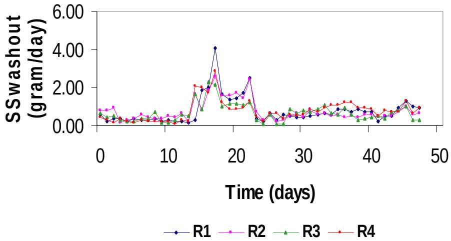


Fig.4.8 SS washout during start-up period.

The performance of the reactors in terms of COD removal efficiency, specific gas production, and SMA of reactor sludge improved continuously along with the operation of the system. It is obvious that the performance of a UASB-reactor treating tapioca wastewater remains quite sustainable up to an OLR of 80 kgCOD/m^3.d, which is very high indeed.

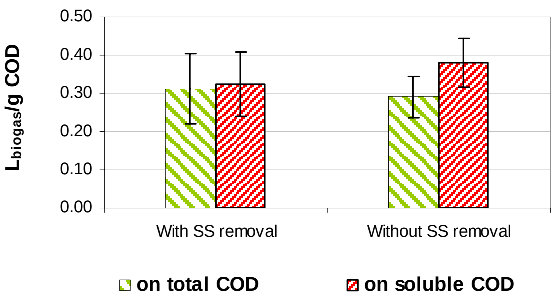


Fig. 4.9 Average biogas reduction with and without SS removal as a pre-treatment step.

Gas production was measured after passing the gas through an alkaline solution. The assessed values fluctuated significantly, i.e., between 0.18-0.55 liter per gram COD removed, but the average value found in all experiments was 0.36 liter biogas per gram COD removed, indicating a quite low sludge yield.

Since we supplied in the experiments a certain amount of sodium hydroxide and sodium bicarbonate to the influent wastewater to neutralize the free VFA and to increase the buffer capacity, it is evident that in practice it is important to recycle effluent in order to reduce the system's chemical needs. To estimate the amount of chemicals needed, raw tapioca wastewater and UASB effluent were analyzed. The initial compositions are shown below:

Table 4.11 The compositions of raw tapioca wastewater and effluent of UASB reactor

Composition	Units	Raw tapioca wastewater	Effluent UASB-reactor
pH	-	3.51	8.62
COD	mg/L	13,729	254
Acidity	$mgCaCO_3/L$	2,300	-
Alkalinity	$mgCaCO_3/L$	-	1,220

The results indicate that in the case of using only sodium hydroxide to adjust the pH of raw wastewater from 3.51 up to 6.61-6.67, the cost for chemicals would be 0.50 Euros per cubic meter of wastewater. While taking advantage of the high pH and alkalinity of the effluent UASB-reactor, the raw wastewater could be mixed with effluent solution in a ratio 1:1; in this way the cost for chemicals could be reduced to 0.38 Euros in the event the feed pH of the mix was increased to 6.61. A further cost reduction is possible by accepting a lower influent pH, because in a well-mixed UASB-reactor a stable operation is still quite possible. For a mix of sodium hydroxide and sodium bicarbonate (using solutions of 5%) the cost reduction would be from 0.69 to 0.51 Euros. In practice this means the recirculation can be applied up to 50% or more of the raw wastewater flow, depending on treatment conditions and on wastewater characteristics for reducing chemical operation costs.

4.4 CONCLUSIONS

- Anaerobic biological treatment – using UASB-reactors – is clearly an extremely feasible system for treating tapioca wastewater, and therefore the application of this system under Vietnamese conditions is highly recommendable, in fact highly logical and necessary;
- Start-up of UASB-reactors at an influent COD concentration of around 1,500mg/L (with HRT 8-10 h) is clearly the best start-up procedure, because a high COD treatment efficiency of 93-96% is attained within only 13 weeks at a maximum OLR of 13-25 kg COD/m^3.day;
- Organic loading rates up to 42 kgCOD/m3.d (even up to 80 kgCOD/m^3.d) can be applied in UASB systems for tapioca processing wastewater treatment at a high treatment efficiency of 82-93%;
- Septic tank sludge available in Vietnam appears to be proper seed sludge in Vietnamese conditions;
- After a period of 20-26 days of the operation, granular sludge clearly manifested visually at an OLR of 6 kgCOD/m^3.d (with pre-treated wastewater);
- One kilogram of COD is biologically converted to around 330 liters of biogas;
- After about 300 days of operation the difference in COD removal efficiency between UASB-reactors operated with UAF-effluent or original wastewater is marginal;
- In order to meet prevailing Vietnamese standards for UASB effluent discharge, some form of post-treatment will be required.

5

Post-Treatment of UASB System Effluent

5.1 GENERAL INTRODUCTION

The activated sludge process has been widely applied in the treatment of industrial wastewater. Among other advantages this system offers operational flexibility, an easy and quick start-up, a high efficiency (low effluent COD concentration) while it also enables nutrient removal. However, a number of pregnant disadvantages also exist, such as its high energy demands, consequently the need to have a connection electricity supply, its high sludge production, its complexity and the fact that these systems are unsuitable to treat very high strength wastewaters. While the UASB reactor with its many advantages (mentioned in Chapter 4) is capable to overcome most of the activated sludge process disadvantages, the treated effluent of AnWT-systems usually does not comply with Vietnamese Industrial wastewater discharge standards, mainly due to the high nutrient content and the fact that organic matter content frequently still is too high.

To balance the pros and cons of both systems, several studies (Catunda and van Haandel, 1996; Odegaard, 1988; van der Steen et al., 1999; von Sperling et al., 2001; Nunez and Martinez, 2001; Lacalle et al., 2001; Torres and Foresti, 2001; Chernicharo and Nascimento, 2001; Polito-Braga et al., 2002; Hong, 2004) demonstrated the benefits of combining the processes, viz. with the anaerobic treatment system as primary treatment system and the aerobic reactor as the secondary (polishing) step. In these instances, the combination process had the following advantages: (1) lower energy consumption, (2) lower chemical consumption for dewatering, (3) much less sludge to be disposed of, (4) the excess sludge generally highly concentrated and well stabilized, (5) less equipment required, (6) higher operational simplicity (von Sperling et al. 2001), (7) possibility of recovering energy from biogas, and (8) compliance of treated effluent with local discharge standards (9) possibilities to use anaerobic effluents during growing seasons for irrigation and fertilization.

The principle aerobic biological treatment processes used for the removal of carbonaceous organic matter include (1) activated-sludge process, (2) aerated lagoons, (3) sequencing batch reactor, (4) trickling filter solids contact system, (5) oxidation ditches, and (6) rotating biological contactors. Of these, the activated-sludge process is the most common for secondary treatment (i.e., following anaerobic treatment in, for instance, UASB reactor). Secondary treatment in the form of the activated sludge process aims at the oxidation and removal of soluble and finely divided suspended materials not removed by the previous treatment or even produced in that step (e.g. sulphides).

Although application of the activated sludge process as secondary treatment was proposed, the treated effluent still remained unacceptable in the case of high organic matter content in raw wastewater (for example, in tapioca processing wastewater); thus, it is necessary to implement a proper post-treatment technology. Since stabilization ponds combine operational simplicity with low costs, energy demands and maintenance, they represent an adequate option for the post-treatment of anaerobically pre-treated high strength wastewaters, despite their high land requirements and the fact that in essence the basics mechanisms underlying these systems are very complex and poorly understood. Nevertheless these systems can frequently be applied quite profitably for attaining a satisfactory quality of effluent, i.e. sufficiently disinfected and low organic matter content. According to Mara (1997), one of the prominent supporters of lagoon systems, stabilization ponds are extremely robust mainly as a result of their large capacity, their long hydraulic retention times, i.e. they can withstand both organic and hydraulic shock-loads. However, this system is only suitable in regions where still cheap land is available, a situation that in many cases not will persist.

To ensure that an effluent quality that complies with the Vietnamese Standards for the effluent discharge (details are presented in Appendix), the objective of this research was to assess the applicability of aeration tanks and stabilization ponds (including algae and water hyacinth ponds) for post-treatment of tapioca-wastewater UASB reactor effluent.

A. USE OF THE ACTIVATED SLUDGE PROCESS

In the present study we investigated the performance of lab-scale activated sludge 20-L reactors for treating (1) 2-h pre-settled tapioca wastewater, i.e. to assess the capacity of the application for activated sludge process during the UASB reactor start up, because during this period a portion of the wastewater remains untreated and therefore needs to be treated before discharge to the receiving water resource (in case of a new factory), and (2) the effluent from UAF-UASB system, to evaluate the feasibility of applying the whole combined treatment system. This research includes an assessment of the treatment efficiency of activated sludge reactor, as well as of the period of time required for organic matter decomposition.

5.2 MATERIALS AND METHODS

5.2.1 Overview of Experiments

The experiments were conducted in two batch reactors and using 2-h pre-settled tapioca wastewater. In the experiment nutrients were added from day 12 to day 19 in order to improve the sludge's settling ability. The imposed hydraulic retention time (HRT) was 24 h and the sludge retention time (SRT) was 10 days. Another similar experiment was conducted with wastewater from the UAF-UASB system effluent. The experiments were carried out in duplicate at ambient temperature (29-35^{o}C) in a CENTEMA laboratory, HCMC, Vietnam.

5.2.2 Reactor

The H*L*W dimensions 20-L glass made reactor were of 40*38*15 (in cm). A schematic diagram of the reactor is depicted in Fig. 5.1, with the angle shape below. This had a 60^{o} delection angle to obtain whirl flow when air was blown through the reactor and to concentrate sludge when the reactor was settling. At the bottom of the reactor were six pumice stones to distribute oxygen. The sludge and

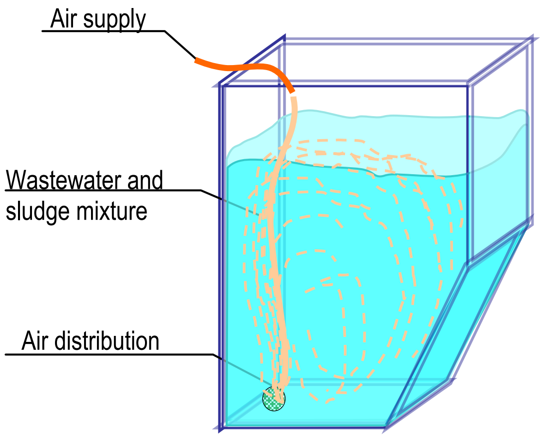


Fig. 5.1 Lab-scale activated sludge reactor.

wastewater in the reactor were mixed, and oxygen was delivered by aircompressor (Rambo 30W). The top of the reactor was covered with a glass plate to prevent wastewater escaping.

5.2.3 Wastewater

Tapioca processing wastewater originating from household factories in Thu Duc district, HCMC stored at an ambient temperature for approximately one week, were used in these studies. The composition of 2-h pre-settled samples of the tapioca wastewater and of the effluents of the UAF-UASB system (UASB effluent running with UAF effluent as pre-treatment step - see Section 4.3.2) are summarized in Table 5.1.

Table 5.1 Composition of pre-settled and UAF-UASB effluent (household tapioca wastewater) used in the experiments

Parameters	Unit	Pre-settled wastewater	UAF-UASB effluent
pH	-	3.7-5.0	7.76-8.30
TDS	mg/l	840-1,395	-
SS	mg/l	450-938	100-203
VSS	mg/l	420-875	85-187
COD	mgO_2/l	7,768-14,738	794-3,070
BOD	mgO_2/l	5,468-9,150	-
$N\text{-}NO_2^-$	mg/l	Trace	0.12-0.90
$N\text{-}NO_3^-$	mg/l	0.68-3.62	Trace
$N\text{-}NH_3$	mg/l	26-112	36.4-110
N-Org	mg/l	164-234	15.0-80.0
Total P	mg/l	18.4-54.5	12.0-60.1

5.2.4 Seed Sludge-Biomass

Septic tank sludge taken from the Hoa Binh fertilizer factory (HCMC, Vietnam) was used as seed sludge. The raw sludge was screened through a 0.6 mm sieve to remove the sand, fibers, and large debris before seeding. The initial characteristics of the sludge were as follows:

Table 5.2 Seed sludge compositions after screening

Parameters	Units	Values
pH	-	7.25
TS	%	7.43
VSS	% dry weight	61.56
$N\text{-}NH_3$	mg/kg	387
N-Org	mg/kg	2465
Total P	mg/kg	497

5.2.5 Nutrient Solution

A nutrient solution was used to stimulate the growth of microorganisms. For the pre-settled wastewater experiment the basal media contained the following nutrients (in mg/l): K_2HPO_4: 320-1600, KH_2PO_4: 160-800, NH_4Cl: 120-600.

5.2.6 Experimental Procedure

The 20-L activated sludge reactor start-up was made at a COD concentration of about 1,000 mg/L and at a biomass concentration of 1,696 mg VSS/L. The imposed HRT and SRT were 24 h and 10 days, respectively. The experiments were carried out with two kinds of wastewater (as mentioned above) and in duplicate. The procedure was as follows:

- Screened septic tank sludge was supplied to the reactor;
- Wastewater and a nutrient solution were prepared and adjusted to a pH around 6.5 and fed into the reactor up to 20 L;
- Aeration was by diffused air for 2 min before sampling for the influent;
- Aeration was continuous by diffusing air in order to ensure a high oxygen content in the system (DO>4mg/L) and to mix the reactor liquor;
- Effluent samples were collected after 23 h;
- The SRT was controlled at 10 days, by a daily discharge of 1/10 of reactor liquor;
- Diffusing of air was terminated, then allowing the sludge to settle in 30 min;
- Supernatant was removed by a siphon system;
- Wastewater with a suitable concentration was supplied into the reactor and the procedure was repeated as described above;
- Once the COD treatment efficiency had stabilized, an experiment on "time treatment profile" was carried out, and the influent COD concentration was increased on the following day;
- Influent COD concentrations in the experiment were 1,000; 1,500; 2,000; 3,000 mg/L in succession, corresponding to the loading rates of approximately 1; 1.5; 2.0; 3.0 $kgCOD/m^3.d$;
- F/M values imposed were different for each experimental period; details are shown in Section 5.3.1 and Table 5.3.

5.2.7 Analytical Methods

To assess treatment efficiency, the pH, COD, SS, VSS, $N\text{-}NH_3$, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, N-Organic and phosphorous parameters were examined according to the Standard Methods For The Examination of Water and Wastewater (APHA, 1995). The COD was analyzed after a 10 min centrifuge of 3,500 rpm to remove suspended solids; the centrifuged COD ($COD_{cent.}$) was used in this Section (5.3) to assess the treatment efficiency.

5.3 RESULTS AND DISCUSSIONS

5.3.1 Activated Sludge Process for The Treatment of Pre-Settled Tapioca Wastewater

The imposed experimental conditions (HRT = 24 h and SRT = 10 days) are summarized in Table 5.3, and the results depicted graphically in Fig. 5.2 and Fig. 5.3. Quite high COD removal efficiencies in the range of 97.0-97.2, 95.1-97.4%, and 97.1-98.1% were obtained during the experimental periods 1, 2, and 3 respectively, with effluent COD_{cen} concentrations ranging from 29-70 mg/l. During period 4 (from day 45 to 51), the treatment efficiency dropped slightly from 97.7% to 92.7% due to high influent COD concentration and effluent COD_{cen} concentrations then exceeded 100 mgO_2/l, as shown in the last days of period 4 (Fig. 5.2).

Table 5.3 Experimental results involving the 24 h HRT and 10 day SRT imposed on the activated sludge reactor in the various experimental periods with pre-settled tapioca wastewater

Parameters	Units	Period 1	Period 2	Period 3	Period 4
F/M	gBOD/gVSS	0.32-0.44	0.43-0.67	0.49-0.68	0.50-0.73
$COD_{cent, inf.}$	mg/l	965-1,071	1,441-1,619	2,033-2,355	3,190-3,510
$COD_{cent, eff.}$	mg/l	29-32	40-70	45-66	77-256
E_{COD}	%	97.0-97.2	95.1-97.4	97.1-98.1	92.7-97.7
$VSS_{inf.}$	mg/l	1,940-2,240	2,120-2,840	2,740-3,960	4,080-5,460
$VSS_{eff.}$	mg/l	2,260-2,420	2,580-3,160	3,160-4,340	4,540-6,060
$VSS/SS_{inf.}$	%	84.3-87.5	89.3-91.3	89.9-91.8	90.6-94.5
$VSS/SS_{eff.}$	%	85.6-87.7	90.2-94.4	90.3-90.9	87.8-90.8
SVI	ml/gSS	30-176	117-141	89-109	84-100
Exp. Time	Days (total)	24	14 (38)	6 (44)	7 (51)
$pH_{inf.}$	-	6.65-7.06	6.55-7.03	6.73-6.96	6.76-7.04
$pH_{eff.}$	-	8.06-8.40	8.40-8.52	8.30-8.44	8.10-8.35
$N\text{-}NH_{3\ inf.}$	mg/l	7.60-55.4	14.6-17.6	13.0-16.0	20.7-28.6
$N\text{-}NH_{3\ eff.}$	mg/l	0.4-34.6	1.9-2.1	0.00	0.0-1.0
$N\text{-}Org_{inf.}$	mg/l	7.8-22.4	29.1-30.0	39.8-40.1	54.4-61.6
$N\text{-}Org_{eff.}$	mg/l	2.0-8.0	4.1-5.0	2.8-3.5	6.0-24.3
$N\text{-}NO_2^-{}_{inf.}$	mg/l	0.0-0.2	trace	trace	Trace
$N\text{-}NO_2^-{}_{eff.}$	mg/l	0.0-2.8	4.0-11.2	trace	Trace
$N\text{-}NO_3^-{}_{inf.}$	mg/l	0.0-0.1	Trace-0.2	Trace-0.2	0.1-0.4
$N\text{-}NO_3^-{}_{eff.}$	mg/l	0.0-0.3	0.3-0.8	Trace	Trace
$P\text{-}PO_{4\ inf.}$	mg/l	0.8-154.7	13.4-14.1	15.1-18.4	17.1-34.9
$P\text{-}PO_{4\ eff.}$	mg/l	0.6-139.5	3.5-6.7	3.9-6.9	0.5-15.9

The DO concentration measured during period 1-3 (after a 0-5 min stop for diffused air) amounted to 6.9-4.4 mgO_2/l, which is more than sufficiently high. In period 4 the DO concentration dropped slightly down to 6.0-3.9 mgO_2/l, but still quite sufficient to supply the biomass with oxygen (Rolf et al. 1991) and to prevent the bulking of filamentous bacteria.

According to Britt and Petter (1998) a too low (<1.5 mg/L) DO concentration might affect detrimentally the effluent turbidity due (1) a poor consumption of substrates present in the wastewater and (2) due biomass degradation due to oxygen limitation, but at the high DO-levels applied in our experiments this looks unlikely.

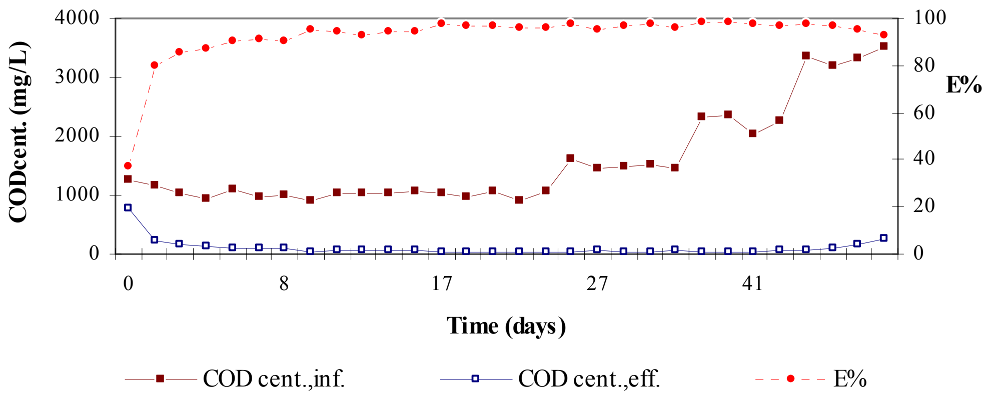


Fig. 5.2 Treatment efficiency involving different pre-settled wastewater.

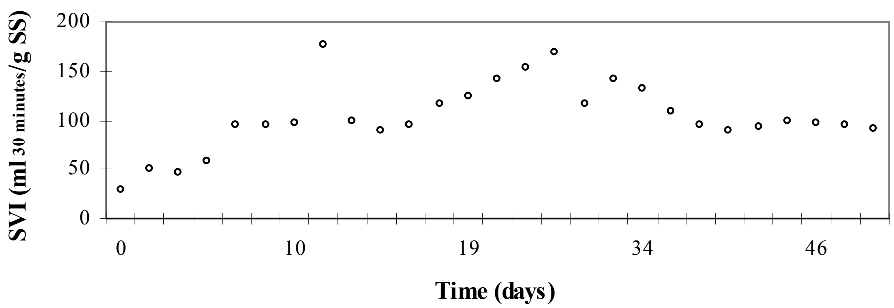


Fig. 5.3 SVI course during the activated sludge process for pre-settled tapioca wastewater.

During the experiment periods 1, 2, and 3 any floating of sludge or foaming on the surface did not manifest. The flocculent activated sludge was fine and brownish in color, the effluent was clear. From the beginning of the experiment up to day 10, sludge settled quite well, viz. with SVI-values in the range of 30-98 ml/gSS. According to APHA (1995), SVI-values below 100 ml/gSS indicate a well settling sludge, SVI-values in the range of 100-200 ml/gSS indicate a moderate settling sludge and SVI values exceeding 200 ml/gSS indicate a poorly settling, i.e., bulking sludge. From day 11 onwards the sludge turned to moderate settling sludge with SVI-values of 176 ml/gSS, and then it easily can pass into bulking type (Sabine et al. 2001, Richard et al. 2003). To avoid this bulking phenomenon, we decided to supply the mixed reactor liquor with 25-50% nutrient A-solution, because nutrients represent one of the factors affecting the settling characteristics of the sludge. Indeed, following the supply of nutrients, the settling of the sludge distinctly improved during the period 12-16. We did not supply nutrient A-solution during period 20 to 39 and the sludge then once again became poorly settling, although it remained of an acceptable quality with SVI-values in the range of 109-142 ml/gSS. From day 40 onward the sludge again became very well settling, with SVI of 26-96 ml/gSS, which might be attributed to a better adoption of the sludge and/or higher sludge activity.

During period 4, the imposed space loading rate was too high with values up to 3.2 to 3.5 kgCOD/m^3.d, much higher that those recommended by Metcalf and Eddy (2003), i.e. comprising only 0.3 to 3 kgCOD/m^3.d. Some sludge floatation manifested on the liquid gas interface of the reactor. The flocculent sludge turned yellow brown, but it remained well setting with SVI in the range of 84-100 ml/gSS (Fig. 5.3). The effluent solution was slightly turbid and yellow in color, which can be attributed to formation of non-biodegradable humic acids. This can be explained by the F/M value becoming too high at the end of period 4; a high concentration of biomass and the provision of nutrients for only a short time can lead to a bulking problem and poor effluent quality. The high biomass concentration can cause a DO deficiency, resulting in poor sludge settling and in turbid effluent (Britt and Petter, 1998; Richard et al., 2003).

One important factor in aerobic suspended-growth treatment processes is the food microorganism ratio (F/M); it is closely related to the specific utilization rate and is used in practice as a design and control parameter. In our experiments, the imposed F/M was in the range of 0.32-0.68 gBOD/gVSS.d and 0.5-0.73gBOD/gVSS.d for periods 1-3 and period 4, respectively. According to Eikelboom (1982), at F/M values exceeding 0.5 gBOD/gVSS.d substrate cannot be metabolized and according to Prendle and Kroiβ (1998) for an effective prevention of bulking the COD loading rate should remain below 0.5 g COD/gVSS.d, and Metcalf and Eddy (2003) propose a ratio of F/M ranging from 0.04 to 1.0. A ratio of less than 0.5 needs to apply for nitrification. Palm et al (1980) indicated that the ratio of F/M is a function of DO concentration in filamentous control. At F/M values of less than 0.5, a DO concentration of 2 mg/L usually controls the filaments, but at F/M values of higher than 0.5 a DO concentration of 4 mg/L (or more) may be needed.

Because the wastewater used for the activated sludge reactors originated from a household factory the composition of the wastewater fluctuated quite heavily, depending on the quality of the fresh cassava roots. According to Richard (2003), extracellular polysaccharides will be produced by all activated sludge bacteria. These compounds are responsible for flock formation. Overproduction of polysaccharides can occur at nutrient deficiency (also at high F/M and DO deficiency), and can lead to an accumulation in the sludge and poor sludge settling, and even to problems in sludge dewatering. When well-settling activated sludge normally contains from 10-20% polysaccharides at a dry weight basis. The higher polysaccharide contents (>20%) prevailing in sludge of younger ages result in poor settling and in dewatering problems.

As mentioned above, the nitrogen and phosphorus can limit the growth of bacteria if not present in a sufficient amount. In general, a BOD:N:P weigh ratio of 100:5:1 is needed for complete BOD removal. However, it should be taken into account that we need to use the total inorganic nitrogen (ammonia plus nitrite plus nitrate) and soluble ortho-phosphorus to estimate the nutrient availability; organically combined nitrogen and phosphorus may not be hydrolyzed sufficiently rapidly by the bacteria to keep pace with BOD use. In our case, the BOD concentration, total inorganic nitrogen, and soluble ortho-phosphorus concentration ranged from 5,400-9,200 mg/L, 26-115 mg/L, and 6-13 mg/L, respectively, consequently values which don't meet the ratio of BOD:N:P = 100:5:1 for complete BOD removal. The results obtained and the observation made indicate that even at a non-optimal BOD:N:P ratio the COD removal efficiency remained high and settleability of the sludge moderate. After the addition of A-solution nutrients, the sludge settling improved significantly, but at the same time the effluent N-NH_3 and total phosphorous concentration became far too high with values of 34.6 mg/l 139.5 mg/l respectively. The experiment involving additional nutrients lasted only a short time, from day 12-16, and was implemented to help us gain insight into a solution regarding slightly settling sludge. Since similar conditions need to be in practice we decided to the remainder of the experiments without supplying nutrients. Details of the experimental results are depicted in Fig. 5.2 and Fig. 5.3.

The results indicate that a high level performance was reached during periods 1-3, resulting in low effluent COD and nutrient concentrations. Occasionally conducted microscopic observations of the reactor contents revealed that the Pseudomonas community was dominant during the experiment, and- in addition, ciliated protozoa were especially observed during periods 1-2, viz. including Carchesium Polipinum, Vorticella Convallaria, and sometimes Opercularia Coarcta. During periods 3-4 the rotifer (Lecane sp.) grew extensively in the reactor medium. This phenomenon demonstrated the stability of the activated sludge process environment.

Assessment of Time Treatment Profiles

During periods 1 and 2, the COD concentration dropped rapidly, i.e., the influent COD_{cen} concentration dropped from 1,038 mg/l to 115 mg/l and from 1,439mg/l to 163 mg/l. Most of the organic matter degraded completely, leaving only effluent COD_{cen} concentrations lower than 100 mg/l after 6 h of aeration. In period 3, the process proceeded similarly to that of the two previous periods; the COD_{cen} concentration of 2,254mg/l dropped to 262 mg/l within 5 h, but the further COD reduction to a COD_{cen} concentration of 95 mg/l took 9 h (Fig. 5.4 C). To reduce the investment cost, this result could be considered and applied for the HRT of activated sludge reactor in operational practice.

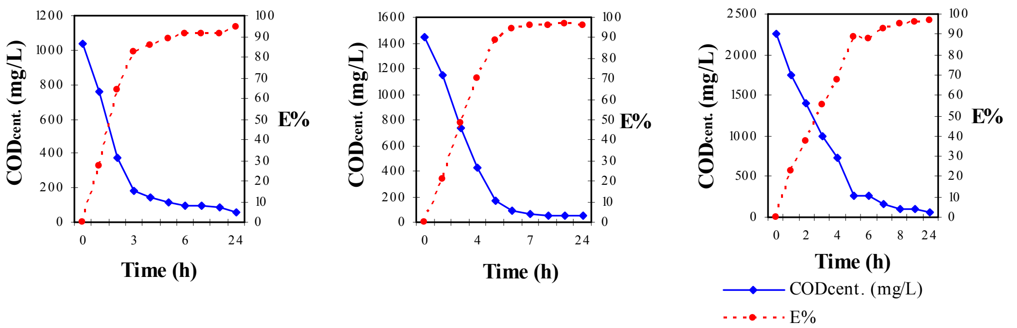


Fig. 5.4 Time treatment profiles involving COD removal in the activated sludge process with pre-settled tapioca processing wastewater as assessed in periods 1, 2, and 3.

5.3.2 Activated Sludge Process for The Treatment of UAF-UASB Effluent

Operational conditions and performances of activated sludge-batch reactor are summarized in Table 5.4. During the three operational periods investigated, the imposed HRT was 24 h and SRT 10 days. In period 1 (day 0-11), the COD_{cen} concentration dropped from 1,214-1,205 mg/l to 28-43 mg/l, corresponding to a COD removal efficiency in the range of 96.4-97.4%. During period 2 (day 12-30), the COD_{cen} concentration dropped from 1,342-1,901 mg/l to 77-110 mg/l, corresponding to a COD_{cen} removal efficiency ranging between 92.4-95.5%, but during day 25-29 the COD_{cen} declined slightly to 92.4-93.1%, likely due to biomass biodegradation. In period 3 (day 31-43), the COD_{cen} concentration dropped from 1,766-2,174 mg/l to 110-129 mg/l corresponding to a COD removal efficiency ranging from 92.9-94.9%.

Table 5.4 24-h HRT and 10 day SRT imposed on the activated sludge-batch reactor in the various experimental periods with the UAF-UASB effluent

Parameters	Units	Period 1	Period 2	Period 3
F/M	gBOD/gVSS	0.23-0.42	0.36-0.56	0.39-0.63
$COD_{cent, inf.}$	mgO_2/l	810-1,205	1,342-1,901	1,766-2,174
$COD_{cent, eff.}$	mgO_2/l	29-43	77-110	110-129
E_{COD}	%	96.4-97.4	92.4-95.5	92.9-94.9
$VSS_{inf.}$	mg/l	1,970-2,140	2,600-3,220	3,450-3,800
$VSS_{eff.}$	mg/l	2,020-2,340	2,760-3,340	3,710-3,920
$VSS/SS_{inf.}$	%	66.3-79.4	84.8-93.1	89.1-94.9
$VSS/SS_{eff.}$	%	67.6-80.1	84.2-93.9	89.9-95.3
SVI	ml/gSS	30-64	64-179	99-137
Exp. Time	days (total)	11	19 (30)	13 (43)
$pH_{inf.}$	-	7.3-8.3	8.3-9.0	8.1-8.8
$pH_{eff.}$	-	8.3-9.0	9.0-9.4	9.2-9.3
$N\text{-}NH_{3\ inf.}$	mg/l	21.8-32.5	38-4-48.7	68.3-128
$N\text{-}NH_{3\ eff.}$	mg/l	Trace	Trace	0.7-48.0
$N\text{-}Org_{inf.}$	mg/l	5.6-10.0	10.8-17.6	15.1-82.9
$N\text{-}Org_{eff.}$	mg/l	1.9-9.3	1.9-4.8	3.8-21.2
$N\text{-}NO_2^-{}_{inf.}$	mg/l	Trace-0.3	Trace	Trace-0.7
$N\text{-}NO_2^-{}_{eff.}$	mg/l	3.1-16.8	6.8-52.0	0.7-70.7
$N\text{-}NO_3^-{}_{inf.}$	mg/l	Trace-0.4	Trace	Trace
$N\text{-}NO_3^-{}_{eff.}$	mg/l	1.2-2.7	0.7-1.6	0.7-4.6
$P\text{-}PO_{4\ inf.}$	mg/l	18.4-23.4	12.8-15.2	51.3-67.3
$P\text{-}PO_{4\ eff.}$	mg/l	2.9-11.9	5.7-10.9	27.9-60.0

The DO concentration amounted to 7.5-4.8 mg/l (corresponding to a diffused air stop from 0-5 min). The F/M ratio ranged between 0.23-0.63 gBOD/gVSS during the experiment. From the beginning of the experiment up to day 15, the sludge was well settling with SVI-values ranging between 30-80 ml/gSS, but from day 15 onwards the sludge settling deteriorated slightly, with

SVI-values in the range from 101-179 ml/gSS, although predominantly between 101-137 ml/gSS (Fig. 5.6).

As we know, the activated sludge process, with its high efficiency and possibility for nutrient removal, has been widely applied in the treatment of industrial wastewater and domestic sewage for that purpose. In view of that we studied the efficiency of the system in the case of tapioca wastewater (post)treatment.

In periods 1 and 2, nitrogen removal efficiency was high, the nitrite nitrogen concentration increased from trace-0.3 to 3.1-52.0 mg/l, the nitrate nitrogen concentration from trace-0.4 to 0.7-2.7 mg/l while the organic nitrogen concentration dropped from 5.6-17.6 to 1.9-9.3 mg/l. But in particular the ammonia nitrogen concentration decreased significantly, i.e., from 21.8-48.7 mg/l in the influent to only traces in the effluent. Also the phosphorus concentration dropped, viz. from 12.8-23.4 mg/l to 5.6-10.9. Since nutrients like inorganic nitrogen and soluble ortho-phosphorus are taken up by microorganisms along with BOD as a growth source for bacterial growth, the removal of soluble ortho-phosphorus, a non-biodegradable compound (contrary to ammonia-N) highly depends on the amount of sludge growth.

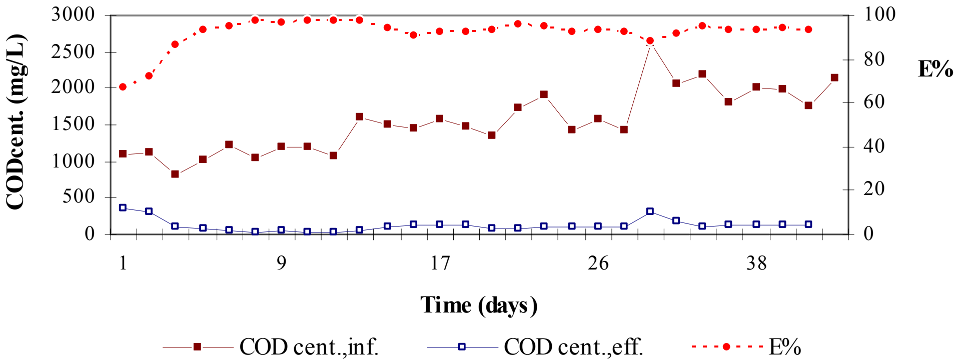


Fig. 5.5 Assessed treatment efficiency of activated sludge involving different UAF-UASB system effluent COD concentrations.

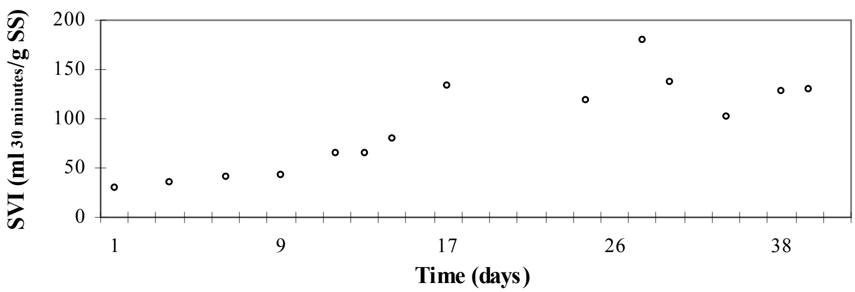


Fig. 5.6 SVI course during the activated sludge process involving UAF-UASB system effluent.

The results indicated that during experimental periods 1-3 a good performance level was reached with the UAF-UASB system effluent, resulting in low effluent COD and nutrient concentrations. The occurrence of microorganism spectrum in the reactor medium was examined twice a week. Pseudomonas sp. community was found to be predominant during the experiment. The ciliated protozoa most commonly observed during periods 1-2 include Carchesium Polipinum, Vorticella Convallaria, and sometimes rotifer (Lecane sp.). During period 3, however, the rotifer was abundant in the reactor, revealing the stability of the activated sludge process environment.

Treatment Efficiency Time Profiles

In period 1 most of the organic matter was degraded within 2 h of aeration. The COD_{cen} concentration dropped from 1,064 mg/l to 63 mg/l after 5 h and the effluent COD_{cen} concentration was very low, with values in the range of 26-43 mg/l. In period 2 the COD_{cen} concentration dropped from 1,412 mg/l to 90 mg/l within 5 h and further to 76 mg/l, although after 24 h it increased to 107 mg/l. Latter can be attributed to biomass biodegradation. In period 3 the influent COD_{cen} concentration dropped from 2,140 mg/l to 106 mg/l after 5 h, and during a 6-8 h period the effluent COD_{cen} concentration became slightly higher, with values ranging between 128-208 mg/l, which very likely can be attributed to the same mechanism (Fig. 5.7).

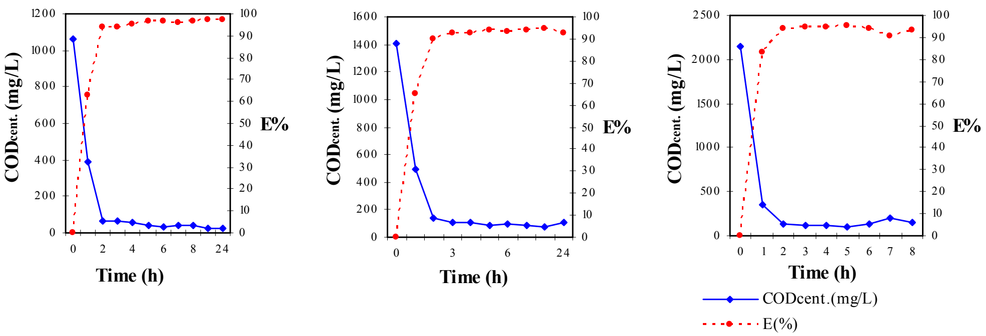


Fig. 5.7 Treatment time profiles during the experiment of period 1, 2 and 3.

5.4 CONCLUSIONS

Results of the experiment indicate that the aerobic activated sludge process can be used not only as a secondary treatment but also used in parallel with UASB reactor during start-up for treating the fraction of tapioca wastewater that remains untreated during that period in the UASB-reactor.

Application of the batch reactor of activated sludge process for the treatment of pre-settled (raw) tapioca wastewater results in a good performance, as indicated by the following:

- With 24-h HRT and 10 days SRT, COD removal efficiency up to 95-98% resulted in CODcen concentration dropping from 965-2,355 mg/l to values of only 29-70 mg/L;

- The biodegradable fraction of CODcen (range of 965-1,619 mg/l and 2,033-2,355 mg/l) was completely biodegraded after 6 and 9 h respectively;
- Operating the system under Vietnamese conditions at a influent CODcen concentration of 2,033-2,355 mg/l, results in effluent COD values of 77-86 mg/l, N-NH3: 0.0-1.0 mg/l, N-Organic: 2.8-24.3 mg/l and Ptt: 0.54-6.9 mg/l. Any further treatment before discharged is not needed.
- At relatively high influent CODcen concentrations, viz. in the high range of 3,190-3,510 mg/l, the quality of the effluent does not comply with the Vietnamese Industrial wastewater effluent discharge standards.

With the effluent of the UAF-UASB system as feed, the batch reactor of activated sludge process performs very well and constitutes a highly acceptable post-treatment system. Observations were as follows:

- A high COD removal efficiency with values in then range 96.4-97.4%, resulting in effluent CODcen concentrations 29-43 mg/l at influent values in the range 810-1,205 mg/l.
- 2 and 5 h are needed for the complete degradation of the biodegradable fraction of the influent COD-values 810-1,205 mg/L and 1,342-2,174 mg/L, respectively.
- With the higher influent COD, i.e., 1,342-2,174 mg/l, the COD removal efficiency remained high with values in the range 92.4-95.5%, but the effluent did not completely comply with the Vietnamese standards.

To ensure that the treated effluent is consistently in accordance with the quality required by the Vietnamese Industrial wastewater effluent discharge standards - B level, it would be necessary to implement a further post-treatment step, e.g. stabilization ponds, but regarding the extremely overall treatment efficiency achieved in the total AnWT-AeWT system, it is highly questionable whether such a pond could remove any additional COD. Likely the contrary will be the case, because growth of algae will proceed easily in these systems. The available land in provinces of Vietnam can better be used for more noble applications.

B. USE OF POND SYSTEMS FOR POST-TREATMENT

Post-treatment of effluents of anaerobic pre-treatment process should lead to a further improved quality of the effluent, e.g. the removal of bacteria pathogens. For this purpose we selected in our research a pond stabilization system consisting of two pond modules: one contained algae (algae pond) and the other - comprising the second step - water hyacinths (water hyacinth pond). The selection of the system was based on the consideration that an algae pond can reduce organic matter and nutrients, though the BOD and SS effluent remain still too high due to the presence of algae biomass (a major bottleneck of these systems!). A water hyacinth pond can be used for the removal of algae and other suspended solids, first of all because of the entrapment characteristics of the plant's long roots and secondly because sunlight penetration in these systems is much lower, consequently biomass (algae) reduced.

5.5 MATERIALS AND METHODS

5.5.1 Overview of Experiments

The experiment was performed using 100-L lab-scale stabilization ponds operated under continuous feeding conditions. The imposed Hydraulic retention time (HRT) was 6-7 days for the algae pond and 7-8 days for the water hyacinth pond (this pond's longer HRT was due to the evaporation by water hyacinth leaves). In period 1, the system was operated on UAF-UASB system effluent; the algae pond and the water hyacinth pond surface loading rates (L_{BOD}) were 207-265 kgCOD/ha.d and 77-153 kgCOD/ha.d respectively, and in period 2 on effluent of UAF-UASB-AeWT system at surface loading rates (L_{BOD}) of the algae and the water hyacinth pond of 31-111 kgCOD/ha.d and 29-54 kgCOD/ha.d respectively. The experiment was conducted to enable a sound evaluation of the feasibility of a whole-treatment system in Vietnamese practice, including the UAF-UASB-AeWT (activated sludge) process and pond system. This research includes an assessment of the pond system treatment efficiency and the quality of the treated effluent. The experiments were carried out in duplicate, lasted almost one year, and were conducted at ambient temperatures. The ponds were exposed to direct sunlight on the terrace at CENTEMA, HCMC, Vietnam.

5.5.2 Pond Modules

The construction of the algae and water hyacinth ponds are very similar. Each system has a 100-L working volume and is made of 5mm glass having the L*W*H* dimensions of 1*0.4*0.25 (in m). The stabilization pond system is illustrated in Fig. 5.8.

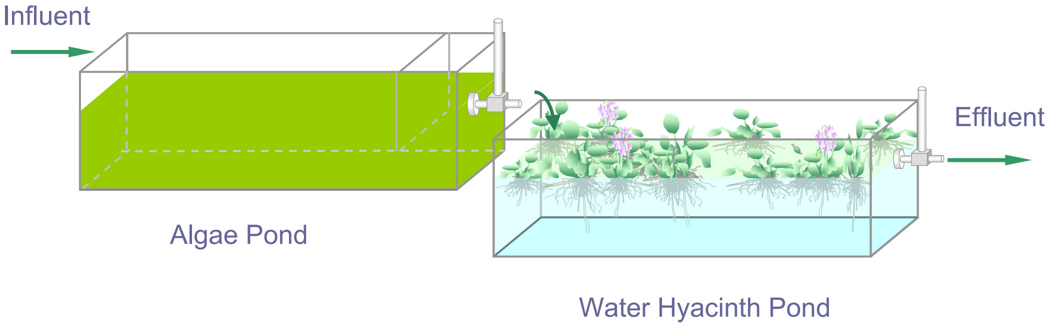


Fig. 5.8 Experimental stabilization pond system used for the post-treatment.

5.5.3 Wastewater

The effluents from the UAF-UASB system and the UAF-UASB-aeration system were used as feed in the experiment. The composition of the effluent is presented in Table 5.5.

Table 5.5 Composition of wastewater from the UAF-UASB and UAF-UASB-aeration system effluent

Parameters	Unit	UAF-UASB Effluent	UAF-UASB-Aeration Effluent
pH	-	7.76-8.30	8.3-9.4
COD_{tt}	mg/l	794-3,070	45-209
BOD	mg/l	-	25-150
SS	mg/l	100-203	15-64
VSS	mg/l	85-187	-
$N\text{-}NO_2^-$	mg/l	0.12-0.90	2.5-52.0
$N\text{-}NO_3^-$	mg/l	Trace	0.7-2.7
$N\text{-}NH_3$	mg/l	36.4-110	Trace
N-Org	mg/l	15.0-80.0	1.9-12.9
Total Phosphorous	mg/l	12.0-60.1	5.6-15.6

5.5.4 Cultivation of Algae and Water Hyacinths

Algae

Before starting up the stabilization pond system with the effluent solution, an algae suspension was cultivated in the pond at an N: P: C ratio of 15: 1: 105 according to Rolf et al. (1991) by using a small amount of algae to initiate their growth, which was achieved by exposing the pond to sunlight over a 5-day period.

Water Hyacinth (Eichhornia crassipes)

In tropical countries, the water hyacinth is abundant and easy to collect. The young and healthy specimens used in the experiment were taken from the Den canal (which is quite polluted by effluent from the Go Cat domestic landfill leachate treatment plant). The water hyacinths were introduced into the pond to an amount of 160 leaves, covering 60-80% of the total surface area. This left enough space for growth.

5.5.5 Experimental Procedure

During period 1, the stabilization pond system was fed with UAF-UASB system effluent. This effluent always is rather high in COD content and therefore needs to be diluted to a COD concentration of about 500 mg/L before being fed to the algae pond. Thus, the BOD concentration was approximately 400 mg/L, corresponding to L_{COD} 179 kgCOD/ha.d and L_{BOD} 143 kgBOD/ha.d. Rolf et al. (1991) proposed a BOD loading range of 56-202 kgBOD/ha.d for stabilization ponds and Mara (1997) a loading range of 331-440 kgBOD/ha.d for the temperature in the range 24-30^{o}C. However, due to the long periods of time needed for BOD analysis and to the relatively stable BOD/COD ratio in tapioca wastewater, a COD loading rate (L_{COD}) was used in this part of the experiment.

In period 2, the stabilization pond system was fed with UAF-UASB-AeWT system effluent (see the characteristics in Table 5.5). Due to the low COD concentration, it was fed undiluted and directly to the stabilization pond system. The operational parameters were as follows:

- Daily feeding at a flow rate of 14-15 L/day, corresponding to an algae pond and water hyacinth pond HRT ranging from 6-7 and 7-8 days, respectively;
- Twice a week, at a fixed time (8:00 AM), samples were taken to assess pH, COD_{tt}, COD_{sol}, SS, VSS, $N\text{-}NH_3$, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, N-Org., and total phoshorous.

5.5.6 Sampling and Analysis

To assess the performance of the treatment processes, viz. efficiency, we examined pH, COD_{tt}, COD_{sol}, $N\text{-}NH_3$, total nitrogen, and SS-content in accordance with the Standard Methods for The Examination of Water and Wastewater (APHA, 1995). The sample was filtered through a 0.45-µm membrane filter before COD_{sol} analysis.

5.6 RESULTS AND DISCUSSIONS

For the post-treatment of anaerobically pre-treated tapioca wastewater, the stabilization pond system was operated for two periods; the first period involved treatment of the UAF-UASB system effluent and the second period treatment of the UAF-UASB-AeWT-tank system effluent. Operational conditions and performances are summarized in Table 5.6, and the details are shown in Fig. 5.9 and 5.10. From the beginning of the experiment up until day 53, the stabilization pond system consisted merely of the algae pond, consequently no water hyacinth pond results were available during that period.

Table 5.6 Experimental results of the stabilization pond system

Parameters	Units	**Period 1 (from day 1 to 205)**		
		Influent Algae pond	**Effluent Algae pond** (HRT 6-7 day)	**Effluent Water Hyacinth** (HRT 7-8 days)
COD_{tt}	mg/l	487-623	248-289	73-154
COD_{sol}	mg/l	335-538	52-98	36-63
L_{COD}	kgCOD/ha.d	207-265	207-265	77-153
$E_{COD\ tt}$	%	-	25-64	46-83
$E_{COD\ sol}$	%	-	73-83	2-58
pH	-	7.20-8.50	8.90-9.30	7.90-8.50
SS	mg/l	22-48	39-118	16-34
$N\text{-}NH_3$	mg/l	11.2-60.5	1.0-2.0	Trace-2.0
$N\text{-}NO_2^-$	mg/l	Trace	Trace	Trace
$N\text{-}NO_3^-$	mg/l	Trace	Trace	Trace
Total nitrogen	mg/l	11.2-60.5	4.3-15.9	4.1-9.2
Total phosphorus	mg/l	8.5-14.2	10.2-11.6	2.3-4.2

Parameters	Units	**Period 2 (from day 206 to 247)**		
		Influent Algae pond	**Effluent Algae pond** (HRT 6-7 day)	**Effluent Water Hyacinth** (HRT 7-8 days)
COD_{tt}	mg/l	72-262	70-135	68-105
COD_{sol}	mg/l	56-164	54-76	51-58
L_{COD}	kgCOD/ha.d	31-111	31-111	29-54
$E_{COD\ tt}$	%	-	5-70	5-38
$E_{COD\ sol}$	%	-	6-63	8-42
pH	-	8.70-9.00	8.90-9.20	8.60-8.90
SS	mg/l	28-61	44-145	18-40
$N\text{-}NH_3$	mg/l	Trace	Trace	Trace
$N\text{-}NO_2^-$	mg/l	2.9-52.0	1.4-16.4	0.0-0.6
$N\text{-}NO_3^-$	mg/l	Trace-2.7	trace-0.9	Trace-1.6
Total nitrogen	mg/l	7.1-57.1	8.2-25,9	2.9-5,6
Total phosphorus	mg/l	9.7-13.3	8.1-9.6	3.6-5.5

During period 1 (day 0-205), the COD_{tt} removal efficiency of the algae and water hyacinth ponds was about 25-64% and 46-83%. The algae pond COD_{sol} removal efficiency ranged between 73-83% and that of the water hyacinth pond between 2-58%. The influent COD_{sol} concentration dropped from 335-538 mg/l to 52-98 mg/l of the algae pond effluent and to 36-63 mg/l of the water hyacinth pond effluent.

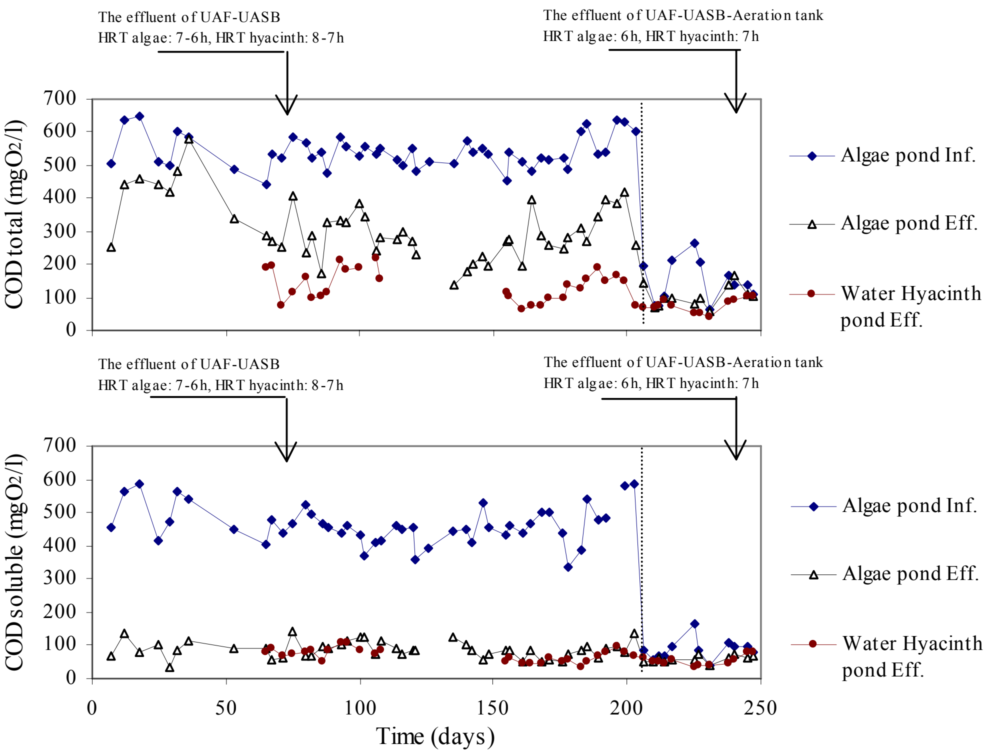


Fig. 5.9 Course of the CODtt and CODsol concentrations in stabilization pond system.

In period 2 (day 206 - 247), the COD content of the influent solution was lower than in period 1, due to the use of UAF-UASB-aeration tank effluent. The influent COD_{tt} concentration dropped from 72-262 mg/l to 70-135 mg/l for the algae pond effluent and to 68-105 mg/l for the water hyacinth pond effluent. The influent COD_{sol} concentration dropped from 56-164 mg/l to 54-76 mg/l of the algae pond effluent and to 51-58 of the water hyacinth pond effluent. These results demonstrate a significant difference between COD_{tt} and COD_{sol}, which can be attributed to the presence of algae and bacteria biomass. According to Arauzo et al. (2000) it seems to be of big importance for improving the performance of stabilization ponds to maintain a balance between bacteria, algae, and plankton. The question obviously is how to accomplish that! It is known, that in stabilization ponds, algae stimulate bacteria (by generation of oxygen) and bacteria stimulate algae (by generation carbon dioxide). In this way, the organic matter and nutrients are biodegradable and a portion accumulates in living cells. This is the reason for the difference between COD_{tt} and COD_{sol} in the treated effluent, as mentioned above. In addition, it is well known that due to its root system the water hyacinth plays an important role not only in the biodegradation of organic matter in wastewater but also in the removal of nutrients and suspended solids. Stabilization ponds that comprise an algae pond followed by a water hyacinth pond therefore constitute an excellence combination of their respective advantages

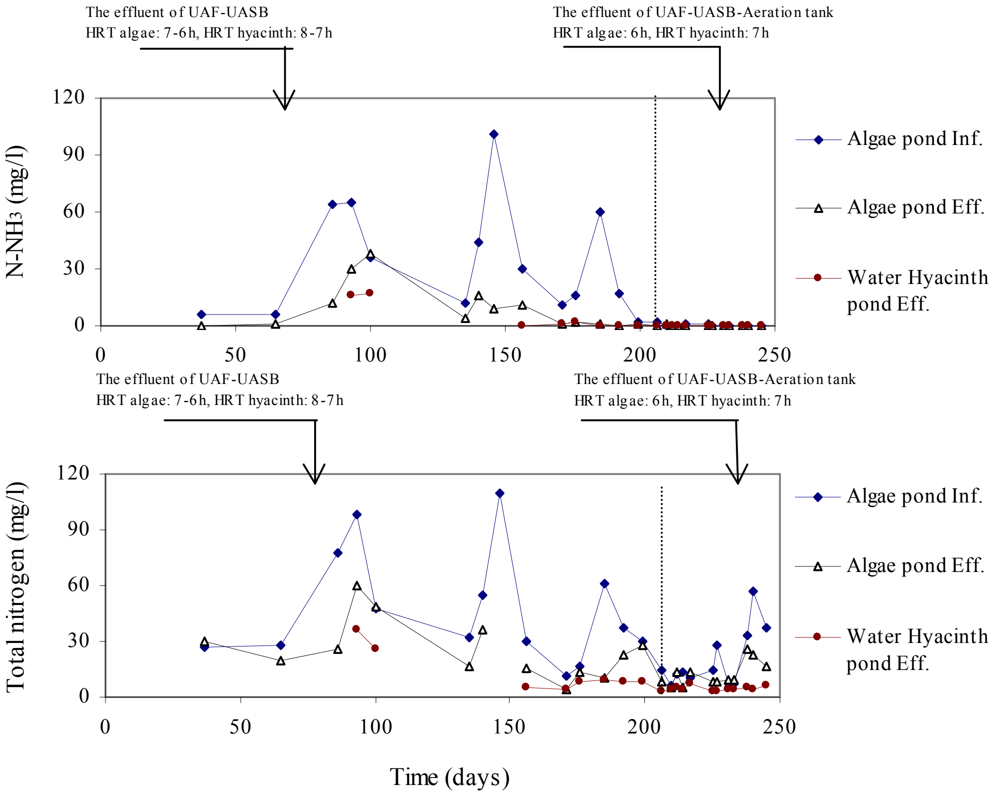


Fig. 5.10 Course of the ammonia and total nitrogen content in a stabilization pond system.

The experimental results proof that post-treatment by stabilization ponds leads to a high nitrogen removal; in period 1, the total nitrogen concentration dropped from 11.2-60.7 mg/l to 4.3-15.9 mg/l in the algae pond and to 4.1-9.2 mg/l in the water hyacinth pond. The total nitrogen removal efficiency in period 2 was very similar to that found in period 1, in particular with regard to the ammonia nitrogen, the concentration of which decreased significantly in period 1, i.e., from 11.2-60.5 mg/l to a maximum of only 2.0. The results also indicate that the pH in algae ponds ranges from 8.9 to 9.3; these high values can be attributed to the consumption of CO_2 and they lead to an improved nutrient removal. Our experimental results are very similar to those found by Catunda and van Haandel (1996) and Cavalcanti et al. (2002). In shallow stabilization ponds the high pH opens the possibility of nutrient removal up to efficiencies exceeding 90%. The ammonia is removed by stripping mechanism, a process that is enhanced by the release of oxygen bubbles from the oversaturated ponds. Phosphates are precipitated at high pH, in the form of a calcium phosphate compound.

During both periods of the experiment, microscopic observations were carried out for the algae pond twice a week. The results show that the Chlorella was predominant. Other kinds of algae cells such as Euglena, Scenedesmus, Ankistrodemus, Oocystis, and Spirulina were occasionally also observed. In addition, protozoa Vorticella, Paramecium, and rotifer were frequently present, thus indicating the optimal performance of the stabilization pond.

The results of our present research show that the Vietnamese Industrial wastewater discharge standards can be met completely (Fig. 5.9 and 5.10) by using the investigated stabilization pond system. This is an important factor, regarding the practical bureaucratic problems that otherwise would prevail.

5.7 DISCUSSIONS

Numerous experimental studies have been made on the application of AnWT using the UASB reactor system, AeWT using the conventional activated sludge process and on the use of separate stabilization ponds for the treatment of industrial wastewater. However, when applied in practice separately, these methods still suffer from some drawbacks. In the meantime a variety of studies have been carried out involving the use of a combined UASB + stabilization pond system (Catunda and van Haandel, 1996; van der Steen et al. 1999) or the combined UASB+ activated sludge system (von Sperling et al. 2001; Isik and Sponza, 2004) for achieving an optimal effluent quality. In most studies, the organic matter concentration of the raw wastewater was not very high and as a result the treated effluent easily complied with local discharge requirements. However, in our experiments, in terms of COD the organic matter was relatively high with values up to 27,000 mg/L and since the Vietnamese Industrial wastewater discharge standards are extremely severe (in fact unrealistic) with standards set for the effluent COD of <100 mg/L, BOD < 50 mg/L, SS < 100 mg/L, total nitrogen < 60 mg/L, total phosphorus < 10 mg/L, it is difficult, in fact even almost impossible, to find a proper treatment system. Hence, our research provides a general view of the whole system’s feasibility.

Due to the (still) high organic matter concentration of UASB effluent, i.e., 2,000-3,000 mg/L, the wastewater would need to be treated in an activated sludge process at HRT-values ranging from 6-9 h in order to be capable to reduce the COD concentration to values below 300 mg/L before it is entering the stabilization ponds. The use of a high rate AnWT-system undoubtedly offers enormous advantages compared to the sole use of a lagoon system for the treatment of tapioca wastewater. First of all the formation (and release) of offensive odors from an anaerobic pond is completely eliminated (see e.g. also Toprak, 1997) and secondly much less land area will be required for the pond post-treatment system. Moreover, the implementation of a high rate AnWT-system as primary treatment system leads to resource recovery and a quite robust approach.

The surface loading rate that can be applied in stabilization ponds (using UAF-UASB-AeWT system effluent) are in the range 111-265 kg COD/ha.d. and then an effluent COD concentration can be obtained in the range 36-58 mg/l at a total HRT from 13-15 days.

The algae pond and water hyacinth pond system represents an effective and technologically fairly plain post-treatment option for UASB reactor effluent under Vietnamese conditions, because this combination indeed provides an efficient removal of dissolved organic matter, suspended solids and nutrients. The treated effluent can be discharged to surface water's or it can be reused for irrigation, even for fertilization although in that case any post-treatment can be omitted.

The result of our study can be applied in practice, not only in tropical countries like Vietnam, but also in temperate climates after appropriate revision the operational parameters.

5.8 CONCLUSIONS AND RECOMMENDATIONS

The combination of a UASB reactor system with an aerobic activated sludge system and stabilization ponds represents an excellent treatment option for high-strength wastewater like tapioca wastewater. In fact it is in various aspects superior over conventional systems, the more so because even without ponds it will suffice provided more realistic – i.e. economically affordable and environmentally acceptable - discharge standards will become implemented. The main conclusions derived from these investigations are:

- Application of the aerobic activated sludge process for post-treatment of UASB reactor effluents of tapioca wastewater provide a high COD removal efficiency with values of 96.4-97.4% at HRT-values less than 5h, which implies overall COD-removal efficiencies (over the total treatment system) of more than 99%.
- The COD concentration of activated sludge process effluent at the maximum is 300 mg/L. Although this already implies an enormous COD-reduction relative to the raw tapioca wastewater COD, the COD even can be reduced further by treating the AeWT-effluent in stabilization ponds;

The combination of an algae pond followed by a water hyacinth pond is effective in the removal of remaining (very likely hardly biodegradable) COD, SS and nutrients, i.e. at an total 13-15 day HRT for the stabilization ponds system (surface loading rate: up to 111-265 kg COD/ha.d.) incredibly low effluent COD-values can be attained with values even down to 36-58 mg/l, while also the nitrogen and phosphorous content can reduced significantly. Therefore the effluent quality of this system complies with extra-ordinary severe effluent standards like those prevailing in Vietnam (standard - B level).

Since we so far only could demonstrate the feasibility of the system on tapioca wastewater treatment under laboratory conditions, it is necessary to start a pilot- or full-scale project or demonstrate its feasibility in practice. In the meantime already a pilot-plant treatment system for tapioca wastewater with a capacity of 10 m^3/d has been designed in detail; the plant was started up in middle of February 2006 in KMC Tapioca Starch Factory, Binh Phuoc Province. The initial results are showed briefly in Section 8.3. In case the results are positive, i.e. the standards for effluent discharge will meet the prevailing standards in Vietnam, we indeed are in the position to recommend starting a full-scale treatment plant soon. The successful application of this relatively low-cost – and resource recovery - robust treatment system is a commendable way to improve the environment and to contribute to sustainable development of the tapioca processing industry in Vietnam.

6

Process and Operational Factors Affecting the Anaerobic Process in the Treatment of Tapioca Processing Wastewater

6.1 GENERAL INTRODUCTION

The anaerobic digestion process is affected significantly by a number of process and/or operating conditions. As the process proceeds via the formation of VFA's, it is important that the HRT, influent organic concentration, and the reactor's alkalinity should be maintained at the appropriate values in order to prevent a serious accumulation of acids, i.e. acidification of the system, because it would result in the failure of the reactor performance. Thus, operational conditions such as the influent strength imposed OLR, reactor medium - pH, operational temperature and availability of nutrients and trace metals are factors governing the UASB performance.

To understand the processes and to improve the reactor efficiency in practice, several critical factors affecting UASB performance were studied by maintaining optimal operation conditions. The studies are discussed briefly below.

6.2 THE EFFECT OF TEMPERATURE ON THE HYDROLYSIS AND ACIDIFICATION PROCESSES OF TAPIOCA WASTEWATER

Anaerobic digestion is strongly influenced by temperature, and a number of specific temperature ranges can be grouped in one of the following categories: psychrophilic (0-20^{o}C), mesophilic (20-42^{o}C), and thermophilic (42-75^{o}C). According to Rajeshwari et al. (2000) and various other researchers, anaerobic bacteria can resist changes in temperature well as long as they do not exceed the upper limit whereby the decay rate exceeds the growth rate. In the mesophilic range, the bacterial activity and growth decreases by one half for each 10^{o}C drop below 35^{o}C. The effect of temperature on the maximum substrate utilization rates of methanogens has recently been evaluated by Yu and Fang (2003); lowering of the operational temperature leads to a decrease in the maximum specific growth and substrate utilization rates. Temperature also effects the maintenance requirements of organisms, e.g. methanogens. However, the temperature effect studies generally have been focused on an overall anaerobic degradation process or methanogenesis, rather than acidogenesis.

In the present study, we investigated the hydrolysis and acidification processes of tapioca wastewater in the presence of a seed sludge, at a temperature of 20^{o}C and 30^{o}C (due to the seasonal temperature range from 18-35^{o}C in South Vietnam).

6.2.1 Materials and Methods

Batch experiments were carried out in the 20^{o}C and 30^{o}C rooms at the Sub-Department of Environmental Technology – of the Wageningen University. Serum bottles of 1,250 ml used in the experiments were inoculated with 500 ml solutions of nutrients and trace elements, septic tank sludge (biomass) at a final content of 2 gVSS/L), and substrate at a concentration of approximate 2,000 mg COD/L. Thereafter, to maintain an anaerobic condition the bottles were tightly sealed by means of an aluminium screw cap and a butyl rubber septum. The bottles are exposed under shaker of 50 rpm, and suitable temperatures (20^{o}C and 30^{o}C rooms). The biogas was measured by a gas pressure meter and other parameters were measured by sampling with a syringe and a needle. The biogas composition was analysed by GC. The concentration of VFA (including acetate, propionate, butyrate, and valerate) and the sugars (including sucrose, glucose, pyruvate, lactate, and formate) were analyzed by GC and HPLC. Tapioca wastewater was used as substrate. Details regarding methodology, experimental procedure, and initial characteristics of the seed sludge as well as the calculations are presented in Chapter 7. The experiment was carried out in duplicate at 20 and 30°C and the applied operational conditions are presented in Table 6.1

Table 6.1 Operational conditions applied at the various temperatures

Temperature	20°C	20°C	30°C	30°C	30°C
Sludge (gVSS/L)	2	2	0.5 and 2	0.5	2
COD (gCOD/L)	No (Blank)	2	No (Blank)	2	2
Nutrients	Present	Present	Present	Present	Present
pH	6.9-7.0	6.9-7.0	6.9-7.0	6.9-7.0	6.9-7.0

Note:

- *At 20°C, the experiment with 0.5 gVSS/L was not done because of the very low sludge activity.*
- *Tapioca wastewater was produced in the lab at Wageningen University with cassava roots using the same procedure for tapioca processing (small-scale) in Vietnam. The ratio of weight of cassava roots / water is 1/3. Cassava roots → Wash → Grind → Mix (with water) → Leach → Settle I & II → Wastewater.*

6.2.2 Results and Discussions

On the basis of the experimental data depicted in Fig. 6.1 – 6.3, we calculated the hydrolysis and acidification rates for various experimental conditions. The details of the calculations are presented in Chapter 7. The results of these calculations are summarized in Table 6.2.

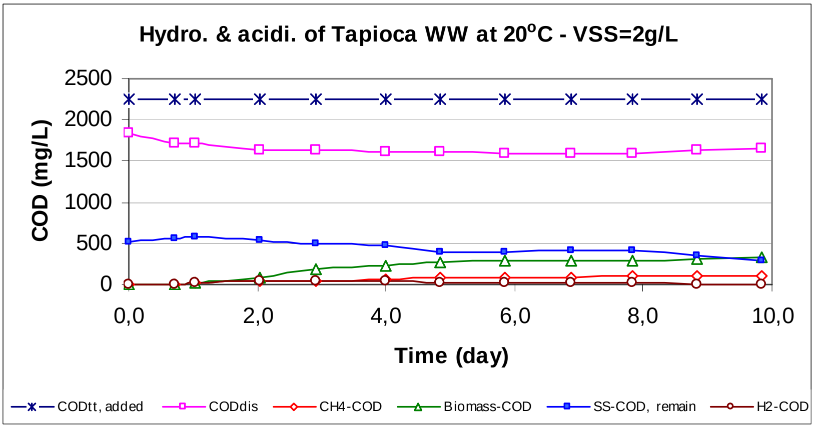


Fig. 6.1 Course of the hydrolysis and acidification processes of tapioca wastewater at 20°C and VSS 2g/L during a 10-day period.

In the experiment conducted at 20^{o}C, it was easy to observe formation of scum layers in the serum bottles; an agglomerated layer at the liquid interface appeared, it looked like flocculent suspended matter. Likely it consisted agglomerated proteins present in the wastewater. Sampling was done after well shaking, but the agglomerate persisted in form of small particle. This may cause a decrease of soluble COD. This phenomenon did not happen in the experiment conducted at 30^{o}C.

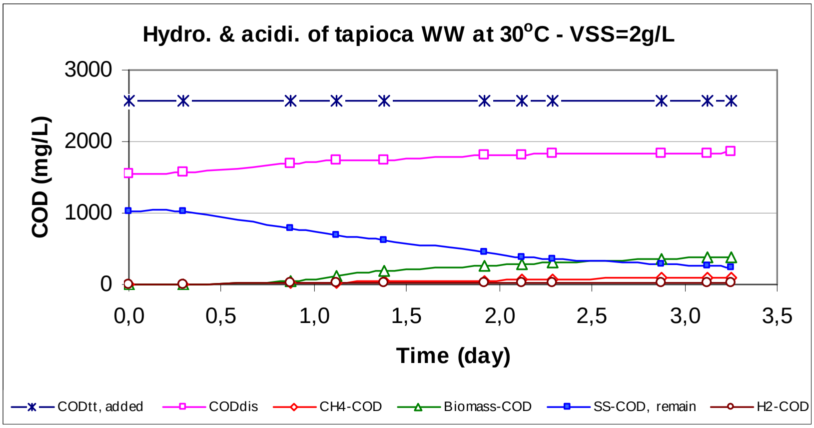


Fig. 6.2 Course of the hydrolysis and acidification processes of tapioca wastewater at 30^{o}C and VSS 2g/L during a 3-day period.

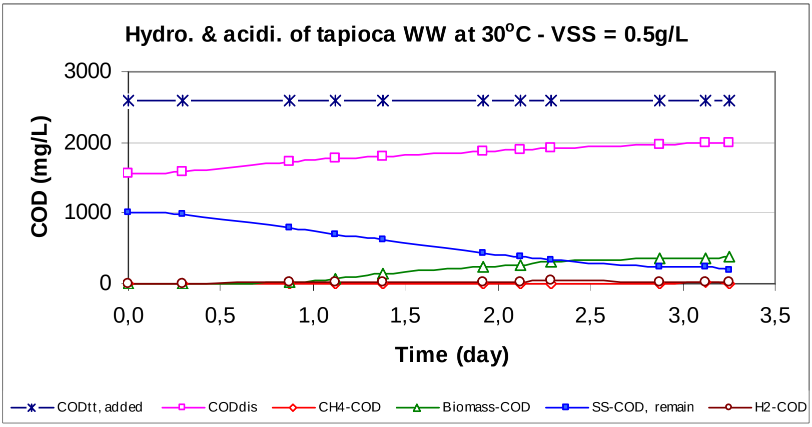


Fig. 6.3 Course of the hydrolysis and acidification processes of tapioca wastewater at 30^{o}C and VSS 0.5 g/L during a 3-day period.

The results of the calculations reveal that the calculated hydrolysis rate is 8 times higher at a temperature of 30°C than at 20°C, i.e. 33 to 255 mgCOD/L.d and the acidification rate is 5 times higher at the higher temperature, i.e. 123 to 637 mgCOD/L.d. Apparently the seed sludge concentration hardly affects the rate of the hydrolysis and acidification, because almost the same values are found in the case of 0.5 and 2.0 gVSS/L. The idea of Rajeshwari et al. (2000) and Metcalf and Eddy (2003) that in the mesophilic range bacterial activity and growth decreases by one half for each 10°C drop, is not confirmed by the results of our present experiments (although obviously the hydrolysis process is an enzymatic and not a bacterial growth dictated process).

Table 6.2 Experimental results regarding the hydrolysis and acidification of tapioca wastewater at different temperatures, with standard deviation in brackets

No	Items	Units	20°C (2gVSS/L)	30°C (2gVSS/L)	30°C (0.5gVSS/L)
1	Hydrolysis rate	mgCOD/L.d	33 (4)	255 (6)	267 (5)
2	Maximum hydrolysis rate	mgCOD/L.d	73 (25)	337 (21)	334 (2)
3	Hydrolysis constant	day^{-1}	0.08 (0.01)	0.58 (0.01)	0.60 (0.01)
4	Specific hydrolysis rate	mgCOD/gVSS.d	37 (12)	169 (11)	668 (4)
5	Acidification rate	mgCOD/L.d	123 (3)	637 (2)	639 (9)
6	Maximum acidification rate	mgCOD/L	239 (24)	1340 (24)	1030 (109)
7	Specific acidification rate	mgCOD/gVSS.d	120 (12)	670 (12)	2060 (218)

6.3 THE EFFECT OF pH ON UASB PERFORMANCE

Reports about the inhibitory effect of low (acidic) pH-values on the anaerobic degradation of starch wastewater are rare in the literature. However adequate information on this topic would be helpful in the both the design and in the operation of UASB-reactors treating such complex types of wastewater.

According to Yu and Fang (2003) and others, many features of the microbial metabolism can become seriously affected by pH and variations in the pH over the pH-range where micro-organisms can grow, i.e. including the utilization of carbon and energy sources and the efficiency of substrate degradation. Moreover, pH variation can affect cell morphology and structure, and the flocculation and adhesion phenomena as well. A substantial number of studies have been carried out on the effect of pH on anaerobic degradation (Sanders, 2001; Yu and Fang, 2002; 2003, Paulo et al., 2003b, Hu et al., 2005), but little attention has been paid to pH influence on UASB performance in treating starch wastewater.

It falls beyond the scope of this thesis to assess the effect of pH on UASB performance treating complex wastewaters in detail; in our investigations we restricted the study to assessing possible problems with low(er) influent pH-values on the UASB-reactor operation.

6.3.1 Materials and Methods

The 8.5 L UASB-reactors used in these experiments were started up using septic tank sludge as seed sludge, i.e. 21 gVSS per litre of reactor. The start-up was done at an OLR of 3 kgCOD/m^3.d, corresponding to a sludge-loading rate (SLR) of 0.14 kgCOD/kgVSS.d. Four levels of volumetric OLR (based on COD) were applied by progressively increasing the influent COD concentration, viz from 3 to 23 kgCOD/m^3.d. The operational conditions are presented in Table 6.3. The experiments were carried out at ambient temperatures and the experimental data was collected over 120 days.

During the start-up period, the original wastewater was diluted to the required concentration with tap water and supplemented with NaOH and $NaHCO_3$ to neutralize free VFA and to provide a sufficient buffer capacity. According to Brummeler et al. (1985), the addition of an average amount of 0.84-1.68 g $NaHCO_3$/L is adequate and the alkalinity in the influent should range between 0.25-0.95 g/L. In fact, in some cases it is quite well possible to operate a UASB-reactor with an acid influent, i.e. when a sufficient amount of neutralized VFA is present and/or when alkalinity is produced in the form of ammonia. However, we still need to define the suitable pH range for UASB-reactor in specific circumstances.

6.3.2 Results and Discussions

Table 6.3 UASB-reactor operating conditions and treatment efficiency using septic tank sludge as seed sludge

Parameter	Units	Organic loading rate (kgCOD/m^3.d)				
		2.2-3.6	**5.1-8.7**	**7.7-13.6**	**10.6-18.3**	**13.8-22.8**
$COD_{total,in}$	mg/L	1,251-1,784	2,677-4,121	3,584-6,684	5,000-8,656	8,177-11,909
$COD_{sol.,in}$	mg/L	1,172-1,581	1,718-3,865	2,400-6,275	3,400-7,357	6,623-9,225
$COD_{total,eff}$	mg/L	166-323	110-273	426-484	676-920	912-1,695
$COD_{sol.,eff}$	mg/L	46-100	55-112	149-173	272-411	466-999
HRT	h	11.4-13.7	11.4-13.7	10.5-12.8	11.4-12.8	16-20
Q	L/d	15-18	15-18	16-19	16-18	16-20
Time	days	1-30 (30)	31-46 (16)	47-86 (40)	87-112 (26)	113-123 (11)
$E_{CODtotal}$	%	90-92	88-97	90-95	90-95	85-94
E_{CODsol}	%	93-97	89-97	94-95	91-95	88-95

The system was started-up at influent COD concentration from 1,200-1,400 mg/L, and HRT ranging of 10.5-12.8 h. The influent pH and alkalinity was maintained in the range 6.7-7.1 and 1,200-1,400 mg$CaCO_3$/L, respectively. Results of the experiment are shown in Fig. 6.5. The results show that the start-up proceeded smoothly, i.e. at a high efficiency.

After 37 days of the operation, the household factory wastewater was replaced by that of a large-scale factory. The influent SS concentration increased from 40-79 mg/L to 257-570 mg/L due to the different characteristics of the wastewater. The ratio of soluble COD/total COD became much lower due to the high fraction of COD_{SS}.

The results show in Fig. 6.4 that the specific methane gas production dropped significantly over 9 days, but then it restored to the original level. The first granules became visible after 40 days of operation, i.e., at OLR 6 kgCOD/m^3.d. The average biogas production was high with values of 0.324 (0.101) and 0.399 (0.109) litre biogas per gram COD converted, calculated on the basis of total COD and soluble COD, respectively, with standard deviation is in brackets.

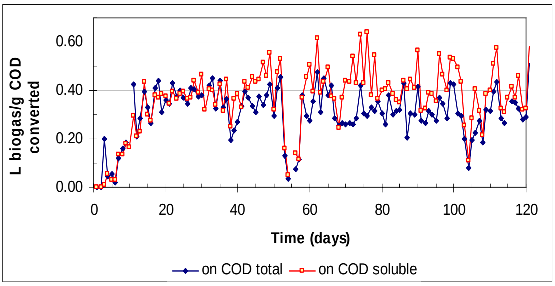


Fig. 6.4 Biogas production from the UASB-reactor (Litre of biogas/1g COD converted).

On day 53 of the operation, the pH of influent suddenly decreased to 6.1, possibly even lower, because of problems with the pH meter. After only 3 h, the sludge bed settled down completely because of no gas production. The problem was solved immediately after it was observed by increasing the influent pH to 6.9 by adding alkalinity (using NaOH and $NaHCO_3$). This means the reactor had been exposed to an influent pH of 6.1 for about 4 h. Nevertheless the performance of the system deteriorated within the next three days, i.e., the COD removal efficiency dropped to 20%, and even to less than 1% the day after. Surprisingly the day after the effluent pH was high with a value of approximately 7.5 at, but COD removal efficiency and gas production remained very low, i.e. only 2 L/d. (see Fig. 6.5). The situation improved gradually, although the complete recovery took 8-10 days; the COD removal efficiency increased to 81-89% and the gas production from 1-2 L/d to 20-25 L/d. As mentioned, two days after the problem the effluent pH attained a value of 7.8 and even increased to pH 8.1 within one week.

Our experimental results clearly demonstrate that in the case of tapioca wastewater even a not really low influent pH of approximately 6.1 can lead to a serious drop in the COD removal efficiency and the biogas production, despite the fact that the exposure period only lasted 4 h. Thus, maintenance of proper alkalinity in the UASB-reactor medium is a factor of vital importance with this particular wastewater! Once the VFA concentration would exceed the bicarbonate buffering capacity of the reactor medium, the pH will drop below the optimum range for microbial metabolism, and the growth rate of the methanons will become severely inhibited which will lead to a highly unbalanced situation (Singh et al., 1998). For neutralization of the wastewater, NaOH 10% (to increase pH from 3.7 to 6.0-6.2) and $NaHCO_3$ to increase pH to about 7.0 was used. During the day the pH dropped to 6.1; the influent bicarbonate alkalinity was 1,980 mg$CaCO_3$/L, while during other days, at the same OLR (7.7-13.6 kgCOD/m^3.d), the bicarbonate alkalinity ranged from 2,780-4,550 mg$CaCO_3$/L and pH 6.7-6.9. However during some days at the same OLR, the pH ranged from 6.7-6.9 and the influent bicarbonate alkalinity from 1,690-1,890 mg$CaCO_3$/L. The influent bicarbonate alkalinity increased when increased OLR – as a result of the higher influent COD concentration because then more chemicals are needed for neutralization. The influent bicarbonate alkalinity was higher at OLR of 10-20 kgCOD/m^3.d, i.e. ranged from 3,880-6,000 mg$CaCO_3$/L.)

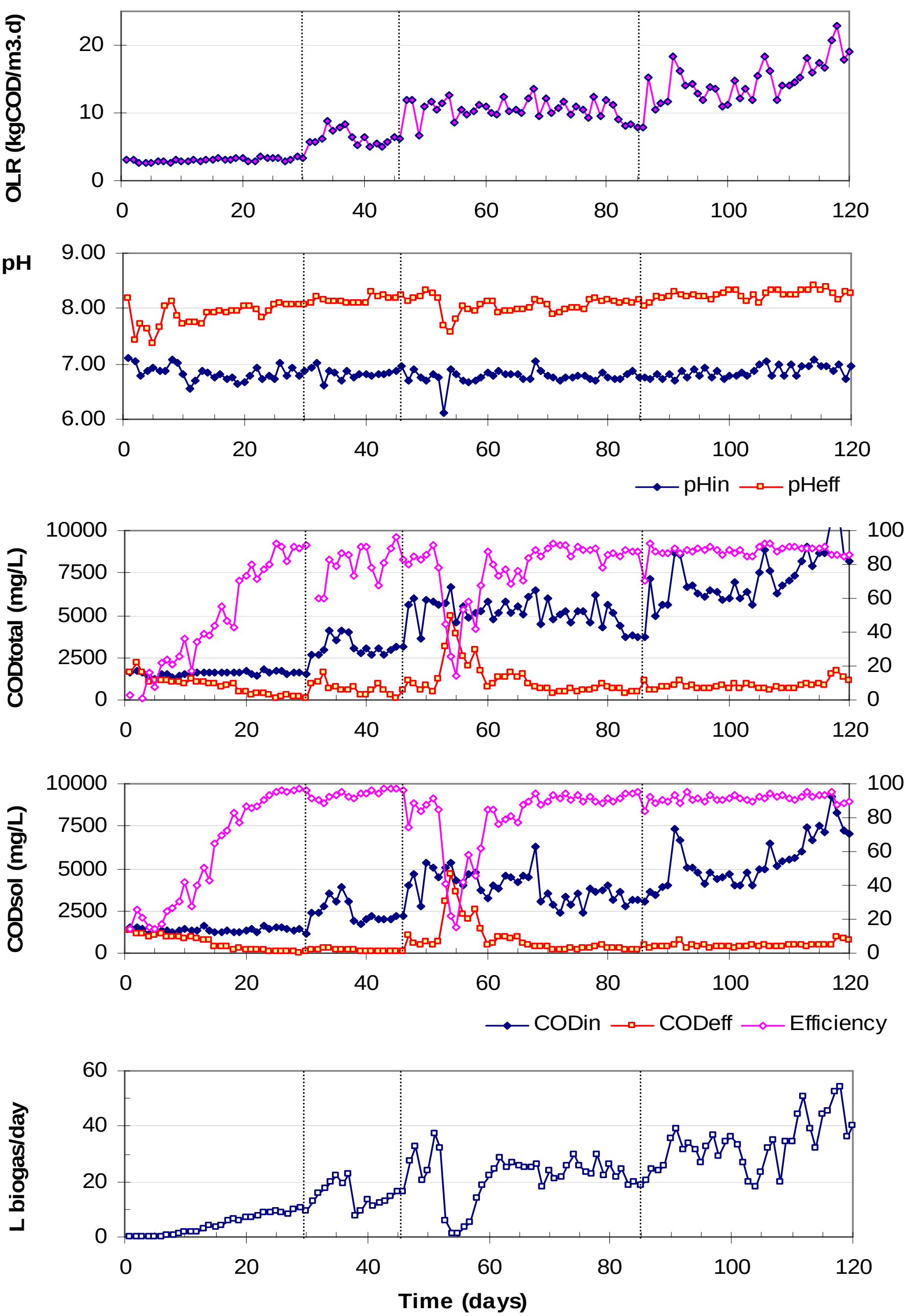


Fig. 6.5 Course of the UASB performance during the experiment.

6.4 EFFECT OF THE PRESENCE AND AVAILABILITY OF NUTRIENTS AND TRACE ELEMENTS ON UASB PERFORMANCE

The effect of the addition of trace metals on the performance of bioreactors has been an important field of study in anaerobic processes, as various metals are involved in the enzymatic activities of acidogenesis and methanogenesis (Osuna et al., 2003a,b). A number of nutrients are essential for metabolic activity. The macronutrients required are carbon, oxygen, hydrogen, nitrogen, phosphorus, and sulphur. Many industrial wastewaters are deficient lacking in nutrients required for the growth of micro-organisms. Hence, in treatment plants, nitrogen and phosphorus occasionally need to be added to the influent (Richard et al., 2003).

Also trace metals are essential micronutrients for growth of both acetogens and methanogens (Metcalf and Eddy, 2003). They are needed for synthesis of co-factors and/or enzymes or essential. In view of that trace element cocktails are commonly supplied to the feed of UASB-reactors, viz mixtures include salts of iron, aluminium, zinc, nickel, cobalt, molybdenum, manganese, copper, boron, and selenium. Although only extremely low concentrations of these elements are needed, a lack of these metals has an adverse effect upon the microbial growth and performance (Lettinga et al, 1998, Singh et al., 1999)

Osuna et al. (2003a) studied the effect of the absence of trace elements on the conversion of a mixture of volatile fatty acids by anaerobic granular sludge; they found that COD removal efficiencies were 99% and 77% for the control and for the trace element deprived reactors, respectively. The lack of trace metals affects the overall process due to the sensitivity of the metabolic pathway of propionate conversion in the UASB-reactor. Similarly, Osuna et al. (2003b) found that maximum specific activity values of granular sludge in the reactor supplied with trace elements were higher than the sludge from the reference reactor not supplied with trace elements. According to Alphenaar et al. (1993), phosphorus deficiency can reduce the methanogenic activity of UASB-reactor to 50% comparison with the control. Erguder et al. (2001) found that a supply of macronutrients and trace metals is vital for the anaerobic treatment of cheese whey. This wastewater can be treated well in a UASB-reactor at an HRT of 2-3 days with a COD removal efficiency of 95-97% and an influent COD of approximately 42-55 g/L. According to Rajeshwari et al. (2000), methane-forming bacteria have a relatively high internal content of iron, nickel, and of cobalt, and it therefore can be essential to supply these elements to the influent of the reactors. Other studies on the effect of cobalt and nickel deprivation on the anaerobic conversion of methanol demonstrated the serious failure of methanogenesis (Bhattacharya et al., 1994, Zandvoort et al., 2002a,b, Paulo et al., 2003a, Zandvoort et al., 2004).

In practice, the supply of nutrient and trace elements may become extremely expensive, i.e., up to approximately 2.2 US$/$m^3$ wastewater, and therefore therefore optimization of the supply of the ingredients is very important. Therefore the aim of our present investigations was to assess the optimal performance of a UASB-reactor treating tapioca wastewater by means of adding nutrients and trace metals to the wastewater.

6.4.1 Materials and Methods

The experimental reactors, the wastewater used for these experiments, and the biomass and the analysis methods have been described in Chapter 4 (the COD concentration in Section 6.4 refers to COD_{total}) concentration. The composition of the nutrient and trace element solution used in the experiment is presented below:

The basal media contained the following nutrients (in mg/l): NH_4Cl: 1,040, KH_2PO_4: 169.8, $(NH_4)_2SO_4$.: 169.8, $MgCl_2.6H_2O$: 150, KCl: 270, Yeast: 19.8. Trace elements (in 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, $C_{10}H_{16}N_2O_8$: 1.0, Resazurine: 0.02, HCl: 0.0001 ml. The nutrients and trace elements were prepared as a concentrated stock solution and diluted when supplied to the reactors.

The experiments were conducted using septic tank sludge as seed sludge. The amount of seed sludge, nutrients, and trace elements supplied to the UASB-reactors are shown in Table 6.4. The start-up of these UASB-reactors was done at a COD concentration of 1.500 mg/L. Total of nine levels of volumetric OLR based on COD were applied by a progressive increase in the influent COD and influent flow rate. The operational conditions are presented in Table 6.5. The organic loadings applied were increased stepwise to minimize any impact on the UASB performance by a sudden increase in loading. The experiment was carried out over 204 days at ambient temperatures.

Table 6.4 Amount of sludge and nutrients supplied to the reactors

Reactor	$gVSS/L_{reactor}$	Nutrients and trace elements (%)
UASB 1	10.5	100
UASB 2	10.4	50
UASB 3	10.4	25
UASB 4	10.4	0

Operational conditions were the same for all four UASB-reactors, i.e. with respect to the amount of seed sludge, flow rate, and influent COD concentrations. NaOH and $NaHCO_3$ were added to neutralize pH from 3.5-4.5 to 6.7-6.9, and to provide sufficient buffer capacity. The amount of chemical for neutralization consumed ranged from 1.8-2.1 gram NaOH and $NaHCO_3$ per litre of original wastewater. The nutrients and trace elements were added separately to the four UASB-reactors’ influent containers, depending on the experimental procedure, i.e., 100, 50, 25, 0%, respectively.

6.4.2 Results and Discussions

The required optimum COD:N:P ratio were obtained from the Anaerobic Lab Work Manual (1995) of the Sub-department Environmental Technology of the Wageningen University and from Lettinga et al. (1998). The minimum concentration of macro- and micro-nutrients can be calculated based on the biodegradable COD concentration of the wastewater, on cell yield, and on nutrient concentration in bacteria cells (Rajeshwari et al., 2000). For carbohydrate, this ratio was 350:5:1. The ratio's of COD:N:P assessed for tapioca processing wastewater's from large, medium, and small factories in South Vietnam are presented in Table 6.6.

Table 6.5 Operation conditions in the experiment are the same for the four UASB-reactors. The COD value expressed the COD concentration at steady UASB performance

Parameters	Units	Period 1	Period 2	Period 3	Period 4	Period 5
CODtt, inf.	Mg/L	1,628-2,053	2,906-3,419	3,484-4,761	6,929-7,830	9,007-10,602
CODsol, inf.	Mg/L	1,405-1,571	1,846-1,942	2,603-3,432	5,535-6,276	6,941-8,130
HRT	H	11.7-13.2	9.9-13.6	12.0-13.2	11.0-13.2	11.0-14.4
Q	L/d	3.8-4.3	3.7-5.1	3.8-4.2	3.8-4.6	3.5-4.6
OLR	kgCOD/m^3.d	2.1-4.1	3.5-8.8	6.5-11.0	9.8-15.7	13-25
Exp. Time	days (total)	11	17 (28)	14 (42)	26 (68)	48 (116)

Parameters	Units	Period 6	Period 7	Period 8	Period 9
CODtt, inf.	mg/L	10,236-11,671	9,194-9,954	7,893-9,023	7,200-9,091
CODsol, inf.	mg/L	8,000-8,927	6,252-8,498	5,760-7,449	5,566-6,075
HRT	h	6.8-8.3	5.2-6.8	4.3-3.7	1.8-2.0
Q	L/d	5.8-7.1	7.1-9.3	9.0-12.9	24-26
OLR	kgCOD/m^3.d	23-38	34-42	38-56	56-101
Exp. Time	days (total)	32 (148)	22 (170)	21 (191)	18 (204)

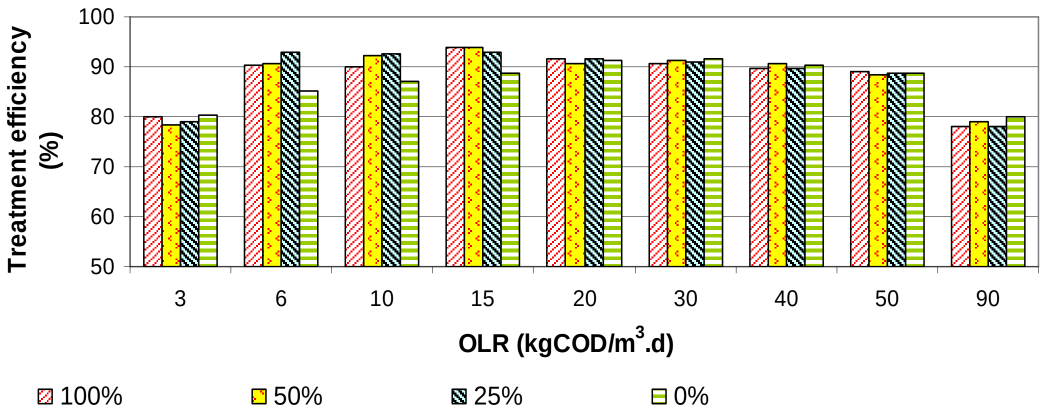


Fig. 6.6 Treatment efficiencies of the UASB at different concentrations of nutrient and trace elements, at various OLR, the treatment efficiency and the OLR values presented in the graph are average values and were collected from the steady UASB performance.

A preliminary calculation indicated that the amount of nitrogen and phosphorus was slightly below the 'theoretical' value. Taking into consideration the results of the literature review and the nature of tapioca wastewater, the experiment was carried out in order to assess the optimal conditions with respect to the supply of nutrients and trace elements for the treatment of tapioca wastewater in UASB-reactors.

Table 6.6 The assessed COD:N:P ratio of tapioca processing wastewaters in the experiment

Type of WW	**COD**	**N**	**P**
Large-scale	350	2.2-9.0	0.2-1.0
Medium-scale	350	1.2-3.0	0.5-0.8
Small-scale	350	1.7-2.1	0.4-0.6

The experimental results are summarized in Table 6.7 and Table 6.8 and Fig. 6.6, and the more detailed data are shown in Fig. 6.7. The results obtained in these experiments indicate that supply of nutrients and trace elements only slightly affect the treatment efficiency of the systems during the initial phases of the operation of the system, i.e., at an OLR below 20 kgCOD/m^3.d. At higher OLR's, the differences in the treatment efficiency at different concentrations of nutrients became insignificant. During the operational period of 204 days in fact no significant difference can be observed among the four UASB-reactors.

Table 6.7 Total COD treatment efficiency at different concentrations of nutrient and trace metals and different OLRs

OLR (kgCOD/m^3.d)	**COD treatment efficiency using different UASB-reactors (different ratio of nutrients and trace elements)**			
	100%	**50%**	**25%**	**0%**
2.1-4.1	79.87	78.37	79.18	82.08
3.5-8.8	90.27	90.75	92.80	85.06
6.5-11.0	87.02	92.11	92.55	87.11
9.8-15.7	94.02	93.93	92.78	88.74
13-25	91.49	90.61	91.70	91.37
23-38	90.63	91.52	90.99	91.65
34-42	89.72	90.52	89.72	90.45
38-56	88.92	88.33	88.70	88.75
56-101	75.09	76.74	78.07	75.55

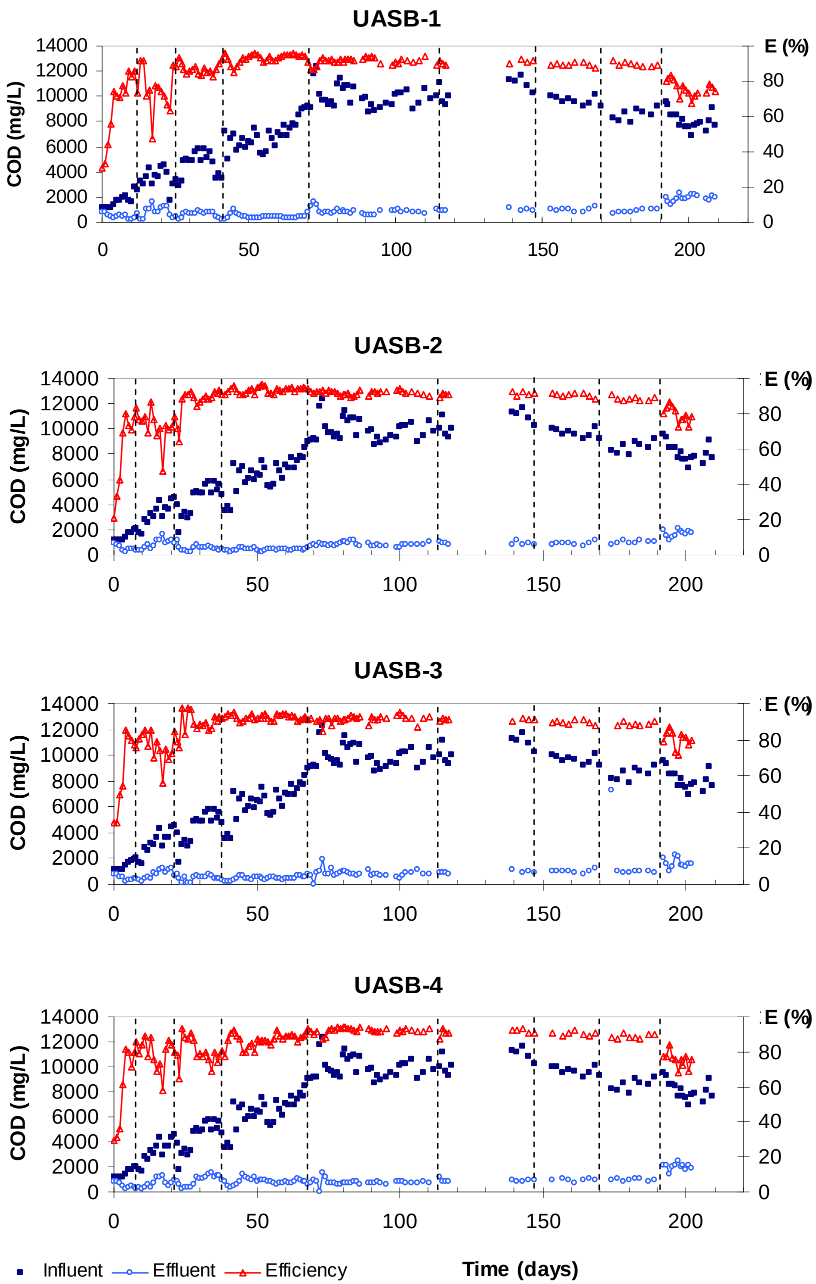


Fig. 6.7 The UASB performance at different of nutrient and trace metals.

Table 6.8 COD_{tt} effluent during a steady UASB performance involving different concentration of nutrients and trace metals

Influent COD_{tt} (mg/L)	Effluent COD_{tt} concentration using different UASB-reactors (different ratio of nutrients and trace elements)			
	100%	50%	25%	0%
1,120-2,053	225-413	242-444	233-427	201-360
1,757-4,550	171-443	163-421	127-328	262-680
3,484-5,800	452-753	275-458	259-432	449-748
5,000-8,459	299-506	304-513	361-611	563-953
9,007-12,335	766-1,049	846-1158	747-1,023	777-1,064
9,290-11,671	871-1,094	795-963	837-1,051	776-975
9,194-10,159	945-1,044	871-963	945-1,044	878-971
7,893-9,244	875-1,024	921-1,079	892-1,045	888-1,040
6,931-9,579	1,732-2,395	1,611-2,228	1,519-2,101	1,697-2,347

Granular sludge manifested visually at the bottom of all four reactors from day 26-28 of operation, in agreement with what was reported by Wiegant and Lettinga (1985) in their experiment with fresh cow manure as seed material and glucose as substrate, viz granulation after 4 weeks of UASB operation. Similarly, Ghangrekar et al. (2005) reported that granular sludge was observed in their UASB-reactor after 25-30 days of operation at an OLR lower than 4.8 kgCOD/m^3.d and with glucose as substrate. Gonzalez et al. (1998) reported that granular sludge manifested after 15 days of UASB-reactor operation treating sugarcane molasses. The volume of biogas produced was very high for UASB-1 and UASB-2, i.e., 1kg of COD is biologically converted to 300-380 litres of biogas, but it was lower in UASB-3 and substantially lower in UASB-4. (See Fig. 6.8 and Fig. 6.9). In our lab conditions we did not measure the biogas composition. This rate of biogas production is comparable to that noted by Rao et al. (2004) with the amount of 300-500 L biogas per kg of converted COD, using bulk drug industry effluent.

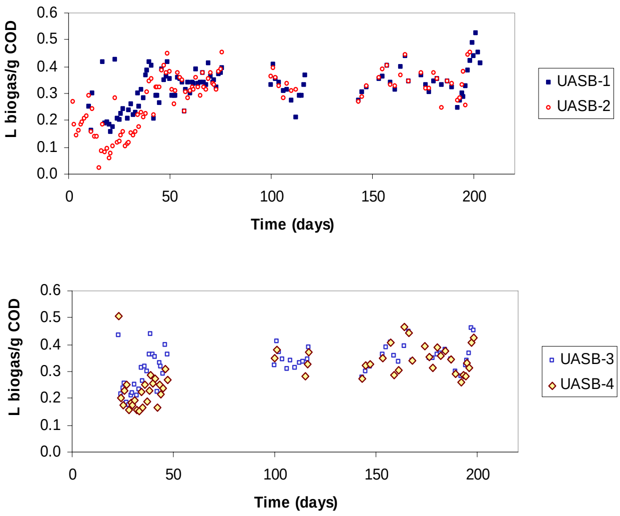


Fig. 6.8 The biogas production for four UASB-reactors during the experimental period (L biogas/1g COD converted).

The results show that nutrient supply perhaps merely is needed to enhance the growth of micro-organisms and to improve the treatment efficiency during the start-up of the UASB-reactors The amount of nutrients and trace elements that needs to be added to the reactor feed can be anyhow kept below ¼ of the amounts recommended according to the Wageningen University's Anaerobic Lab Work Manual (1995). The experimental result confirms that of Gonzalez et al. (1998), who studied the treatment of sugarcane molasses using a UASB. Addition of the nutrient solution was stopped at day 80, but the process performance and sludge granulation was not affected.

The biogas production data show that 1g biologically converted COD leads to 0.38-0.40 L of biogas (with an expected methane content of 70%). Theoretical calculations show that 1g of COD will convert to 0.323L methane gas and to 0.118g new biomass-COD.

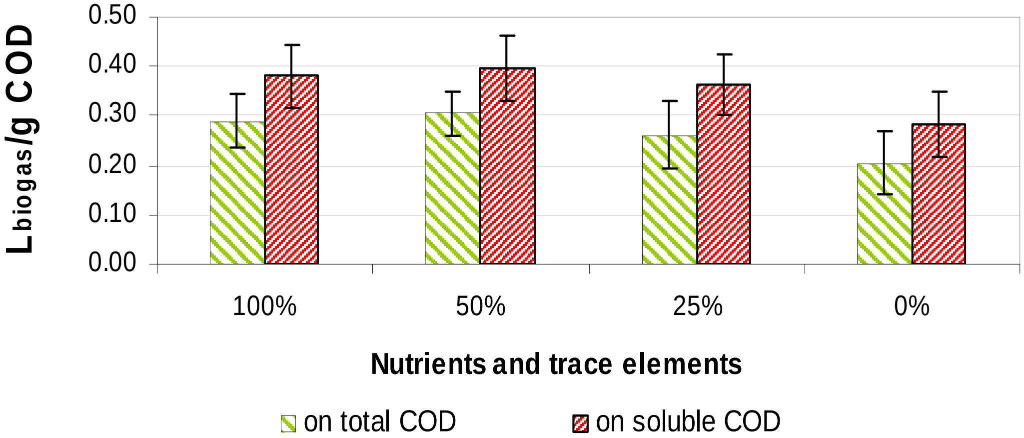


Fig. 6.9 The biogas production average (and standard deviation) at different concentrations of nutrient and trace metals. The presented results are arithmetic means, collected during the whole 200-day period, due to the fluctuation of biogas production (Fig. 6.8).

6.5 THE EFFECT OF ORGANIC LOADING RATE ON UASB PERFORMANCE

In anaerobic wastewater treatment, similarly as in other microbial treatment processes, the applied organic loading rate (OLR) plays an important role, because it significantly affects the microbial ecology and performance characteristics of the system. According to Rajeshwari et al. (2000), Fixed Film, Expanded Bed, and Fluidized Bed reactors can accommodate a higher organic loading rate than other high-rate anaerobic reactors. Fluidized Bed systems would be capable of handling maximum loading rates up to 100 kgCOD/m^3.d compared to other reactor systems only 50 kgCOD/m^3.d. According to Rao et al. (2004), the optimum OLR is 10 kgCOD/m^3.day in AFFR with bulk drug industry wastewater; an increase in the OLR would lead to a drop in substrate removal, which would indicate inhibition of the biomass activity.

The maximum organic loading rate applied for a UASB-reactor in various studies is presented in Table 6.9. Normal OLRs reported for UASB-reactors are in the range of 3 - 39 kgCOD/m^3.d, but values up to 104 kgCOD/m^3.d have been reported for UASBs using VFA and yeast extract substrate under thermophilic conditions.

Table 6.9 Maximum OLR applied for UASBs in various studies

No.	Substrate type	OLR (kgCOD/m^3.d)	HRT (h)	Temperature condition	Reference
1	Sugar	16-104	2.1-3.2	Thermophilic	Wiegant and Lettinga, 1985
2	Sucrose	6-9	1.3-2	Mesophilic	Soto et al., 1997
3	Sucrose and VFA	1-45	4.2	Thermophilic	Syutsubo et al., 1998
4	Slaughter-house	13-39	2-7	Mesophilic	Torkian et al., 2003
5	Dairy wastewater	2.4-13.5	3-12	Mesophilic	Rasmasamy et al., 2004
6	Glucose	2.9-9.5	8-16	Mesophilic	Ghangrekar et al., 2005
7	Piggery waste	1.0-4.0	2-8	Mesophilic	Sanchez et al., 2005

Since the applicable loading rate in treatment systems depends on a number of factors, such as operational temperature, wastewater characteristics, type of reactor system, start-up regime applied, and researcher experience with the various available anaerobic treatment systems, many of the above-mentioned reports are in fact highly specific. It is incorrect to generalize, but unfortunately this is frequent practice. In view of that the objective of this investigation was to assess the capability of the UASB-reactor system to handle high organic loading rates under conditions of high COD removal efficiencies using tapioca wastewater as feed.

6.5.1 Materials and Methods

Two series of experiments were carried out using septic tank sludge as seed sludge (See also Chapter 4). The details of operational conditions are mentioned in Table 4.7 and Table 4.9 and in a briefly in Table 6.10 and Table 6.11. The start-up of these UASB-reactors was made at a COD influent concentration of 1.500 mg/L. Six and nine levels of volumetric OLR were applied to the system by increasing the influent COD and/or influent flow rate progressively. The organic loadings were increased stepwise to minimize any impact on UASB performance, as would be the case with a sudden drastic increase in loading (the sudden increase in influent COD concentration is called shock loading, which we will investigate in Section 6.6). The experiment was carried out over 294 and 239 days for experiment 1 and experiment 2, respectively, and at ambient temperatures.

6.5.2 Results and Discussions

Results of the experiment are summarized in Table 6.7 and Table 6.8. They are also depicted in detail in Fig. 6.10.

Table 6.10 UASB-reactor operational conditions in experiment 1, with wastewater from household-scale factory with SS removal as pre-treatment step

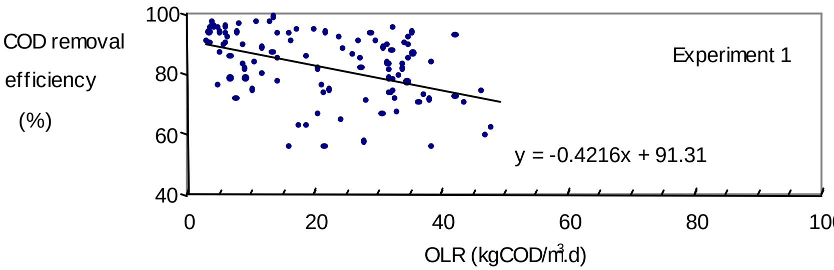
Para-meters	Units	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6
OLR	kgCOD/m^3.d	2.9-4.8	5.3-9.2	10.7-13.7	14.1-21.6	23.7-42.4	28.6-42.7
$COD_{tt,\ inf.}$	mg/l	1,426-1,817	2,384-3,389	4,748-5,751	6,590-7,654	11,200-12,400	9,211-9,500
HRT	h	9.0-11.0	9.0-12.6	10.1-11.2	9.4-12.0	8.3-8.4	6.2-6.3
Exp. Time	days (total)	27	39 (66)	27 (93)	72 (165)	105 (270)	24 (294)

Table 6.11 UASB-reactor operational conditions in experiment 2, with wastewater from large scale factory

Para-meters	Units	Period 1	Period 2	Period 3	Period 4	Period 5
OLR	kgCOD/m^3.d	2.1-4.1	3.5-8.8	6.5-11.0	9.8-15.7	13-25
$COD_{tt,\ inf.}$	mgO_2 /L	1,628-2,053	2,906-3,419	3,484-4,761	6,929-7,830	9,007-10,602
HRT	h	11.7-13.2	9.9-13.6	12.0-13.2	11.0-13.2	11.0-14.4
Exp. time	days (total)	11	17 (28)	14 (42)	26 (68)	48 (116)

Para-meters	Units	Period 6	Period 7	Period 8	Period 9	Period 10
OLR	kgCOD/m^3.d	23-38	34-42	38-56	56-101	36-108
$COD_{tt,\ inf.}$	mgO_2 /L	10,236-11,671	9,194-9,954	7,893-9,023	7,200-9,091	4,286-9,105
HRT	h	6.8-8.3	5.2-6.8	4.3-3.7	1.8-2.0	1.8-2.0
Exp. time	days (total)	32 (148)	22 (170)	21 (191)	18 (209)	30 (239)

The results clearly demonstrate that a stepwise increase in the UASB-reactor's OLR leads to a stable and quite satisfactory performance up to OLR's as high as 56 kgCOD/m^3.d, particularly in experiment 2. The performance remained quite stable and at a high treatment efficiency up to bout 40-50 kgCOD/m^3.d. In experiment 1 distinctly more fluctuations in the treatment efficiency manifested in the OLR-range up to that value and the treatment efficiency dropped off faster. The reason for this difference can be attributed to the origin of the influent (wastewater). Wastewater from large-scale is more stable in composition, such as with respect to the total COD, which ranged from 7,850-12,244 mg/L (experiment 2), while in experiment 1, where we used wastewater from the household-scale installations, the total COD concentrations ranged from 5,585-14,476 mg/L. Besides that, in the experiment 1, the UASB performance showed more fluctuations in the treatment efficiencies in comparison with experiment 2 (See Fig.4.6 and Fig 4.7). From the results obtained in this section no general relation between the OLRs and COD removal efficiencies can be established. Nevertheless, high treatment efficiencies were attained at high OLR-values following various successive stepwise increments of the OLR's to successively 3, 6, 10, 15, 20, 30, 40, 50 kgCOD/m^3.d and even higher in experiment 2. Once the UASB achieved a satisfactory steady performance at a certain imposed OLR, like the case in experiment 2, the OLR apparently can safely be elevated further. This gradual OLR increase under steady-state conditions clearly gives the UASB-reactor an excellent stability and operational reliability.



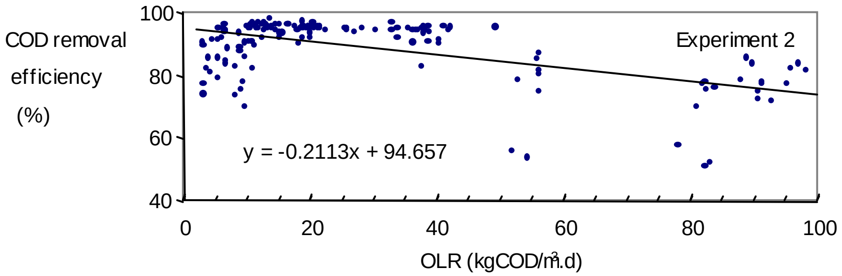


Fig. 6.10 Course of the COD treatment efficiency at different OLRs in experiment 1 and experiment 2.

6.6 THE EFFECT OF ORGANIC SHOCK LOADS ON UASB PERFORMANCE

Regarding the rather high variations in the COD concentration of tapioca wastewater, the stability of the UASB-reactor for imposed organic shock loads comprises one of the most important aspects of reactor design and operation. Organic shock loads can be divided into two categories: short-term lasting only for a few hours, or long-term, which stretches over days and even weeks before a reversion to the original operating conditions.

A number of researchers studied the effect of short-term and long-term organic shock loads on anaerobic reactors. Bello-Mendoza and Castillo-Rivera (1998) subjected an anaerobic hybrid reactor treating wastewater from a coffee-processing plant and operated at an OLR of 1.89 kgCOD/m^3.d to an OLR exceeding 2.4 kgCOD/m^3.d at an HRT of 22 h. Although this hardly can be designated as a shock load it resulted in deterioration in treatment efficiency, i.e., dropping from 77% to 25%, and in a 9-day reactor shutdown. After a feed interruption of 9 days, the reactor performance recovered. In this case obviously we are dealing with a system, which did not (yet) contain (or perhaps even is incapable to retain) a sufficient amount of viable sludge.

Similarly, using an 8.7-L UASB-reactor Eng et al. (1986) found that the sudden increase in influent COD concentration from 1g/L to 50; 14 and 12 g/L (by sucrose) in 3 days in each separate experiment resulted in a severe UASB performance upset, i.e., inhibition of methanogenesis, which led to an accumulation of lactate. Nachaiyasit and Stuckey (1997) found that the performance of an ABR (anaerobic baffled reactor) operated at 20 h HRT, 4 g/L COD, and 35^{o}C remained almost unaffected after the feed COD was increased instantaneously to 8 g/L COD for a period of 20 days. However, when the concentration was increased to 15 g/L (from 4 g/L) for a 20-day period, the treatment efficiency decreased slightly from 98% to 90%. The ABR system apparently prevents most of the biomass being exposed to low pH during shock loads and thus enhances reactor stability. Barnes et al. (1983) examined the stability of an anaerobic fluidized bed for shock loads when treating a high BOD synthetic feed applied over period of 1 h; they found a deterioration in effluent quality in terms of BOD and VFA concentrations. Studies of Leitao (2004) revealed that UASB-reactors comprise a robust system with regards to COD removal efficiency and pH stability when exposed to shock loads. They are robust regarding their ability to cope with a five-fold organic or a three-fold hydraulic shock loads lasting a period of 6 h. However the reactor-system cannot attenuate the imposed fluctuations in the influent COD.

In general the response of anaerobic processes to an organic shock loads will be reflected by: i) an increase in volatile fatty acids, ii) a decrease in COD removal efficiency, iii) a decrease in methane content, iv) a temporary higher effluent suspended solids concentration, v) an increased sludge volume index, and vi) a lower effluent (reactor medium) pH, i.e. depending on the buffer capacity of the influent and the system. The degree of deterioration in the performance depends on the duration and extent of the shock, the amount of active sludge present in the reactor system and – especially – the amount of active sludge which can be retained in the system during exposure to the shock, and on the rate of the microorganism's adaptability. Thus, the function of higher (viz. an excess of) viable biomass in an anaerobic reactor is usually to improve its stability rather than improve COD removal (Nachaiyasit and Stuckey, 1997).

6.6.1 Materials and Methods

The experimental reactors, the wastewater for experiment, the biomass, and the analytical procedures used in our experiments are described in Chapter 4. The term COD concentration presented in this section (6.6) refers to the COD_{total} concentration. The three UASB-reactors were initially started up at an applied 10 gVSS per litre of reactor, HRT of 12 h and a COD concentration of about 3,000 mg/L, which then was increased to 5,000 mg/L. The reactors were operated for 30 days with a feed COD ranging from 4,500 to 5,300 mg/L and an HRT of 12 h to provide a steady reactor performance for the purpose of the research. The feed used in the experiments consisted of raw tapioca wastewater. The amount of chemical for neutralization consumed is ranged from 1.8-2.1 gram NaOH and $NaHCO_3$ per liter of original wastewater with pH ranged from 3.7-4.5.

6.6.2 Results and Discussions

In the UASB-1 experiment, during the first imposed 24 h shock-load, the COD concentration was instantaneously increased from 5,250 mg/L to 13,055 mg/L, after which it was returned to

5,091 mg/L for several weeks to allow the reactor to recover completely. In our investigations, the period between the two experimental shock loads was 7 weeks, because of the high fluctuations in the COD concentration of the raw wastewater (we had to wait until we obtained a wastewater with a high COD concentration). In the second 24-h shock load the influent COD concentration was instantaneously increased from 3,541 mg/L to 14,822 mg/L. In the first imposed shock load, the COD concentration was increased from 5,253 to 13,055 mg/L. The bicarbonate alkalinity increased from 2,480 to 4,400 $mgCaCO_3/L$ due to the increasing of chemical neutralization. Similarly, in the second imposed shock load, the COD concentration was elevated from 3,541 to 14,822 mg/L and the bicarbonate alkalinity from 1,880 to 3,840 $mgCaCO_3/L$. The detailed experimental results are summarized in Table 6.12 and depicted in Fig. 6.11. They show that the response of the reactors was very similar in both events.

Table 6.12 Operational conditions used in 12-h HRT UASB-reactor shock loads

Reactor	**Influent total COD (mg/L)**			**Duration of shock load**
	Before shock load	**During shock load**	**After shock load**	
UASB 1				
- Experiment 1	5,253	13,055	5,091	24 h (short-term)
- Experiment 2	3,541	14,822	5,779	24 h (short-term)
UASB 2	4,712-5,369	12,697-14,330	4,469-5,885	5 days (longer-term)
UASB 3	4,712-5,369	12,697-14,330	9,400-11,800	5 days (longer-term)

Table 6.13 The imposed space loads and sludge loads before and after shock load

	Imposed Space loads ($kgCOD/m^3.d$)	**Imposed Sludge loads** (kgCOD/kgVSS.d)
Before shock	10.5-11.5	1.05-1.15
During shock	34-41	3.4-4.1
After shock	16	1.6

The experimental results indicate that during a sudden elevation of the influent COD the treatment efficiency in terms of COD drops quite significantly. This can be attributed to an imbalance in the metabolic rates of acid-forming and methane-forming bacteria, i.e. in fact a severe overloading of the retained sludge (regarding the imposed extremely high sludge loads). It results in a steep increase of the VFA-concentration; VFA are still rapidly produced by the acidogens during the shock, but the amount of methanogens present in the system obviously is far too small to accommodate that excess of substrate and accordingly the effluent pH declines, although not values such low that we face a serious inhibition of methanogenic bacteria. On the other hand the experimental results clearly show a distinct, in essence even serious drop in the biogas production, i.e., from 6.9 L/d to 2.1 L/d! This can merely be attributed to an inhibition effect of accumulated VFA. The complete recovery took 2-3 days, consequently was far from immediate.

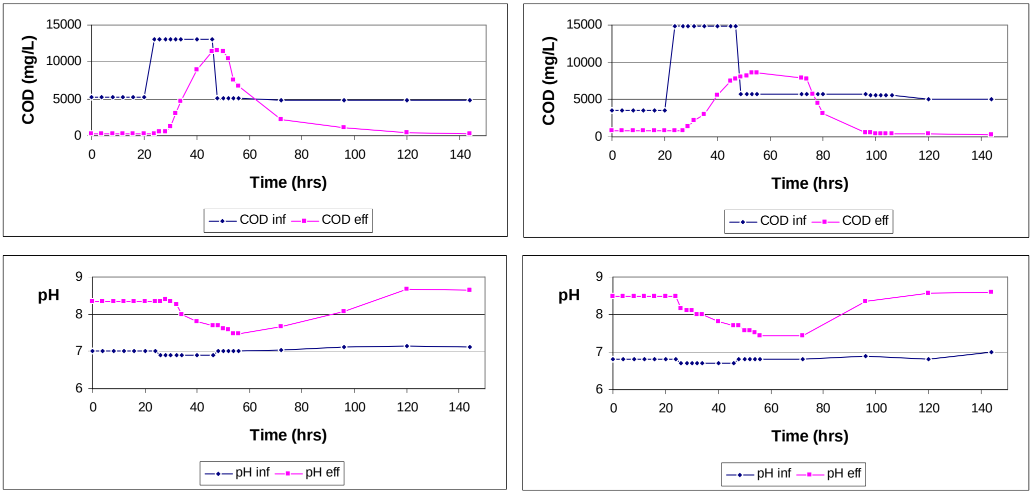


Fig. 6.11 The response of organic shock loads imposed on UASB-1 presented in terms of COD_{total} at HRT 12 h.

The results clearly demonstrate the capability of the UASB-system to withstand a quite heavy – in essence quite risky – organic COD shock load, viz. in the underlying case amounting to three times the original load. A severe and lasting upset in UASB performance did not manifest, but regarding the already high sludge load applied during the steady operation, we can conclude that the system was operated under fairly critical conditions. It in fact looks recommendable to operate the system on the basis of sludge load conditions, because it then surely will be capable to accommodate high organic shock loads. In the present case things could have gone seriously wrong, especially in case the shock would have been accompanied with heavy wash-out of viable sludge. According to Eng et al. (1986), but many other researcher deal this opinion, when viable bacteria remain retained in the reactor-system during such a heavy shock load and provided the pH will not drop into the acidic range, methanogens may resume their normal activity soon after the accumulated metabolites have been rinsed out of the system and the pH value has returned to optimal ranges.

The other two reactors, UASB-2 and UASB-3, were operated using the same amount of seed sludge and wastewater (see detail in Materials and Methods Section). The imposed organic shock lasted for 5 days, and here the space COD loads (consequently sludge loads) were also almost three times higher, i.e. the influent COD concentration was elevated from 4,884 mg/L to 14,330 mg/L, and then returned to 4,469-5,885 mg/L for UASB-2, and to 9,400-11,800 mg/L for UASB-3. The system here indeed was exposed to very critical conditions. The experimental results (see Fig. 6.12) reveal a serious drop in treatment efficiency; the complete recovery took a long period of time, i.e. 15-18 days after the feeding conditions had been returned to their original value. UASB-2 reached again a high treatment efficiency (in terms of COD), i.e. 91-93% after 18 days, with COD effluent values ranging from 582-792 mg/L. The UASB-3 also recovered, but under conditions of higher influent COD concentrations, consequently lower treatment efficiencies i.e., 83-89% after 20 days; after termination of the shock load the effluent

COD concentration attained values ranging from 1,152-1,240 mg/L. With UASB-3, we intended to apply a long-term shock load, but due to fluctuation of the COD concentration of raw wastewater from the factory we were unable to do this; 5 days after initiating the shock load, the influent COD dropped to 9,400-11,800 mg/L. In order to make the graphs more illustrative, in Fig. 6.12 merely the results obtained during the imposed shock load are depicted, not those of the period of steady operation during the pre-shock load. The details are shown in Fig. 6.12.

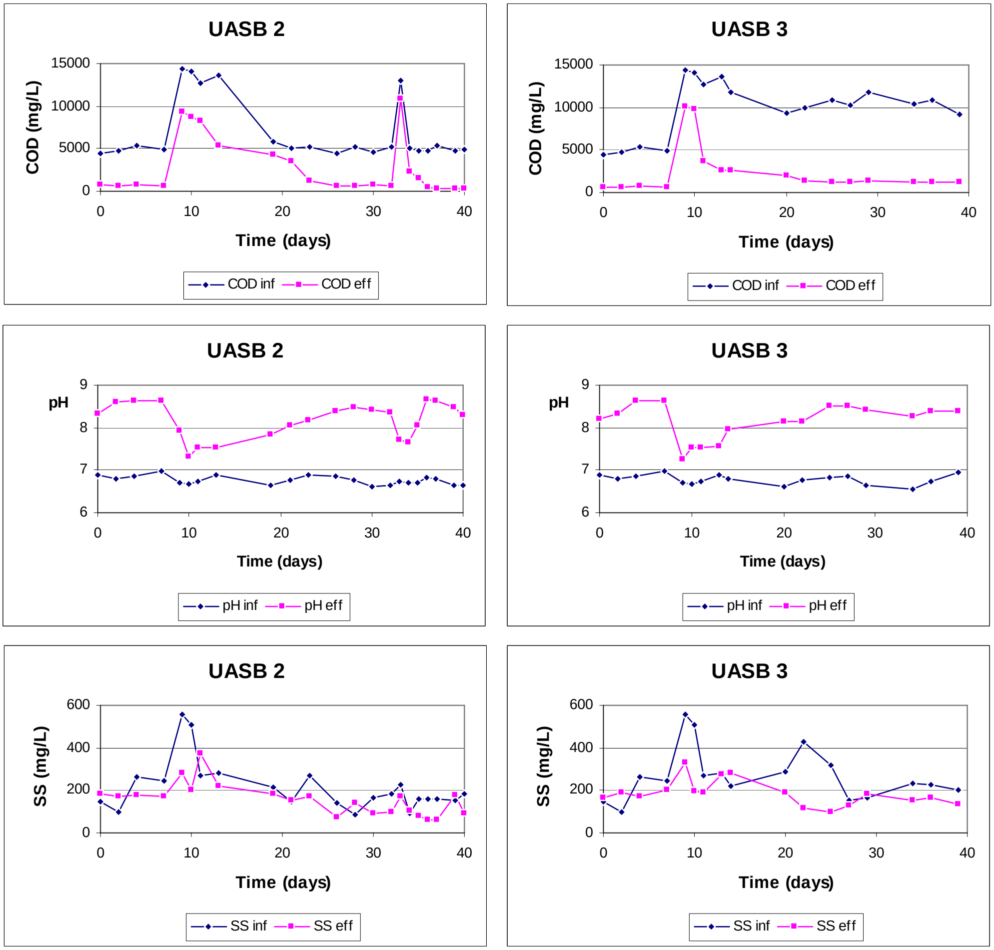


Fig. 6.12 Response of UASB-2 and UASB-3 reactors to long term (5 days) organic shock loads presented in total COD. Systems were operated at an HRT of 12 h. After the imposed shocks the influent COD were decreased to 4,469-5,885 mg/L and 9,400-11,800 mg/L in UASB-2 and UASB-3, respectively (Table 6.12).

The results obtained in UASB-3 demonstrate that the system is capable to accommodate a quite heavy a prolonged organic shock load of three times higher than the normal OLR (which already was 'critical in term of the imposed sludge load); the influent-COD was increased from 5,000 to 15,000 mg/L and the bicarbonate alkalinity from 1,880-2,160 $mgCaCO_3$/L up to 3,840 $mgCaCO_3$/L due to increasing chemical for neutralization, i.e. NaOH and $NaHCO_3$. Despite the heavy overloading of the system (i.e. of the sludge!) in fact a devastating upset did not manifest, although obviously the time needed for recovery became fairly long. It should be taken into account that during the whole recovery period in fact the treatment efficiency was far from optimal!!! The situation for UASB-reactor 2 was less positive, because the system here needed even more time to recover, despite the fact that after the shock load the influent COD was returned to the pre-shock value. The reason for the different responses of these reactors probably can be attributed to the lower sludge content of reactor 2 as compared to reactor 3. In almost all cases the effluent pH did not drop below 7.2; the bicarbonate buffer capacity in the UASB-reactors sufficed.

Sludge-washout temporarily manifested from the reactor only occurred part of the days during the shock load, but then soon the effluent SS concentration reached the same values as during the pre-shock load and even better. This phenomenon of the temporary sludge-washout generally can be attributed to the expansion of the sludge bed, likely due to the higher biogas production during shock loads. However, in our experiments, the biogas production always decreased during first day of imposed shock load after which it recovered stepwise.

6.7 CONCLUSIONS

Based on the experimental results presented in this chapter, it can conclude that UASB-reactors indeed are affected by changes in external factors, such as temperature, pH, available nutrients and trace elements, imposed OLRs, shock loads, viz.:

- An increase in temperature can affect the hydrolysis and acidification processes of tapioca processing wastewater. The calculated hydrolysis rate is 8 times higher at 30^{o}C than at 20^{o}C;
- A drop in the influent-pH can strongly affect UASB performance, because the optimum pH range for methanogensis 6.5-7.5. Therefore the process of methanogenesis can become inhibited at a lower pH, even as we found when the pH is around 6, consequently not really in the acidic range. The effect of the inhibition can become quite detrimental and lead to a serious drop in the COD removal efficiency and biogas production, even when the low-pH period lasts only 4h;
- In the case of tapioca processing wastewater, likely little if any nutrients and trace elements need to be supplied. The experimental results show that supply of nutrients merely is needed during the start-up of UASB-reactors, viz. to improve the treatment efficiencies and biogas production;
- The height of the OLR imposed to the system plays an important role, because it significantly can affect the microbial ecology and performance characteristics of the system. The results clearly show that a stepwise increase of OLR leads to a stable and quite satisfactory performance up to OLR's as high as 56 kgCOD/m^3.d. Once in the UASB a steady satisfactory performance at a certain imposed OLR is attained, the OLR can safely be elevated further stepwise. Such a stepwise gradual increase of the OLR under steady-

state conditions clearly gives the UASB-reactor an excellent stability and operational reliability. Fluctuations in wastewater compositions affect the UASB performance, because the balance between the various metabolic groups of microorganisms depends on the composition of the wastewater;

- The results of shock load clearly demonstrate that a high rate AnWT-system like a UASB-reactor represents a quite stable system; the system even is capable to recover from a serious overloading, although obviously during the period of severe overloading the treatment efficiency can drop seriously. Moreover the time of recovery is substantial, depending on the duration of the shock. It therefore is essential to take care for i) a sufficient buffer capacity, ii) prevention of severe overloading, i.e. especially sludge overloading (even in case of an excess of bicarbonate buffer capacity), iii) the influent strength and the applied OLR.

7

The Effect of Cyanide on the Hydrolysis and Acidification Processes Involving Tapioca Starch Particles

7.1 GENERAL INTRODUCTION

Cassava (*Manihot esculenta)* is a cyanogenic plant containing two cyanoglucosides: lotaustralin and linamarin (this being the major one). They are present in all of the plant tissues. Different cassava varieties also display wide variation in tuber linamarin content, i.e., in the range from 25-450 µg cyanide equivalent per gram (Elias et al., 1997). The roots are used during cassava starch production in tropical countries, and large amounts of cyanoglycosides are released and hydrolyzed, producing glucose, acetone, and cyanidric acid in equimolar quantities. This leads to cyanide concentrations in the wastewater ranging from 3-5 mgCN$^-$/L (Annachhatre, 1999), 10-30 mgCN$^-$/L (Mai et al., 2001), and to 200 mgCN$^-$/L (Siller, 1998). Since cyanide is a well-known metabolic inhibitor, cyanide-containing effluents cannot be discharged without sufficient detoxification. Swiss and German regulations place the limits for surface water at 0.01 ppm CN$^-$ and for sewers at 0.5 ppm CN$^-$. For fish, 0.1 ppm CN$^-$ has been given as an upper tolerance. As most microorganisms lose their biological activity at 0.3 ppm cyanide (Basheer et al., 1992; Connell and Miller, 1984), this can obviously cause severe problems for aerobic and anaerobic wastewater treatment. For the detoxification of cyanide, microbiological degradation may be a more elegant solution than chemical oxidation (Siller, 1998; Akcil et al., 2003; Luque-Almagro et al., 2005).

A large number of studies exist that deal with the aerobic cyanide degradation by pure cultures (Schygulla-Banek, 1993; White et al., 2000) and by activated sludge systems (Mudder, 1983; Richard and Shien, 1987; Wild et al., 1994; Zacharias, 1996). But the anaerobic degradation of cyanide has also been studied extensively. Siller and Winter (1998a,b) have reported the treatment of cyanide-containing wastewater from cassava processing in a laboratory-scale fixed-bed methanogenic reactor. The results show that for establishing a proper biofilm a start-up phase is required of about 6 months at a cyanide concentration of 10 mg/L. Cyanide could then be degraded up to a concentration of 150 mgCN$^-$/L at a hydraulic retention time of 3 days. The maximum cyanide space loading that could be maintained was 50 mgCN$^-$/L.day, while shock loading rates up to 75 mgCN$^-$/L.day could be well accommodated. Under steady-state conditions, the cyanide concentration of the effluent was below 0.5 mg/L. In another study, Siller and Winter (1998) reported the degradation of cyanide in an acidification reactor and in a single-step methane reactor by bacteria enriched from soil and cassava peels. A pre-acidification reactor was capable of removing up to 4 g CN$^-$/L of wastewater at a hydraulic retention time of 4 days, equivalent to a maximal cyanide space loading of 400 mgCN$^-$/L.day. The residual cyanide concentration was 0.2-0.5 mg/L. Rojas et al. (1999) investigated the effects of cyanide on methanogenic bacterial populations in continuous (UASB) and batch reactors. In those experiments, sucrose as a carbon source and potassium cyanide was used as a free cyanide source. The results show that a 0.96 mg/L concentration of cyanide caused a 50% inhibition of the methanogenic activity during the exposure stage, and 6.1 mgCN$^-$/L during the recovery stage in batch experiments. In continuous experiments using UASB-reactors, the cyanide concentration could be increased from 0.5 and 130 mgCN$^-$/L after the anaerobic sludge had become acclimatized. The hydraulic retention time remained constant at 12 h. Results indicate that while partial inhibition occurred at concentrations below 100 mgCN$^-$/L, severe inhibition manifested at 130 mgCN$^-$/L. In a similar study, Gijzen (2000) reported the effect of cyanide on anaerobic treatment. In his s experiments, a synthetic wastewater containing starch particles and volatile fatty acids was used as substrate. The acclimatization was achieved using an initial addition of cyanide at 5 mgCN$^-$/L at a hydraulic retention time of 12 h. Influent levels of cyanide were then gradually increased up to values of 125 $mgCN^-/L$. The results obtained show that the methane production and COD conversion temporarily decreased, while at the same time the CN^- levels in the effluent temporarily increased, i.e., directly after the cyanide concentration had been elevated. Sludge activity measurements demonstrated an increased tolerance against CN^-, once the sludge had been acclimatized. Annachhatre and Amatya (2000) studied the toxicity and anaerobic degradation of cyanide in batch reactors using serum bottles with granular sludge from UASB-reactor, and using a synthetic wastewater. The UASB-reactor was fed with synthetic wastewater containing cyanide and glucose at a COD loading rate of about 50 $kgCOD/m^3$.day. The activity of the sludge was 0.63 kgCOD/kgVSS.day. Under steady-state conditions of the UASB-reactor operation, samples of granular sludge were taken periodically to assess the effect of cyanide toxicity and biodegradability in a batch reactor. In the batch experiments, the sludge was exposed for 48 h to initial cyanide concentrations ranging from 1-100 mg/L. The results showed that the cyanide degradation rate increased along with the initial cyanide concentration in the solution of the batch reactor. A maximum cyanide degradation rate of 35-40 mg/L.day was recorded for initial cyanide concentrations of 100 mg/L. The methane production rate decreased with an increase in the initial cyanide concentration of the solution. A report by Oliveira et al. (2001a,b) dealt with a study on the biological treatment of wastewater from the cassava meal industry. As a pre-treatment, method flocculation and sedimentation with aluminium salts was employed, in order to reduce the organic matter from 14,000 to 2,000 mgCOD/L. This pre-treatment resulted in a cyanide concentration reduction from 400 to 18 $mgCN^-/L$. After biological treatment (a combined aerobic-anaerobic process), the COD and cyanide concentrations were 200 mgCOD/L and 0.020 $mgCN^-/L$, respectively. Another study was carried out in a continuous regime with wastewater from the cassava industry using a completely stirred tank reactor for the acidogenic phase and a hybrid reactor for the methanogenic phase at ambient temperatures (Paixao et al., 2000). The results indicated that the predominant end products of the acidogenic phase were propionic, n-butyric, and n-valeric acids, while the acidogenic biomass was composed of 95% fermentative bacilli, which was responsible for a 90% reduction in free cyanide. As expected, methanogenic bacteria dominated in the methanogenic phase, during which the cyanide concentration decreased further, from 5-30 $mgCN^-/L$ to 0.4-2.8 $mgCN^-/L$.

According to Elias et al., (1997), the active biomass decomposes linamarine to acetone, glucose, and cyanide by linamarase [Eq.(1)] and [Eq.(2)]. The cyanide is next converted directly to ammonia and formate or to formamide and then to ammonia and formate as [Eq.(3)] and [Eq.(4)] (Basheer et al., 1992; Annachhatre and Amornkaew, 2000). The main product of enzymatic decomposition by fungi is formamide (Knowles, 1986), but this compound could not be detected in the experiments described above.

$$\text{Linamarin} \xrightarrow{\textit{Linamarase}} \text{glucose} + \text{acetone cyanohydrin} \quad (1)$$

$$\text{Acetone cyanohydrin} \rightarrow \text{acetone} + \text{cyanide} \quad (2)$$

$$HCN + 2H_2O \rightarrow HCOO^- + NH_4^+ \quad (3)$$

$$HCN + H_2O \rightarrow \underset{\textit{Formamide}}{HCOONH_2} \rightarrow HCOO^- + NH_4^+ \quad (4)$$

The chemical formulas of Linamarin and Lotaustralin have been described by Elias et al. (1997) as follows:

Linamarin		Lotaustralin
CH_3		$CH_2 - CH_3$
|		|
$CH_3 - C - O -$ glucose	and	$CH_3 - C - O -$ glucose
|		|
CN		CN
Linamarin		**Lotaustralin**

Cyanide can form ionic complexes of varying stability with many metals, and most of these complexes are much less toxic than free cyanide. On the other hand, weak acid-dissociable complexes such as those of copper and zinc are relatively unstable and can easily release cyanide back into the environment. Iron-cyanide complexes are of particular importance due to the abundance of typically available iron in soils and to their extreme stability under most environmental conditions. The complexes of cyanide and iron such as $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ can be considered to be essentially non-toxic (Wild et al., 1994; APHA, 1995). However, iron cyanides are subject to photochemical decomposition and will release cyanide when exposed to ultraviolet light. Metal- cyanide complexes are also subject to other reactions that reduce cyanide concentrations in the environment (Wild et al., 1994; UNDP & ECME, 2005).

Although the effect of cyanide on anaerobic degradation processes has been investigated (as mentioned above), little if any work seems to have been done on the process of (anaerobic) hydrolysis and acidification, and particularly not on the effect of cyanide, even though, in practice, wastewaters are generally exposed to these processes during transport and storage. This obviously is the case when applying anaerobic treatment to these wastewaters. For this reason, also taking into account the subject's enormous scientific relevance, we decided to conduct experiments dealing with the effect of cyanide on the anaerobic processes of hydrolysis and acidification of tapioca starch particles. In our investigations we used batch reactors and as seed sludge we applied septic tank sludge. The objective of this study was to assess the effect of cyanide on the anaerobic hydrolysis and acidification of tapioca starch particles. To this end we attempted to assess the following: (i) the maximum hydrolysis rate and hydrolysis constant of starch particles at different concentrations of cyanide; (ii) the adaptation of bacteria to cyanide; (iii) the effects of cyanide (or toxicity of cyanide) in the anaerobic reactor.

7.2 MATERIALS AND METHODS

7.2.1 Experimental Conditions

The experiments were divided into two groups, with the first - including series (1), (2), (3) - carried out in the Sub-Department of Environmental Technology laboratory at Wageningen University (The Netherlands). This group of experiments focused on the effect of cyanide and sulphide on the hydrolysis process involving tapioca starch particles. The second group - series

(4) - was carried out in Vietnam in the CENTEMA laboratory, and focused on the effects of cyanide in the anaerobic batch reactors at ambient temperatures.

7.2.2 Batch Experimental Reactor

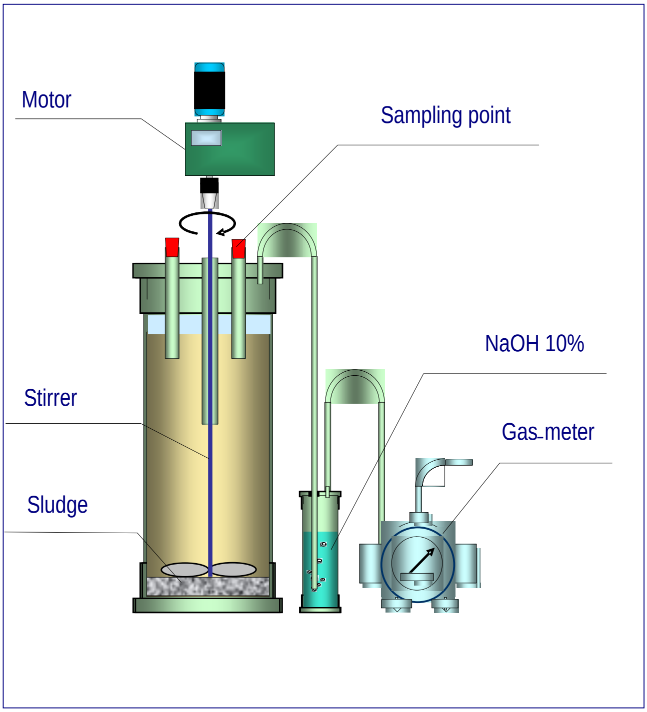


Fig. 7.1 Schematic of 5-L vessel for batch experiment.

In the experiments dealing with the effect of cyanide and sulphide on the hydrolysis and acidification of tapioca starch particles, the 1,250 ml serum bottles were inoculated with 500 ml of nutrients and trace elements solution, septic tank sludge (biomass) up to a final content of 2gVSS/L, and substrate at a concentration of 2,148 mg/L in terms of COD (corresponding to 2g/L of tapioca starch). Following that, the bottles were tightly sealed by means of an aluminium screw cap and butyl rubber septum in order to maintain anaerobic conditions. The biogas production was monitored by measuring the gas pressure using sampling with a syringe and a needle.

For the experiments dealing with the detoxicification of cyanide by supplying Fe^{2+}, 5,000 mL working volume acrylic vessels with a 155mm diameter were used (see Fig. 7.1). The reactors were supplied with nutrients, a trace element solution, and sludge (biomass) up to a final content of 2gVSS/L and 2,148 mg/L substrate in terms of COD (corresponding to 2g/L of tapioca starch). The biogas production was measured by a wet-test gas-meter (Meterfabriek, Schlummbergen). Other parameters were tested by sampling with a pipette through the hole in the cover.

The experiments dealing with the effect of cyanide and sulphide concentration on the anaerobic hydrolysis and the acidification of tapioca starch particles were performed in duplicate using serum bottles at a temperature of 30 ± 2^{o}C in three series. Together with those of the detoxification experiments involving cyanide with Fe^{2+}, the applied experimental conditions are presented in Table 7.1.

Table 7.1 Experimental conditions in four series dealing with the effect of cyanide on the hydrolysis and acidification processes of tapioca starch particles at a COD of 2,148 mg/L

Items	Unit	Effect of cyanide (1)	Effect of sulphide (2)	Effect of cyanide and sulphide (3)	Detoxicity of cyanide (4)
Sludge	mgVSS/L	2,000	2,000	2,000	2,000
$NaHCO_3$	mg/L	2,000	2,000	2,000	2,000
S^{2-}	mg/L	32	0-32-64	0-32	32
CN^-	mg/L	0-1-6-20-60-120	no	0-60	120
Fe^{2+}	mg/L	no	no	no	0-60-120

Note:

- *The experiments (1), (2), (3) are carried out in Wageningen University, the Netherlands, while experiment (4) is carried out in CENTEMA, Vietnam.*
- *The experiment without cyanide in series (1), without sulphide in series (2), without both cyanide and sulphide in series (3), and without Fe^{2+} in series (4) are used as CONTROL EXPERIMENTS.*
- *In each series, the additional experiments without substrate are used as BLANK.*
- *KCN chemical is used as stock solution (solution of 10 gCN^-/L).*

7.2.3 Substrate Characteristics

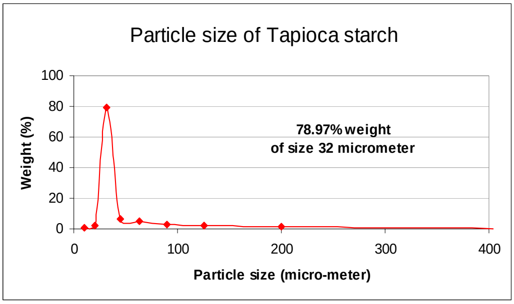


Fig. 7.2 Particle size distribution.

Dried tapioca starch taken from the Tan Chau factory in Vietnam was used as substrate. The particle size was determined by the sieving. The results of this particle size estimation are shown in Fig. 7.2. We estimated that 79% of the weight was distributed in a particle size range of 32-45 micrometer.

7.2.4 Biomass

Septic tank sludge taken from the Hoa Binh fertilizer factory in Vietnam was used in the experiments. The seed sludge characteristics are summarized in Table 7.2.

Table 7.2 Initial characteristics of seed sludge in the experiments

Items	**Unit**	**In series (1), (2), (3) (the Netherlands)**	**In series (4) (CENTEMA-Vietnam)**
Water content	%	91.2	89.9
TS	%	8.8	10.1
VSS/wet sludge	%	5.46	6.22
SMA	gCOD/gVSS.d	0.149 (at 30^{o}C)	0.089 (at ambient temp.)

7.2.5 Experimental Procedure

For the 1,250-ml serum bottle – carried out in Wageningen University, the Netherlands

a. Measuring the volume of each serum bottle using water and a 2 decimal balance;

b. Calculating the head space volume for each bottle;

c. Filling the 1,250-ml serum bottles with 500 ml of medium (use cylinder), including nutrients, trace elements, starch, sodium bicarbonate, cyanide, and sulphide (see Table 7.1);

d. Sealing the bottles with thick soft rubber stoppers and caps;

e. Flushing the bottles' head space with helium gas for 3 min;

f. Supplying 1 ml/L of Na_2S 1M - which is equivalent to 32 mgS^{2-}/L - to assure complete anaerobic conditions. (Na_2S 1M stock solution, fresh prepared);

g. After the addition of Na_2S, reducing pressure in the bottle to a level slightly above atmospheric pressure using a pressure meter and an extra needle;

h. Thereafter, bringing the temperature of the bottles to 30^{o}C under shaking at 50 rpm;

i. Starting from time zero and then 3 times per day, (start at 8.00 then 14.00 and 20.00), taking gas samples using a gas-tight syringe (100 μl) followed by liquid sampling (2.5 ml) of supernatants;

j. Analyzing gas samples using a GC on their H_2 and CH_4 content;

k. Centrifuging liquid samples at 10,000 rpm for 10 min, then supplying 0.20 ml of the supernatant with 0.80 ml formic acid (3%) to assess VFA - acetate, propionate, and butyrate using GC. A further 0.2 ml was supplied with 0.80 ml 0.5% sulphuric acid (for assessment of sucrose, glucose, pyruvate, lactate and formate. About 1.5 ml of the supernatant was filtered through a filter membrane (0.2 μm) for analyzing COD;

Based on the results, the data obtained in serum bottle experiments enabled us to assess a complete COD balance and to calculate the hydrolysis and acidogenesis rate.

For the 5-L vessel – carried out in CENTEMA, Vietnam

a. Measuring the volume of each vessel cylinder;

b. Filling the reactor to the 5-L mark, i.e., including nutrients, the supply of trace elements, starch, sodium bicarbonate, cyanide, Fe^{2+} (see Table 7.1), and tap water;

c. Sealing the vessels using a cover and screws (Fig. 7.3);

d. Supplying 1 ml/L of Na_2S 1M (equivalent to 32 mgS^{2-}/L) to assure completely anaerobic conditions (Na_2S 1M stock solution, fresh prepared);
e. Exposing the reactor at ambient temperatures (during the experiment, the temperature ranged from 28-34^oC);
f. Intermittently mixing for 1 min every 3 min, with a stirrer speed of 100 rpm;
g. Taking samples daily from the vessel reactors to assess the concentration of VFA, CN^-, COD soluble, and SS, as well as the pH. In these experiments, VFA was analyzed by the distillation and titration method, CN^- was analyzed by the distillation (Fig. 7.4) and colorimetric method ;
   + Cyanide soluble (CN_{sol}) and also cyanide absorbed into the sludge (CN_{abs}) was analyzed to assess the effect of cyanide in the process;
   + Calculation: CN_{tt}, added = CN_{sol} + CN_{abs} + CN_{deg}

     Where CN_{tt}*, added* = *cyanide total added at the beginning*

     CN_{sol} = *cyanide soluble*

     CN_{abs} = *cyanide absorbed on sludge*

     CN_{deg} = *cyanide degraded*

7.2.6 Analytical Methods

Methane was determined using a Gas Chromatograph (GC-Hewlett Packard 5890) equipped with a 2m x 2mm stainless steel column packed with Poropack Q (80 to 100 mesh). The temperatures of the column, injection port, and flame ionization detector (FID) were 60, 200, and 220^oC, respectively. Argon was used as the carrier gas at a flow of 45 ml/min.

Hydrogen was determined using the same GC with a thermal conductivity detector and a molecular sieve 25H (60-80 mesh). The column size was 1.5m x 6.4mm. The temperatures of the column, injection port, and thermal conductivity detector were 40, 110, and 125^oC, respectively.

Sugar (including sucrose, glucose, pyruvate, lactate, and formate) was measured by High Performance Liquid Chromatograph (HPLC) equipped with an organic acids column (ion 300), using a Refractive Index detector (RI). The temperature of the column was 20^oC. H_2SO_4 at 1.25 mM was used as a carrier phase at a flow rate of 0.5 ml/min.

VFA was determined in centrifuged samples (10,000 rpm in 10 min) by gas chromatography (Hewlett Packard 5890A) equipped with a 2m x 2mm (inner diameter) glass column and packed with Speck port (100-120 mesh) coated with 10% Fluorad FC 431. The temperatures of the column, injection port, and flame ionization detector were 130, 200, and 280^oC, respectively. N_2 saturated with formic acid at 20^oC was used as a carrier gas at a flow of 30 ml/min.

All the other parameters were assessed following the methods as described in APHA (1995). The dissolved COD was analyzed from membrane filtered samples (0.2 µm) using the closed reflux-colorimetric. Cyanide was analyzed using total cyanide after distillation.

Fig. 7.3 5-L vessels in the experiments

Fig. 7.4 Cyanide distillation apparatus.

7.2.7 Calculations

a. Raw samples were used to assess total COD (COD_t);

b. Paper-filtered samples were used to assess paper-filtered COD (COD_{pf});

c. Membrane-filtered samples were used to assess the dissolved COD (COD_{dis});

d. Suspended COD was calculated using the equation: $COD_{ss} = (COD_t - COD_{pf})$;

e. Colloidal COD was calculated using the equation: $COD_{col} = (COD_{pf} - COD_{dis})$;

f. The viable biomass-COD production was calculated using the equation: COD-biomass = acido-biomass COD + methano-biomass COD

Where: *Acido-biomass COD = (cumulated methane + produced VFA) * 0.196*
*Methano-bimass COD = cumulated methane * 0.028*

g. **COD-SS remain** = COD_{tt}, added - (produced COD_{dis} + cum-methane + COD-biomass)

h. **COD-acid** = COD-VFA+ COD-CH_4 + COD-biomass+ COD-lactic acid+ COD-formic acid

In all cases, the results of a blank sample were taken into account, which implies that the final result was the difference between the sample and the blank. All results presented in this report were final. From the results of the measurements and calculations, we obtained the curves of COD-dissolved, COD-CH_4, COD-H_2, COD-biomass, COD-VFA, and COD-SS_{remain} versus time. From the curves of COD-SS_{remain}, we calculated the hydrolysis rate, maximum hydrolysis rate, and specific hydrolysis rate. From the curves of COD-acid, we then calculated the acidification rate, maximum acidification rate, and specific acidification rate.

+ From the slope of the COD-SSremain curve versus time, we calculated the hydrolysis rate. In practice, the results of the COD-SSremain curve versus time is a curve, and the straight line that best fits the data was calculated by using the least squares method.
+ From the slope of the steepest part of the COD-SS remain curve versus time, we obtained the maximum hydrolysis rate.
+ From the quotient of maximum hydrolysis rate with the amount of biomass in the experiments, we obtained the specific hydrolysis rate.

Similar calculations were used to determine the acidification rate; we obtained the maximum acidification rate from the COD-acid curve.

7.3 RESULTS AND DISCUSSIONS

Along with the presentation we'll discuss the results of inhibition/toxicity experiments for cyanide and sulphide when present solely and in mixture this paragraph.

7.3.1 Effect of Cyanide Concentration on The Hydrolysis Process Involving Tapioca Starch Particles

These experiments are – as far as we could trace in literature rather unique, particularly wit respect to the effect of cyanide and sulphide on the processes of hydrolysis and acidogenesis. So far very little attention has been afforded to occurrence of inhibition on hydrolysis. As a matter of fact our studies are still firstly preliminary, the main objective in fact was to assess whether or not the process of hydrolysis is amenable for inhibition since it in essence is an enzymatic process. On the basis of the experimental data obtained, the hydrolysis rate is calculated for the various experimental conditions investigated. The results of these calculations are summarized in Table 7.3. The hydrolysis of tapioca starch particles was assessed on the basis of the concentration of particles remaining at time t in the experimental bottles, calculated as $COD\text{-}SS_{remain}$. Fig. 7.5 presents the $COD\text{-}SS_{remain}$ versus the time at the different applied concentrations of cyanide. The experiment without cyanide (0 $mgCN^-/L$) was used as the control.

It is very clear, and in fact surprising, that cyanide exerts such a strong detrimental effects on the rate of the hydrolysis process, particularly at concentrations exceeding 6 mg/l. The anaerobic degradation of starch particles only proceeds once the bacteria acclimatized to CN^- and/or if this compound can be degraded in some manner. As mentioned in the introductory section of this chapter, certain micro-organisms are indeed capable of converting cyanide to carbon dioxide and ammonia (Knowles et al., 1998), while others can adapt to grow in the presence of cyanide; they achieve this either by inducing synthesis of enzymes needed for the degradation of cyanide or by synthesizing cyanide-resistant enzymes (Amornkaew, 1999). The (partial) elimination of cyanide leads accordingly to reduced toxicity, e.g., to a partial or (ultimately) even completes detoxification. The results in Fig. 7.5 clearly demonstrate that the effect of cyanide on the hydrolysis of starch particles is relatively small at cyanide concentrations below 6 mg/L, although the curves clearly deviate from the control curve. But at cyanide concentrations of 20, 60, and 120 mg/L the detrimental effect of CN^- is quite significant. At concentrations of 20 and 60 $mgCN^-/L$ a lag phase of 1-1.5 days manifests, during this period bacteria either adapts to or they degrade the cyanide according to the reaction equation (2) and (3). First, the $COD\text{-}SS_{remain}$ only dropped slightly, but thereafter the hydrolysis apparently reaches a maximum, as can be concluded by the steep part of the curves. Our experimental results did not allow us to draw a conclusion about the exact mechanism. Regarding the rather preliminary character of our present investigations, but considering the quite strong affect of cyanide obviously more detailed studies should be conducted on this matter in the near future.

Table 7.3 Calculated results of the hydrolysis process involving tapioca starch particles at different concentrations of cyanide with 2g starch particles and 2 gVSS/L. The values presented are average; the standard deviation is in brackets

CN^- concentration (mg/L)	Hydrolysis rate (mgCOD/L.d)	Maximum hydrolysis rate (mgCOD/L.d)	Hydrolysis Constant (1/day)	Specific hydrolysis rate (gCOD/gVSS.d)
0	430 (4)	1,332 (9)	1.31 (0.02)	0.666 (0.004)
1	389 (7)	1,167 (10)	1.05 (0.01)	0.584 (0.005)
6	398 (6)	1,116 (2)	0.98 (0.02)	0.558 (0.001)
20	479 (9)	1,042 (16)	0.65 (0.08)	0.521 (0.008)
60	438 (15)	614 (14)	0.56 (0.06)	0.307 (0.007)
120	297 (26)	606 (61)	0.33 (0.17)	0.303 (0.031)
20 – 2nd feed	435 (57)	1,166 (15)	1.00 (0.25)	0.583 (0.007)
60 – 2nd feed	219 (61)	528 (93)	0.21 (0.06)	0.264 (0.064)

The results of the calculated maximum hydrolysis rate and hydrolysis constant are depicted in Fig. 7.6 and Fig. 7.7. The maximum hydrolysis rate in all instances was calculated from the highest slope.

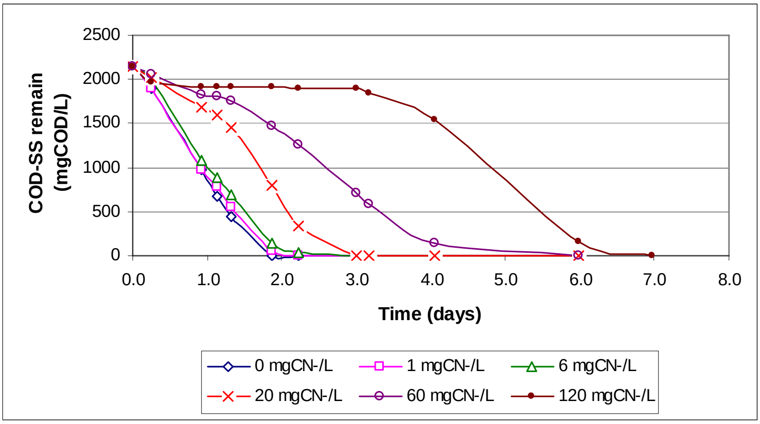


Fig. 7.5 COD-SS remaining at time t for the different concentrations of cyanide.

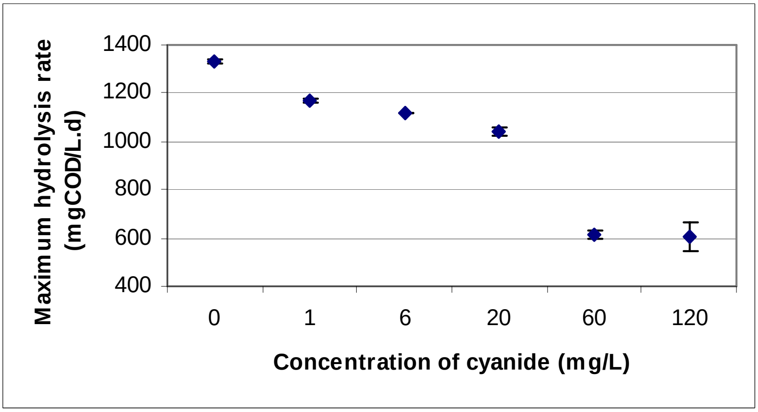


Fig. 7.6 Course of the calculated maximum hydrolysis rate in relation to the applied cyanide concentrations.

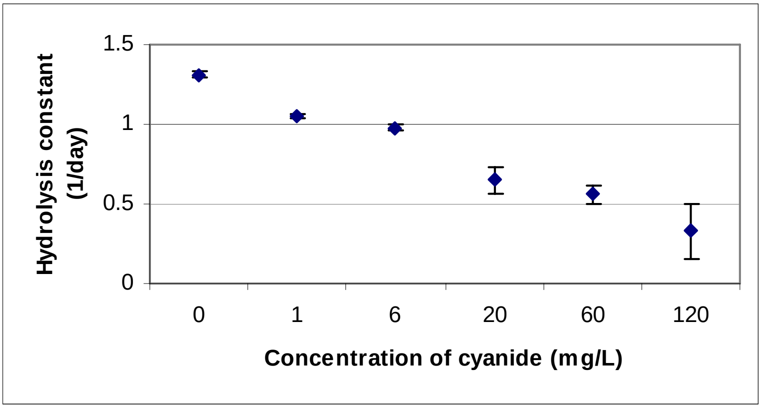


Fig. 7.7 Course of the calculated hydrolysis constants in relation to the applied cyanide concentrations.

The assessed maximum hydrolysis rate and hydrolysis constant of tapioca starch particles for the control experiment were 1,332 mgCOD/L.d and 1.31 day^{-1}, respectively. Due to the strong inhibitory effect of CN^-, the assessed maximum hydrolysis rate and hydrolysis constant for the experiment with 120 $mgCN^-/L$ were much lower with values of 606 mgCOD/L.d and 0.33 day^{-1}, respectively.

The maximum acidification rate amounted to 1,452 mgCOD/L.d for the control experiment, but it dropped at increasing cyanide concentrations, i.e., to 1,174, 1,197, 1,017, and 852 mgCOD/L at 1, 6, 20, and 60 $mgCN^-/L$ respectively. For the 120 $mgCN^-/L$ experiment, a higher value was found for the maximum acidification rate with 916 mgCOD/L, but it should be taken into account that the lag phase much longer, i.e., of 4 days instead of a few hrs up to one day in the experiments with no or relatively low initial cyanide concentrations (see Fig. 7.8).

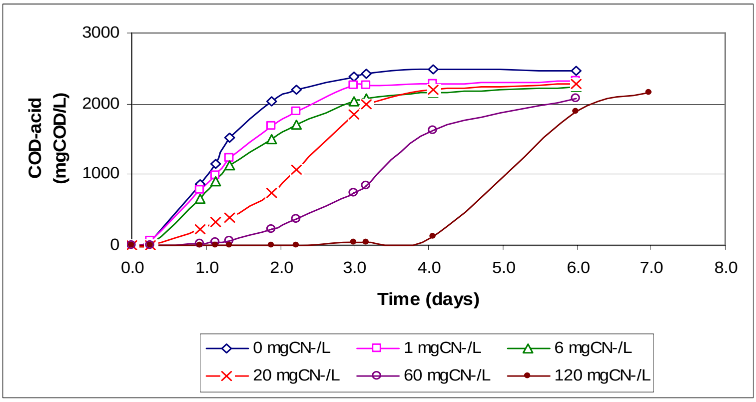


Fig. 7.8 COD-acid at time t for the different concentrations of cyanide.

Results of methane production measurements (Fig 7.9) show that a higher initial cyanide concentration leads to lower methane generation. The big differences between the curves in Fig. 7.9 reveal that the process of methanogenesis is heavily affected by cyanide, even at a concentration of 1 $mgCN^{-}/L$.

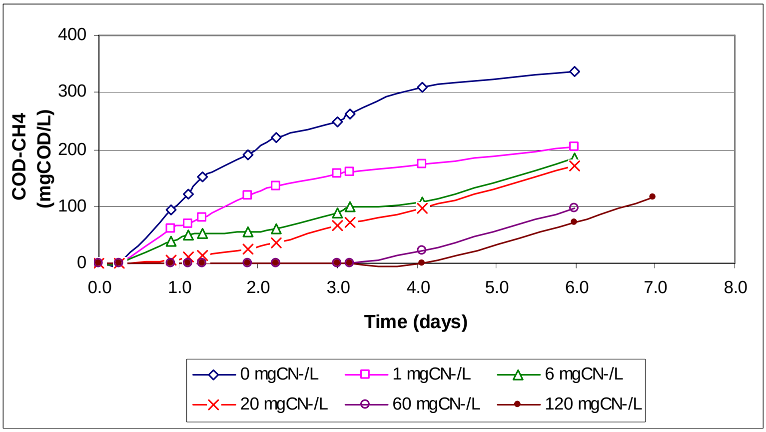


Fig. 7.9 Accumulated methane in relation to the imposed cyanide concentration.

To examine the capacity of bacteria to adapt to cyanide, we exposed it to a concentration of 20 and 60 $mgCN^{-}/L$ -, and then gave it a second feed at the same concentration. The experimental results shown in Fig. 7.10 clearly reveal that the bacteria adapt in the case of cyanide concentrations of 20 $mgCN^{-}/L$ but not at 60 $mgCN^{-}/L$.

In the experiment involving a concentration of 20 $mgCN^{-}/L$, the recovery of hydrolysis occurred very quickly during the second feed. The COD-dissolved and COD-VFA values were much higher than in the first feed. However, this was not the case at a concentration of 60 mgCN⁻/L, because then the recovery proceeded very slowly, i.e., taking about 8-10 days. The results also indicate that the values of COD-dissolved and COD-VFA in the first feed were more stable than in the second. The curves of the first feed were smooth, whereas they fluctuated considerably in the second. This can perhaps be attributed to an accumulation of cyanide on the biomass layer, leading to a decreased stability of the hydrolysis process.

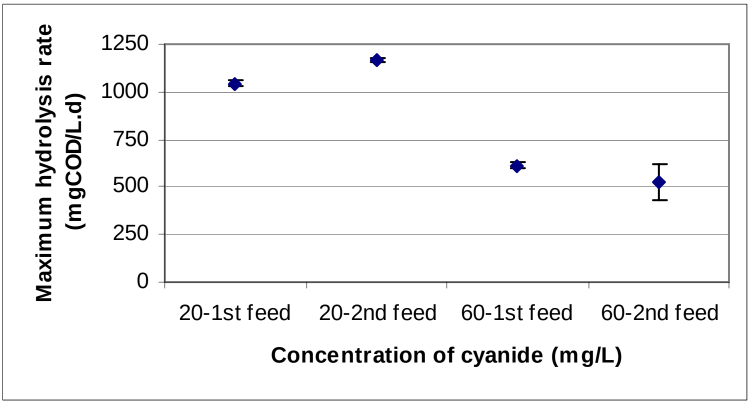


Fig 7.10 Difference in maximum hydrolysis rate between the first and second feed.

7.3.2 Effect of Sulphide (as total sulphide) on The Hydrolysis Process Involving Starch Particles

An additional experiment we conducted dealt with the effect of sulphide on the hydrolysis and acidification processes of starch particles (Fig. 7.10). The assays were prepared according to the procedure as described for the cyanide experiments, except that no cyanide was supplied.

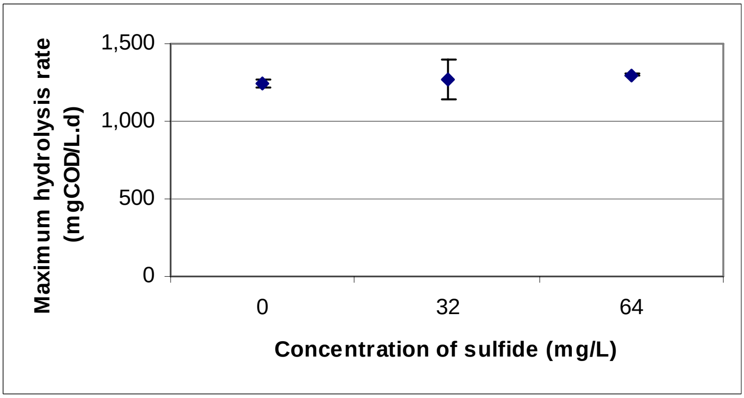


Fig. 7.11 Calculated maximum hydrolysis rate of starch particles at different sulphide concentrations.

The experimental results show that up to concentrations of 64 mgS^{2-}/L any clear detrimental effect on the various distinct process steps is absent. The assessed maximum hydrolysis rate and maximum acidification rate with an initial sulphide concentration of 0, 32, and 64 mgS^{2-}/L were almost the same (See Fig. 7.11). More details are summarized in Table 7.4.

Table 7.4 Calculated results of the hydrolysis process of starch particles at different concentrations of sulphide only, and of sulphide + cyanide, found with 2g starch particles and 2 gVSS/L. The values presented are average; the standard deviation is in brackets

Sulfide only S^{2-} (mg/L)	**Hydrolysis rate (mgCOD/L.d)**	**Maximum hydrolysis rate (mgCOD/L.d)**	**Hydrolysis constant (1/day)**	**Specific Hydrolysis rate (gCOD/gVSS.d)**
0	690 (8)	1,242 (28)	1.37 (0.01)	0.261 (0.014)
32	672 (7)	1,270 (123)	1.27 (0.01)	0.635 (0.061)
64	683 (3)	1,300 (2)	1.33 (0.04)	0.650 (0.010)
CN^- & S^{2-} (mg/L)				
CN=0 S=0	690 (8)	1,242 (28)	1.37 (0.01)	0.261 (0.014)
CN=0 S=32	430 (4)	1,332 (9)	1.31 (0.02)	0.666 (0.004)
CN=60 S=0	488 (13)	927 (6)	1.18 (0.02)	0.464 (0.003)
CN=60 S=32	438 (15)	614 (14)	0.56 (0.06)	0.307 (0.007)

Certain literature indicates that sulphide might be capable of quickly converting cyanide (CN^-) into thiocyanate (SCN^-), a compound that is much less toxic and also more environmentally acceptable than cyanide (Ganczarczyk et al., 1985; APHA, 1995). Moreover, thiocyanate can be used by microorganisms as a source of nitrogen and carbon (Goncalves et al., 1998) for growth. For this reason we conducted a further experiment dealing with the effect of sulphide on the toxicity of cyanide. These experiments were performed in the same manner, with 60 mg/L cyanide and with and without sulphide (32 mgS^{2-}/L). The results of the experiment obtained without sulphide and cyanide (control experiment), with only sulphide (32 mg/L), with only cyanide (60 mg/L) and with both sulphide and cyanide are illustrated in Fig. 7.12.

The results of the experiment conducted with merely sulphide are very similar to those of the control experiment; sulphide was seen to have little if any effect. Surprisingly, however, in the presence of cyanide, sulphide seems to reinforce the toxicity, i.e. it exerts a synergistic effect. Apparently the conversion of cyanide to thiocyanate did not occur (or not sufficiently quickly) because then the toxicity of cyanide would have become lower.

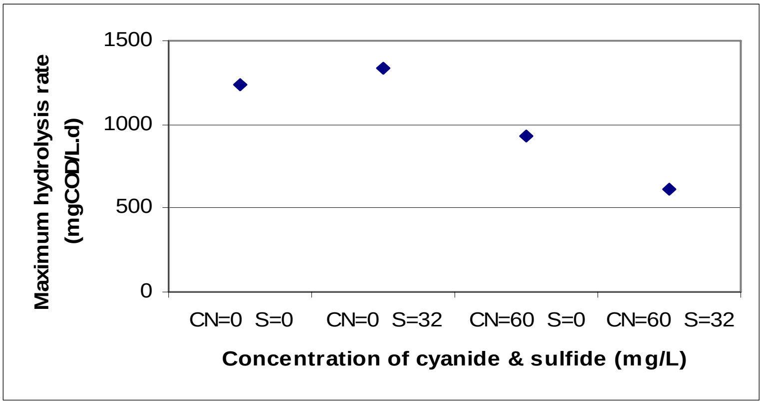


Fig. 7.12 Maximum hydrolysis rate found at different cyanide and sulphide concentrations.

7.3.3 Reduction of Cyanide Toxicity by The Fe^{2+} Compound

Our additional complementary experiment involved assessing the effect of cyanide in the anaerobic degradation of starch particles. The results obtained at a cyanide concentration of 119 mg/L and at a Fe^{2+}-concentration varying from 0, 60 and 120 mg/L demonstrate that ferro-ions did not affect the degradation of cyanide in the solution, but they could reduce the toxicity of cyanide, as they increased the rate of substrate degradation. In our laboratory conditions, the methane gas and sugar concentration were not analyzed. Thus, we did not calculate the hydrolysis and acidification rates, but simply focused on the course of the cyanide during the experiment.

The cyanide measurement concerned the total amount of cyanide, i.e., including all free cyanide, all dissociable cyanide complexes, and all heavy-metal cyanide, with the exception of cyanate (CNO^-) and thiocyanate (SCN^-). The total cyanide measurement was carried out with a raw sample and a filtration sample. In this way, we could calculate the cyanide absorption into the sludge.

Experimental results dealing with the effect of cyanide in the absence of additional ferro-ions (Fig. 7.13) showed that after day 17 the degradation of cyanide (CN_{deg}) amounted to only 48 mg/L of a total of 119 mg/L cyanide added. However, the amount of soluble cyanide (CN_{sol}) decreased gradually. Combining these results with those in Section 7.3.1, we can conclude that the lag phase (2-6 days) during the hydrolysis and acidification processes in the presence of different concentrations of cyanide likely is mainly spent to the adaptation of bacteria. Cyanide decomposition occurred only to a minor extent.

A comparison of the results in Fig. 7.13, Fig. 7.14, and Fig. 7.15 shows that the addition of ferro-ions increased the absorption of cyanide complexes (in the form of ferro-cyanide $[Fe(CN)_6]^{4-}$) into the sludge, but it did not stimulate the degradation of cyanide compounds.

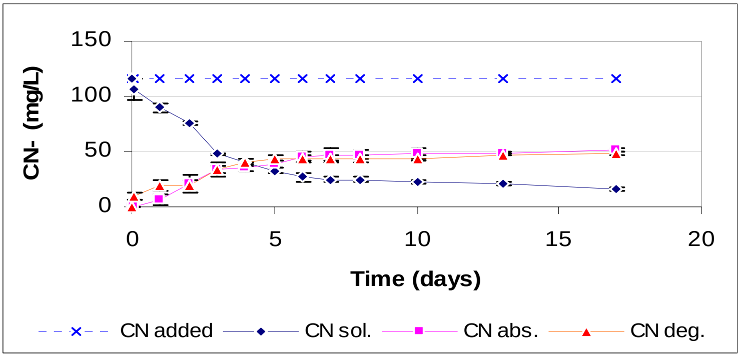


Fig. 7.13 Course of the cyanide concentration and calculated amounts of absorbed and degraded cyanide during the period when no ferrous-ions were supplied.

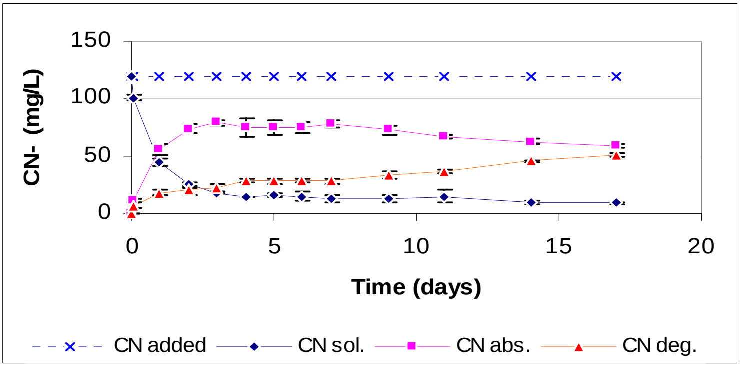


Fig. 7.14 Course of the cyanide concentration and calculated amounts of absorbed and degraded cyanide during the period when 60 mg/L Fe^{2+} was supplied.

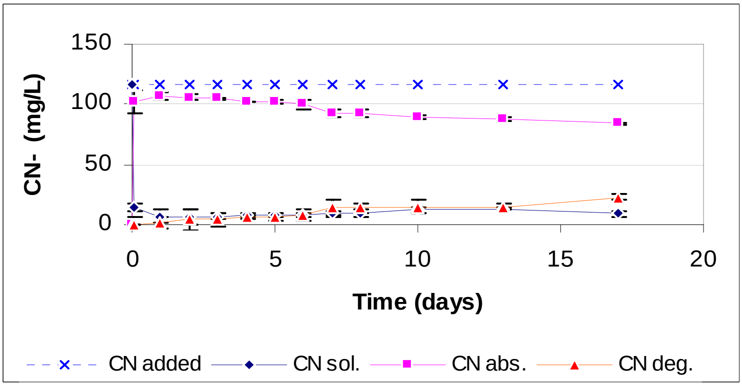


Fig. 7.15 Course of the cyanide concentration and calculated amounts of absorbed and degraded cyanide during the period when 120 mg/L Fe^{2+} supplied.

According to Luque-Almagro et al. (2005), the iron complexes are extremely stable; for this reason they are much less toxic, but with respect to degradation also much more recalcitrant. Compared to the control experiment without ferro-ions added at 48 mg/L, after 17 days of exposure to anaerobic conditions at a cyanide concentration of 119 mg/L, the amount of cyanide degraded (CN_{deg}) amounted to 51 and 23 mg/L in the experiment with 60 and 120 $mgFe^{2+}/L$ supplied respectively. In addition, the cyanide absorption (CN_{abs}) increased steeply when ferro-ions were added; the higher the amount of ferro-ions supplied, the higher the CN_{abs} increase.

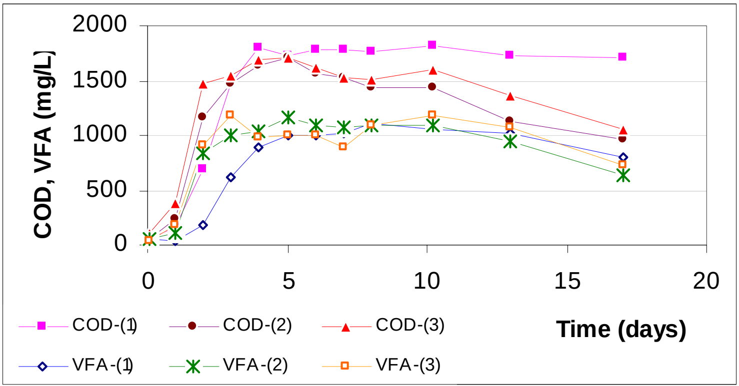


Fig. 7.16 Course of the concentration of COD-dissolved and VFA during the experiment. (average values): (1) without Fe^{2+} added, (2) Fe^{2+} = 60 mg/L, (3) Fe^{2+} = 120 mg/L.

The experiment was carried out with 2g tapioca starch particles, corresponding to 2,148 mg COD/L; 119 $mgCN^{-}/L$ was added together with different concentrations of ferrous-ions. The experimental result shows that the course of the VFA-concentration remained the same with or without ferro-ions. However, the COD-dissolved concentration decreased significantly in the presence of ferro-ions, i.e., from 1,716 mg/L to 960-1,047 mg/L at day 17, although the ferro-ion concentration seems to affect the VFA values much less. They remained almost the same, i.e., 1,047 and 960 mg/L in the case of 60 and 120 $mgFe^{2+}/L$, respectively. This means that a certain amount of COD-dissolved had been converted to VFA and the end-product methane. Apparently the presence of Fe^{2+} reduced the toxicity of cyanide on methanogenic bacteria.

The curves of COD-dissolved and VFA in this experiment show that the lag phase lasted only one day, while the same experiment with 120 $mgCN^{-}/L$ carried out in a laboratory at 30°C in the Netherlands (Section 7.3.1) gave a 4-day lag phase. This was surprising, since the operational conditions were almost identical, apart from the ambient temperature, which in Vietnam was 28-34°C. A 1,250-mL (with 500 mL medium solution) serum bottle was used in Wageningen (The Netherlands), while in Vietnam a 5 L vessel was used; the samples were exposed to 50 rpm shaking instead of stirring inside the reactors at 100 rpm (intermittent 1-min mixing for each 3 min). On comparing the curve of COD-dissolved with 120 $mgCN^{-}/L$ with the curve of COD-dissolved with 20 $mgCN^{-}/L$ found under Vietnamese conditions, it appears that they almost coincide. Our experimental results don't allow yet drawing a conclusion about this difference in the results.

7.4 CONCLUSIONS

The following conclusions can be drawn from the our investigations:

- Cyanide exerts a distinct toxicity, in particular on the hydrolysis process of tapioca starch particles. Hence, hydrolysis of these particles was completed within 2 days in the control experiment (using 2g starch particles and 2 gVSS/L in the experiment conducted at 30oC), while at a high cyanide concentration of 120 mgCN-/L it took up to 6 days;
- Compared to the hydrolysis process, the acidification process is much less affected by cyanide; acidification always proceeded immediately after hydrolysis of the starch particles;
- The adaptation of bacteria to cyanide proceeds well in the second feed at a cyanide concentration of 20 mg/L, but distinctly less well at 60 mg/L;
- Like the hydrolysis step, also the methanogenesis step is strongly affected by cyanide, even at a concentration of 1 $mgCN^-/L$;
- Sulphide concentrations lower than 64 mg/L (as total sulphide) do not affect the hydrolysis process;
- Sulphide ions do not reduce the toxicity of cyanide through the formation of thiocyanate, but instead reinforce the toxicity of cyanide;
- The prevalence of lag phase due to the presence of cyanide on the hydrolysis and acidification process is probably due to bacteria adaptation as well as to cyanide degradation;
- The addition of Fe^{2+} significantly reduces the toxicity of cyanide on the hydrolysis and methanogenesis through the formation of the ferro-cyanide complex, but it does not stimulate the degradation of cyanide.

8

Summary, Conclusion and Recommendation

8.1 THE NECESSARY

Agro-industries play a major role in the world's economy. At the same time, they are major contributors to worldwide industrial pollution problems, especially in Asian countries. Agro-industries use a variety of raw materials. Wastewater generated from the processing of these raw materials generally varies significantly during the year, both in quantity and characteristics. In the framework of this thesis, the tapioca processing industry was studied. The main sources of wastewater from this industry originate from the settling or the centrifugation stage of the production process of tapioca. The specific flow-rate ranges from 3 - 5 cubic meters per ton of fresh cassava root. About 1 ton of starch can be produced per 3.5 - 4.0 tons of fresh cassava root, and therefore a factory with a capacity of 100 tons starch discharges 1,200-2,000 cubic meters of wastewater per day. The wastewater originating from household-scale factories is almost completely discharged untreated into rivers or lakes, while using a series of anaerobic and facultative ponds generally treats that from large-scale factories. However, with this technology it is impossible to meet the prevailing discharge standards in Vietnam. For Tay Ninh province with the total capacity of approximately 6,580 tons of fresh roots per day (at a crop) an amount of 30,000 cubic meters of wastewater is released everyday, which results in a serious environmental deterioration and water resources. Treatment of these wastewaters prior to discharge obviously is of urgent concern of the Government manager staffs.

8.2 THE ACHIEVEMENTS

Wastewater from tapioca processing factories are high in COD (7,000-41,500 mg/L), BOD (6,200-23,000 mg/L) and SS (500-8,600 mg/L), their pH is low with values in the range 4.2-5.7 while the content of the highly toxic CN^- is high with values of 19-96 mg/l. The anaerobic biodegradability of raw tapioca wastewater is excellent, viz. between 92.3 – 93.3 %, and of pre-settled tapioca wastewater even higher, i.e. 94.6 – 94.7 %. Therefore this treatment biotechnology was selected for lab-scale investigations as main treatment step with an Anaerobic Upflow Filter (UAF) as pre-treatment step for reducing the SS content of the raw wastewater (influent). The core of the treatment system is – as mentioned above - a high rate anaerobic wastewater treatment (AnWT) step – using UASB-reactor, because it is capable to remove major part of organic pollutants. As post-treatment finally an aerobic (aeration tank) and/or aquatic pond system will be used in order to eliminate the remaining organic pollutants, nitrogen compounds and phosphorus. The experimental results obtained in our investigations are briefly presented as below:

8.2.1 Study on Appropriate Technology for Treatment of Tapioca Processing Wastewater

Based on the results reported in Chapter 3, Chapter 4 and Chapter 5, it can be demontrated that the proposed technology is well feasible for treatment of tapioca processing wastewater.

The experimental results of the investigations carried out with UAF-reactor show that the main mechanisms of SS removal in the UAF-reactor are sedimentation, entrapment and sorption, and straining through the filter media. The studies in Chapter 3 reveal that UAF-reactors packed with RPF, PPF, and PW filter material give high treatment efficiencies, i.e., 68-85%, 64-74%, 75-83%, respectively, resulting in a SS reduction in the raw wastewater from 900-1,183 mg/L to 180-352 mg/L. For Vietnamese conditions the PW filter material is most suitable for application in view of its low price and high availability.

Experimental results in Chapter 4 clearly show that the best procedure for UASB reactor start-up is maintaining an influent COD concentration around 1,500mg/L and a HRT 8-10 h, because a high COD treatment efficiency of 93-96% can then be attained within only 13 weeks at a maximum OLR of 13-25 kg COD/m^3.d. An OLR up to 56 kgCOD/m^3.d (even up to 80 kgCOD/m^3.d) can be applied in UASB systems with tapioca processing wastewater at a high treatment efficiency of 82-93%. The results of our investigations also demonstrate that septic tank sludge appears to be a proper seed sludge in Vietnamese conditions. The first granules using this seed sludge were visible at day 20-26 of the operation at an OLR of 6 kgCOD/m^3.d. After about 300 days of operation the observed differences in COD removal efficiency between UASB-reactors operated with UAF-effluent (as SS removal step) and the original wastewater were marginal, indicating that the effect of suspended solids on UASB performance is insignificant, i.e. even at the influent SS values up to 1,100-1,800 mg/L. The UAF-reactor therefore mainly implies a useful optional unit in the system when the original wastewater contains a very high SS-content.

Although the UASB reactors gave excellent treatment efficiencies, COD effluent values below 300 mg/L at steady operation could not be obtained in any of our experiments. In order to meet prevailing Vietnamese standards for UASB effluent discharge, therefore some form of post-treatment is required. The combination of a UASB reactor system, an activated sludge reactor and stabilization ponds were shown to represent an excellent solution for the treatment of high-strength wastewaters like tapioca processing wastewater.

Application of the activated sludge process as post-treatment step for the UASB effluent indeed gives high COD removal efficiencies, i.e. 96.4-97.4%, which comprises a very high overall treatment efficiency for the total system. However, in view of the severe Vietnamese standards this still would not be enough and therefore following post-treatment with an activated sludge process a further polishing step with stabilization ponds was studied. This system consisted of an algae pond followed by a water hyacinth pond. This combined system gave the required overall removal efficiency of COD, SS and nutrients. With a total HRT of 13-15 days for the stabilization ponds system, comprising a surface-loading rate up to 111-265 kg COD/ha.d, an effluent COD concentration was reached of 36-58 mg/l. In addition to the exceptionally high COD removal, also the total nitrogen and phosphorus concentrations are reduced significantly. This ensures that the effluent complies with the Vietnamese industrial wastewater discharge standards - B level (details are presented in the Appendix).

8.2.2 Factors Affecting The UASB Performance

Based on the experimental results presented in Chapter 6, it is clear that UASB-reactors are affected by changes in external factors such as temperature, pH, available nutrients and trace elements, imposed OLRs and shock loads. When UASB-reactors are exposed to changing operational conditions, generally the response of the system is an incomplete methanogenesis, which results in a drop in pH, in biogas production, COD removal efficiency and an increase sludge washout.

A drop of the influent pH value can strongly adversely affect the UASB performance when it results in a lower reactor pH, because the methanogens have an optimum pH within the range of 6.5-7.5. Consequently an AnWT-system can become inhibited at lower pH-values. This even can be the case when the pH is not really very low, e.g. pH around 6. Our results indicate that such pH-values - around 6.10 - can be quite detrimental, because we found a serious drop in the COD removal efficiency and biogas production, even though the period only lasted 4h. This is a surprising new observation.

In anaerobic treatment nutrients and trace elements are essential ingredients for the metabolic activity and microbial growth. Our experimental results show that in case of tapioca wastewater, nutrients – including N, P, and also trace elements: Fe, Zn, Mn, Mo, Co, Ni, Se… - need to be supplied merely during the start-up of the UASB-reactors in order to improve the treatment efficiencies and biogas production.

The imposed OLR plays an important role; it significantly affects the microbial ecology and characteristics of the system. The results clearly show that a stepwise increase of the OLR leads to a stable and quite satisfactory performance up to values as high as 56 kgCOD/m^3.d. Once the system reached a steady satisfactory performance at a certain imposed OLR, the OLR can safely be elevated further.

The results of shock load experiments with 2-3 times higher than normal OLR (short-term: 24 h and long-term: 5 days) demonstrate that a high rate AnWT-system like a UASB-reactor indeed comprises a quite stable system; it even is capable to recover from a serious overloading (in case of UASB-3, the imposed shock load was 5 days, with influent COD concentrations 3 times higher than normal – from 4,884 mg/L to 14,330 mg/L - and then kept high influent COD concentrations in range of 9,400-11,800 mg/L) , although during periods of severe overloading the treatment efficiency may decline seriously and then the period of time for complete recovery can be substantial, depending on the duration of the shock.

8.2.3 Cyanide Toxicity on Hydrolysis and Acidification Processes of Tapioca Starch Particles

The cyanide concentration in tapioca processing wastewater ranges from 19 – 96 mg/L, with typical values between 22 – 34 mg/L. At these concentrations the performance of UASB-reactors remained almost completely unaffected, while the effluent cyanide concentrations were always below 1 mgCN^-/L.

Experiments to study CN^- toxicity on the hydrolysis of tapioca starch particles reveal a distinct toxicity of cyanide. In the control experiment (using 2g starch particles and 2 gVSS/L in the experiment conducted at 30^{o}C) the hydrolysis of these particles was complete within 2 days, while at a high cyanide concentration of 120 mgCN^-/L it took up to 6 days. The adaptation of bacteria to cyanide proceeds well in the second feed at a cyanide concentration of 20 mg/L, but is distinctly poorer at 60 mg/L. The prevalence of lag phase due to the presence of cyanide on the hydrolysis and acidification processes probably due to bacteria adaptation as well as to cyanide degradation.

Sulphide ions – lower than 64 mg/L – do not reduce the toxicity of cyanide (through the formation of thiocyanate), but instead they reinforce the toxicity. However addition of Fe^{2+}

significantly reduces the cyanide toxicity, both on the hydrolysis and methanogenesis process through the formation of the ferro-cyanide complex. However, it does not stimulate the degradation of cyanide.

8.3 THE APPROPRIATE TECHNOLOGY FOR TREATMENT OF TAPIOCA WASTEWATER

Conventional treatment technologies do not provide a sustainable solution for wastewater treatment and management in developing countries like Vietnam. Based on the quite satisfactory experimental results obtained with anaerobic treatment of tapioca wastewater under laboratory conditions, the following combined treatment system for the full treatment of tapioca wastewater is proposed (see Fig. 8.1)

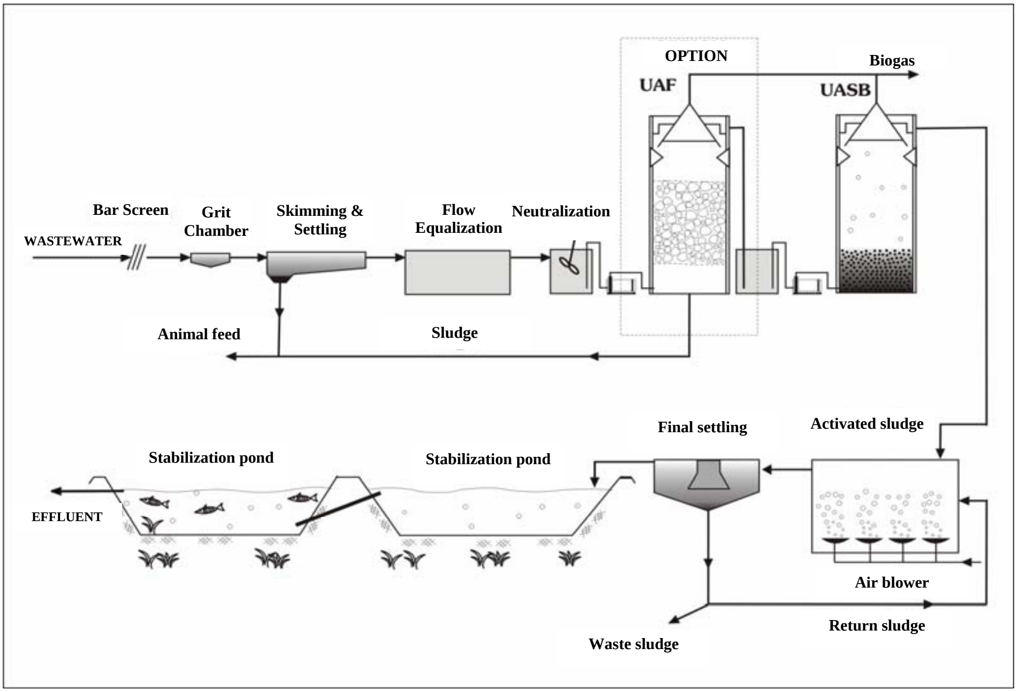


Fig 8.1 Approriate technology for treatment of tapioca processing wastewater.

The AnWT step offers numerous important advantages, including the absence of extensive electricity requirements, the production of useful energy carrier in the form of biogas, a very substantial reduction in land area requirements for subsequent treatment step, e.g. pond systems. On the other hand – in fact well known - an AnWT-system produces an effluent with a still relatively high concentration of organic pollutants. For that reason, a post-treatment using an activated sludge system followed by a facultative pond system can be used to reduce the organic matter concentration down to levels below the Vietnamese effluent discharge standard

(B-level) for discharge of industrial wastewater. The aerobic (or micro-aerobic) step serves as a means to reduce offensive smell and to prevent pollution of ground water resources just maturation ponds are needed (if at all), the use of the anaerobic ponds can be completely omitted. The UAF-pre-treatment step included in the proposed concept is just an option, because our experimental results clearly demonstrated the absence of any seriously detrimental effect of suspended solids on UASB performance during 300 days of operation.

A pilot-plant scale version of this technology-concept with a capacity of 10 m^3/d has already been designed and installed (but without UAF-reactor). The system start-up was commenced in the middle of February 2006 at KMC Tapioca Starch Factory, Binh Phuoc Province. After 73 days of operation, the UASB-reactor in the system is operating already at an OLR of 6.2 – 7.4 kgCOD/m^3.d, and the results show a relatively good performance. The COD concentration decreases from 3,020 – 3,660 mg/L to 620 – 1,040 mg/L, i.e. giving a COD removal efficiency in the range of 72 – 82%. The performance data collection show that the biogas production fluctuates from 260 – 350 liter per kilogram COD removal. This amount is measured after biogas passed through an alkaline solution to remove CO_2 and H_2S. The exact composition of the gas could not be analyzed. A successful application of this treatment system can contribute significantly to a further sustainable development of the tapioca processing industry in Vietnam by minimizing the environmental pollution.

8.4 ADVANTAGE OF BIOGAS RECOVERY

As mentioned in Chapter 1, at present in Vietnam, almost all tapioca processing factories treat their wastewater in a series of stabilization pond system. A pond system requires a vast area of land and furthermore it wastes a valuable energy resource. As a matter of fact a pond system – despite the fact that they have been applied for years – is a poorly understood off-site outdated technology. Several of the early ponds installed in the past have become anaerobic and release large quantities of methane, consequently apart from the fact that energy is wasted huge amounts of greenhouse gases into atmosphere. Besides, these designed (poorly understood) ponds release bad smell and they frequently lead to ground water pollution. Moreover, when applying merely stabilization pond systems generally the effluent the severe Vietnamese industrial wastewater discharge standards cannot be met.

With the technology proposed in Section 8.3 above, energy can be recovered in the form of biogas. For a wastewater flow-rate of around 2,000 m^3/d and wastewater COD-concentration ranging from 10,000-15,000 mg/L, the estimated output for the amounts biogas recovered of tapioca processing factory with capacity of 100-120 tons starch per day are summarized in Table 8.1. Such a factory consumes an average amount of energy of approximately 53,000 MJ for electrical - and 160,000 MJ 75% for thermal energy -, which is equivalent to 3,000-3,600 L of fossil oil (FO) per day. This energy is required to dry the starch, viz. reducing its moisture content from 40-60% to 11-13% for bagging and shipment.

Table 8.1 The estimated output for biogas recovery from tapioca wastewater

	Items	Influent UASB	Effluent UASB
1.	Flow-rate	2,000 m^3/d	2,000 m^3/d
2.	COD concentration of WW	10 – 15 kg/m^3	3.0 – 4.5 kg/m^3
3.	Average biogas production per 1 m^3 wastewater (Based on pilot-scale data)		2.1 – 3.1 m^3
4.	Methane content		> 60%
5.	Total amount of biogas produced per day		4,200 – 6,200 m^3/d
6.	Total amount of energy equivalent (1m^3 biogas with 60% CH_4 # 26 MJ)		109,200 – 161,200 MJ/d
7.	Total amount of FO equivalent		2,600 – 3,838 L FO/d
8.	Saving energy cost (0.33 US$/L FO)		858 – 1,266 US$/d
9.	Emission reductions eCO_2 per day		34.44 – 50.78 tons/d
10.	Emission reductions eCO_2 per year		12,054 – 17,773 tons/year
11.	Benefit equivalent (10-20 US$ per ton of eCO_2 emission reduction)		120,000 – 355,000 US$/year

The estimate shows that the required treatment system with a capacity of 2,000 m^3/d will produce 4,200 – 6,200 m^3 biogas per day (>60 % methane gas), which is equivalent to 2,600 – 3,800 liters of FO per day. And energy cost savings to the plant are estimated at 850 – 1,260 US$ per day. If 1 m^3 biogas (with 50% methane) is equal to 1.7 kWh of electricity (data from the power plant using biogas of Go Cat landfill, HCMC, Vietnam), then the power plant can generate 7,100 – 10,500 kWh per day.

The proposed wastewater treatment system combined with energy recovery can also benefit from international carbon trading and help support financing projects through the Clean Development Mechanism (CDM). Or the project can sell Certified Emissions Reduction credits under the Kyoto Protocol’s proposed CDM. In this project – based on converting wastewater to energy and profit - both the technology and the business model are highly possibility.

This solution, comprising the implementation of the AnWT-technology combined with aerobic post-treatment, clearly demonstrates the big benefit of the energy cost savings and resource conservation together with its feasibility to meet really extremely severe discharge standards. It also shows how strong returns can be generated for investors using CDM.

8.5 RECOMMENDED SUSTAINABLE DEVELOPMENT FOR TAPIOCA PROCESSING INDUSTRY

Based on the results of our research, we can recommend an almost perfect wastewater treatment system for the tapioca industry for Vietnam, but not merely Vietnamese conditions. It combines pollution prevention with energy recovery and resource protection. With the proposed integrated treatment system, which incorporates waste minimization and reuse of valuable compounds from the 'waste', a sustainable development of the tapioca industry can be achieved. Waste and wastewater can therefore really comprise a resource instead of a headache. The treated wastewater can be reused in aquaculture or for irrigation in the area. Peel waste can be used for composting, and the compost produced can be applied for the cassava cultivation or other industrial crops. Fibrous residues can be used for animal feed production. In this way, an (zero waste) industrial ecosystem can be created (see Fig. 8.2).

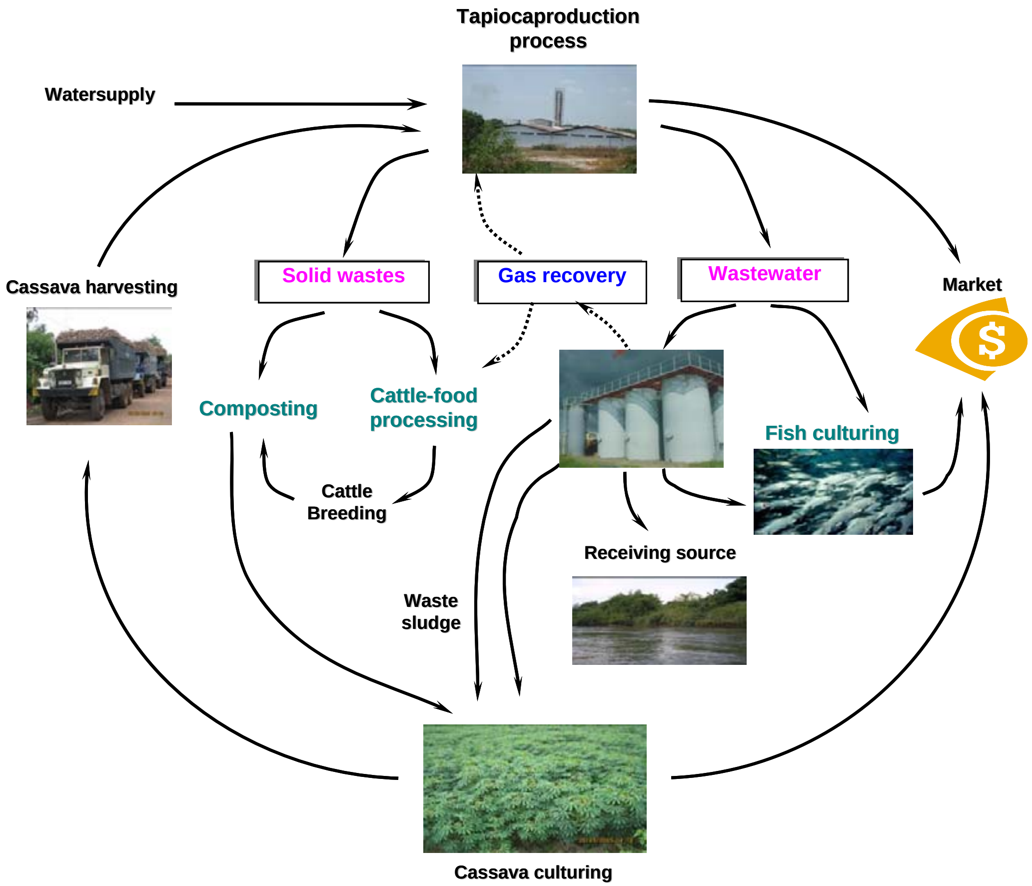


Fig. 8.2 Recommended sustainable development for tapioca processing industry.

8

Samenvatting, Conclusies en Aanbevelingen

8.1 DE VEREISTEN

De agro-industrie speelt een belangrijke rol in de wereld economie, maar draagt daarnaast wezenlijk bij aan de industriële vervuilingproblemen in de hele wereld, vooral in Aziatische landen. De agro-industrie gebruikt een verscheidenheid aan ruwe grondstoffen en de hoeveelheid afvalwater gegenereerd bij de verwerking van deze grondstoffen wisselt in het algemeen aanzienlijk in de loop van het jaar, zowel qua hoeveelheid als eigenschappen. In het kader van dit proefschrift is de tapiocaverwerkingsindustrie onderwerp van studie geweest.

De belangrijkste bronnen van afvalwater die bij deze industrie vrijkomen zijn afkomstig van de bezinkings- of centrifugeerfase van het tapiocaproductieproces. De specifieke afvalstroom varieert van 3 tot 5 kubieke meter per ton verse maniokwortels. Uit 3,5–4,0 ton verse maniokwortels kan één ton zetmeel worden geproduceerd. Daardoor loost een fabriek met een capaciteit van 100 ton zetmeel per dag 1200–2000 kubieke meter afvalwater per dag. Het afvalwater dat van de familie-schaal fabriekjes vrijkomt wordt vrijwel geheel geloosd in rivieren of meren, terwijl bij grote fabrieken het in het algemeen wordt behandeld in een vijversystemen bestaande uit anaërobe en facultatieve vijvers. Met deze methode is het echter onmogelijk aan de Vietnamese lozingsnormen op B-niveau te voldoen. Voor de provincie Tay Ninh, met een totale productiecapaciteit van ongeveer 6580 ton verse wortels per dag (tijdens oogsttijd), komt dagelijks 30.000 kubieke meter afvalwater vrij, hetgeenbij lozing resulteert in een ernstige achteruitgang van het milieu en van waterbronnen. Het is duidelijk dat de behandeling van dit afvalwater alvorens het wordt geloosd een eerste prioriteit voor het overheidsmanagement vormt.

8.2 DE PRESTATIES

De vervuiling van het afvalwater van tapiocaverwerkingsfabrieken is hoog, t.w. COD :7000–41.500 mg/l, BOD: 6200–23.000 mg/len SS: 500–8600 mg/l; de pH van het afvalwater is laag: 4,2–5,7 en het bevat een hoog gehalte aan het zeer giftige CN^- (19–96 mg/l). De anaërobe biologische afbreekbaarheid van ruw tapioca-afvalwater is uitstekend (92,3–93,3%), en voor voorbezonken tapioca-afvalwater ligt dit nog hoger (94,6–94,7%). Daarom is deze biotechnologische behandelingswijze uitgekozen als de belangrijkste behandelingsstap voor onderzoek op een laboratoriumschaal, waarbij een Anaerobic Upflow Filter (UAF) werd gebruikt als een voorbehandelingstap om het gehalte aan SS van de (binnenstromende) ruwe afvalwater terug te dringen. De kern van het behandelingssysteem is behandeling met hoge snelheid van het afvalwater met anaërobe bacteriën (AnWT) met behulp van een UASB-reactor omdat die het mogelijk maakt de meeste organische verontreiniging te verwijderen. Ten slotte werd een aëroob (beluchtingstank) systeem en/of een watervijver gebruikt om de resterende organische verontreiniging, stikstofverbindingen en fosfor te verwijderen. De experimentele resultaten van ons onderzoek worden hierna samengevat.

8.2.1 Een haalbare behandelingstechnologie voor het afvalwater afkomstig van tapiocaverwerking

Op basis van de resultaten beschreven in de hoofdstukken 3, 4 en 5 kan worden geconcludeerd dat de voorgestelde technologie zeer bruikbaar is voor de behandeling van afvalwater afkomstig van tapiocaverwerking.

De resultaten van het onderzoek met de UAF-reactor laten zien dat de belangrijkste mechanismen voor de verwijdering van SS met de UAF-reactor berusten op bezinking, invangen en adsorptie, alsmede afvangst in de filtermedia. Het onderzoek beschreven in hoofdstuk 3 wijst uit dat UAF-reactors gevuld met RPF, PPF en PW filtermateriaal een hoge behandelingsefficiëntie geven, namelijk respectievelijk 68–85%, 64–74% en 75–83%, waardoor de hoeveelheid SS in het ruwe afvalwater wordt teruggebracht van 900–1183 mg/l tot 180–352 mg/l. Onder de Vietnamese omstandigheden is het PW filtermateriaal het geschiktst voor toepassing vanwege de lage prijs en ruime beschikbaarheid van dit materiaal.

De experimentele resultaten beschreven in hoofdstuk 3 laten duidelijk zien dat een UASB-reactor het best kan worden opgestart bij een influent COD-concentratie rond 1500 mg/l en een HRT (hydraulische retentietijd) van 8–10 uur, omdat zo een hoge efficiëntie bij de behandeling van COD kan worden bereikt van 93–96% binnen een periode van slechts 13 weken bij aan maximale OVB (orgnische volumebelasting) van 13–25 kg COD/m^3.d. Een OVB tot 56 kg COD/m^3.d (en zelfs tot 80 kg COD/m^3.d) kan worden toegepast in UASB-systemen met afvalwater uit de tapiocaverwerking met een hoge behandelingsefficiëntie 82–93%. Onze onderzoeksresultaten laten zien dat slib afkomstig uit een septic tank onder de omstandigheden in Vietnam een uitstekend entmateriaal is. De eerste korrels in dit entslib werden zichtbaar na 20–36 dagen continue bedrijf bij een OVB van 6 kg COD/m^3.d. Na ongeveer 300 dagen waren de waargenomen verschillen in efficiëntie tussen UASB-reactors werkend met UAF-effluent (toegepast voor de verwijdering van SS) en het oorspronkelijke afvalwater marginaal, wat erop wijst dat het effect van gesuspendeerde vaste stoffen op de prestaties van de UASB-reactor niet significant is, zelfs bij waarden voor instromende SS tot 1100–1800 mg/l. Daarom is de UAF-reactor een bruikbare optionele eenheid in het systeem, vooral als het oorspronkelijke afvalwater een hoog SS-gehalte heeft.

Hoewel de UASB-reactors een uitstekende behandelingsefficiëntie lieten zien kon in geen enkel experiment een effluent-COD-waarde lager dan 300 mg/l worden bereikt bij continue operatie. Daarom is hoe dan ook nabehandeling nodig om aan de Vietnamese normen voor lozing van UASB-effluent te kunnen voldoen. De combinatie van een UASB-reactor met actief slibsysteem en stabilisatievijvers bleek een uitstekende oplossing te zijn voor de behandeling van sterk vervuild afvalwater zoals dat bij tapiocaverwerking.

Toepassing van het proces met het aërobe actief slibproces als nabehandelingstap voor UASB-effluent geeft inderdaad een hoge efficiëntie ten aanzien van de verwijdering van COD (96,4–97,4%); dit betekent dat aldus een zeer hoge behandelingsefficiëntie voor het gehele systeem wortd bereikt, maar gezien de uiterst strenge Vietnamese lozingsnormen zou dit echter nog niet genoeg zijn. Daarom is een extra nabehandeling met stabilisatievijvers als polishingstap van het effluent van actief slib onderzocht. Dit systeem bestond uit een algenvijver gevolgd door een waterhyacint. Met dit gecombineerde systeem werd de vereiste totale efficiëntie voor verwijdering van COD, SS en voedingsstoffen bereikt. Met een totale HRT van 13–15 dagen voor het systeem met stabilisatievijvers, dat werd geopereerd bij een oppervlaktebelasting tot 111–265 kg COD/ha.d, werd een COD-concentratie in effluent van 36–58 mg/l bereikt. Naast de uitzonderlijk hoge COD-verwijdering werd ook de concentratie aan totaal stikstof en fosfor significant verlaagd, waarmede het behandelde afvalwater dan voldoet aan de Vietnamese normen voor lozing van industriële effluent op B-niveau (details hiervan zijn te lezen in de Appendix).

8.2.2 Factoren die van Invloed zijn op de Werking van het UASB-systeem.

De resultaten van experimenten beschreven in hoofdstuk 6 maken duidelijk dat de werking van UASB-reactoren wordt benvloed door externe factoren als temperatuur, pH, beschikbare voedingsstoffen en spoorelementen, opgelegde OVB's en stootbelasting. Als UASB's bloot staan aan veranderende operationele omstandigheden, kan het systeem reageren met een volledige verzuring, resulterend in een drastische daling van de biogasproductie en COD-verwijderingsefficiëntie van en/of in een sterk verhoogde uitspoeling van slib.

Een lage pH-waarde van het te behandelen afvalwater kan een sterk nadelig effect hebben op de prestaties van de UASB-reactor wanneer die zou resulteren in een te lagepH van de reactorinhoud, omdat het pH-optimum van methaanbacteriën bij 6,5–7,5 ligt. Dientengevolge kan de werking van een AnWT-systeem sterk achteruitgaan bij lagere pH-waarden. Onze resultaten geven aan dat reeds bij pH-waarden rond 6,10 een duidelijk remmende werking optreedt, t.w. een duidelijke daling van de CODverwijderingsefficiëntie en biogasproductie, ook al duurde deze blootstelling aan de wat lagere pH slechts 4 uur. Dit was een verrassende nieuwe observatie.

Bij de behandeling met anaërobe bacteriën vormen voedingsstoffen en spoorelementen essentiële ingrediënten voor stofwisselingsactiviteit en de groei van bacteriën. De resultaten van onze experimenten laten zien dat in het geval van tapioca-afvalwater voedingsstoffen als N en P, alsmede spoorelementen als Fe, Zn, Mn, Mo, Co, Ni en Se ter verbetering van efficiëntie en verhoging van de biogasproductie alleen 'moeten' worden toegevoegd tijdens het opstarten van de UASB-reactoren.

De toegepaste OVB speelt een belangrijke rol gezien zijn sterke effect op microbiële ecologie en de eigenschappen van het systeem. Onze resultaten laten duidelijk zien dat een stapsgewijze toename van de OVB tot stabiele en bevredigende prestaties leidt tot waarden van wel 56 kg COD/m^3.d. Als het systeem eenmaal gestage bevredigende prestaties levert bij een zekere opgelegde OVB, kan de OVB veilig worden verhoogd.

De resultaten van experimenten uitgevoerd bij OVB-schokbelasting 2–3 keer de normale belasting (kortdurend: 12 uur en langdurig : 5 dagen) tonen aan dat een hoog belastbaar AnWT-systeem zoals een UASB-reactor inderdaad een zeer stabiel systeem is. Het is zelfs in staat zich te herstellen van ernstige overbelastingen zoals het geval is in reactor UASB-3, waarin de schokbelasting met COD-concentraties in het afvalwater die 3 keer zo hoog waren als normaal (14.330 i.p.v. 4.884 mg/l) 5 dagen duurde waarna hoge COD-concentraties in het afvalwater werden gehandhaafd van 9.400–11.800 mg/l . De zuiveringsefficiëntie kan aanzienlijk dalen gedurende de periode van overbelasting. De tijd die nodig is voor een volledig herstel kan dan aanzienlijk zijn, een en ander afhankelijk van de duur van de schokbelasting.

8.2.3 Toxische Invloed van Cyanide op Hydrolyse en Verzuringprocessen bij Tapiocazetmeelkorrels

Het cyanidegehalte in het afvalwater bij tapiocaverwerking ligt tussen 19 en 96 mg/l, meestal tussen 22 en 34 mg/l. De prestaties van UASB-reactors blijkt bij deze concentraties nauwelijks of niet te worden aangetast en het cyanidegehalte in de effluent bereikt waarde die steeds lager waren dan 1 mg CN^-/l.

De experimenten uitgevoerd ter vaststelling van de toxische werking van CN^- op de hydrolyse van zetmeeldeeltjes van tapioca hebben uitgewezen dat cyanide een uitgesproken toxische werking heeft. In een controle-experiment (uitgevoerd met 2 g zetmeeldeeltjes en 2 g VSS/L bij 30 °C) was de hydrolyse voltooid binnen 2 dagen, terwijl hiervoor 6 dagen nodig bleken te zijn bij een hoge cyanideconcentratie van 120 mg CN^-/l. De adapatatievan de betreffende bacteriën aan cyanide blijkt goed te verlopen bij een tweede blootstelling aan een cyanideconcentratie van 20 mg/l, maar is duidelijk slechter bij 60 mg CN^-/l. Een zich manifesterende lagfase bij aanwezigheid van cyanide op de hydrolyse- en verzuringprocessen kan waarschijnlijk worden verklaard doordat tijd nodig is voor adaptatie van bacteriën evenals voor het op gang komen van de afbraak van cyanide.

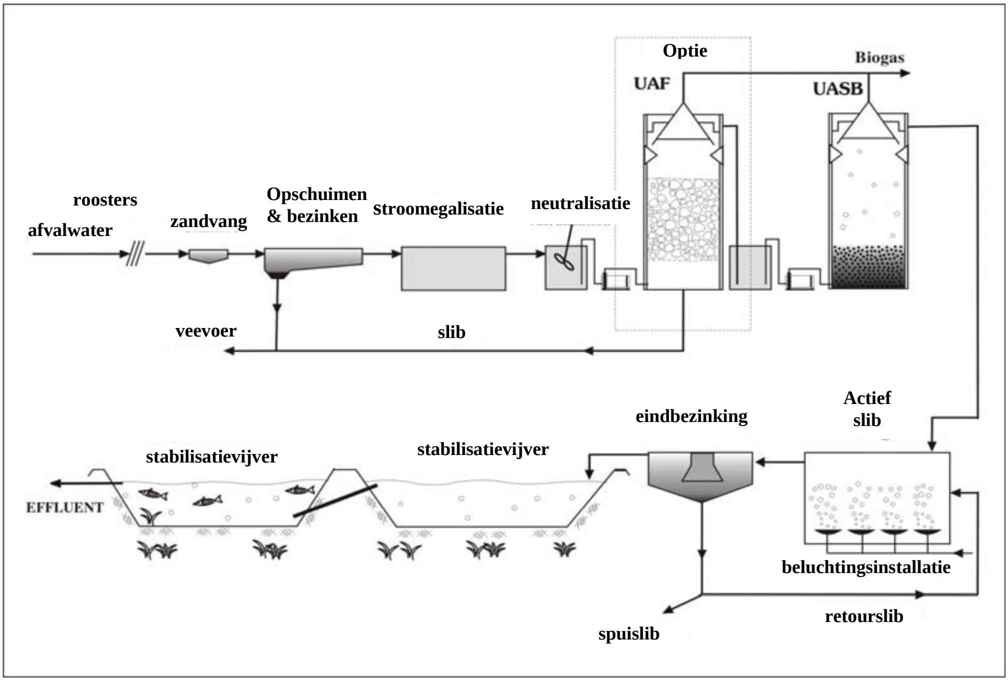
Sulfide-ionen – bij een concentratie beneden 64 mg/l – verminderen de toxiciteit van cyanide niet (t.w. door de vorming van het veel minder giftige thiocyanaat) maar versterken juist de cyanide-toxiciteit.

Daarentegen resulteert de toevoeging van Fe^{2+} in een zeer significante verlaging van de toxische werking van cyanide, t.w. zowel op de hydrolyse als op de methanogenese, hetgeen is toe te schrijven aan de vorming van het ferrocyanidecomplex. De afbraak van cyanide wordt echter door Fe^{2+} niet merkbaar gestimuleerd.

8.3 DE GEËIGENDE TECHNOLOGIE VOOR DE BEHANDELING VAN AFVALWATER BIJ DE TAPIOCAVERWERKING

Conventionele behandelingstechnieken bieden geen duurzame oplossing voor de afvalwaterbehandeling en het te voeren beleid dienaangaande in ontwikkelingslanden als Vietnam. Op basis van de verkregen hoogst bevredigende resultaten van onze experimenten met de anaërobe behandelingstechnologie voor tapioca-afvalwater onder laboratoriumcondities stellen wij het volgende gecombineerde systeem voor de volledige behandeling van tapioca-afvalwater voor (zie figuur 8.1).

De AnWT-stap biedt diverse belangrijke voordelen zoals de afwezigheid van de behoefte aan elektriciteitsvoorziening van buiten, de productie van een nuttige energiedrager in de vorm van biogas en aanzienlijk lagere ruimtebehoefte voor de nabehandelingsstappen, zoals vijversystemen. Anderzijds is ook bekend dat een AnWT-systeem een effluent produceert dat nog steeds een relatief hoge concentratie aan organische verontreinigende stoffen kan bevatten. Daarom kan nabehandeling met een actief-slibproces gevolgd door een vijversysteem met facultatieve bacteriën worden gebruikt om de concentraties aan organische stof terug te brengen tot een niveau beneden de Vietnamese norm voor lozing van effluent op B-niveau voor het lozen van industrieel afvalwater. De aërobe (of micro-aërobe) stap dient als een middel om overlast door stankstoffen de wereld uit te helpen en de verontreiniging van grondwater te voorkomen. Omdat slechts rijpingsvijvers nodig zijn (of zelfs helemaal geen vijvers) kan het gebruik van anaërobe vijvers geheel achterwege worden gelaten. De UAF-voorbehandelingstap die onderdeel uitmaakt van het hier voorgestelde concept is eenvoudigweg een optie, omdat de resultaten van onze experimenten, uitgevoerd over een periode van 300 dagen, duidelijk hebben aangetoond een dat gesuspendeerde vaste stoffen geen enkele merkbare schadelijke werking hebben op de prestaties van een UASB-proces hebben.



Figuur 8.1. Stroomdiagram van het gecombineerde systeem voor de behandeling van afvalwater bij de verwerking van tapioca.

Een proeffabriekversie van deze technologie, met een capaciteit van 10 m^3/d, werd ontworpen en is inmiddels geïnstalleerd, zij het zonder UAF-reactor. De aanloopfase van het systeem begon midden februari 2006 bij de KMC Tapioca Starch Factory in de provincie Binh Phuoc. Na 73 dagen werkte de UASB-reactor van het systeem al met een OVB van 6.2–7.4 kg COD/m^3.d en de resultaten laten redelijke prestaties zien. De COD-concentratie wordt teruggebracht van 3020–3660 mg/l tot 620–1040 mg/l, overeenkomend met een COD-zuiveringsefficiëntie van 72–82%. Uit de verzamelde gegevens over de werking van het systeem blijkt dat de biogasproductie fluctueerde tussen 260 en 350 liter per kilo $COD_{verwijderd}$. De biogasproductie werd gemeten nadat het door een alkalische oplossing was geleid om CO_2 en H_2S te verwijderen. De exacte samenstelling van het gas kon niet worden vastgesteld. De succesvolle toepassing van dit afvalwaterbehandelingssysteem kan aanzienlijk bijdragen tot een verdere duurzame ontwikkeling van de tapioca-industrie in Vietnam, aangezien er paal en perk wordt gesteld aan de milieuverontreiniging.

8.4 VOORDEEL VAN HET TERUGWINNEN VAN BIOGAS

Zoals in hoofdstuk 1 is uiteen gezet behandelen momenteel vrijwel alle tapioca-fabrieken in Vietnam hun afvalwater in een reeks systemen met stabilisatievijvers. Vijversystemen vragen niet alleen om veel landoppervlak maar het gebruik van die systemen impliceert ook dat een waardevolle energiebron wordt verkwist. In feite is een vijversysteem, hoewel het al jaren wordt gebruikt, een nauwelijks begrepen en achterhaalde off-site technologie. Verschillende van die vijversystemen die in het verleden werden geïnstalleerd zijn anaëroob geworden en er komen grote hoeveelheden methaan uit vrij. Daardoor, nog afgezien van het feit dat er energie wordt verspild, worden gigantische hoeveelheden broeikasgassen in de atmosfeer geloosd. Bovendien komen uit deze pover ontworpen en amper begrepen vijvers veel kwalijke geuren vrij en leiden ze vaak tot verontreiniging van het grondwater. Daarnaast voldoet het effluent van stabilisatievijvers doorgaans niet aan de zeer strenge Vietnamese lozingsnormen voor industrieel afvalwater.

Met de technologie voorgesteld in 8.3 kan energie worden teruggewonnen in de vorm van biogas. Bij een doorstroomsnelheid van ongeveer 2000 m^3/d en een COD-concentratie in het afvalwater van 10.000–15.000 mg/l bedraagt de geschatte opbrengst aan te winnen biogas in een tapiocabedrijf met een capaciteit van 100–120 ton/dag zetmeel zoals samengevat in tabel 8.1. Een dergelijke fabriek verbruikt gemiddeld 53.000 MJ aan elektriciteit en 160.000 MJ 75% aan warmte-energie, wat overeenkomt met 3000–3600 liter fossiele olie (FO) per dag. Deze energie is nodig om het zetmeel te drogen, dat wil zeggen het vochtgehalte van het zetmeel terug te brengen van 40–60% naar 11–13% om te kunnen verpakt en vervoerd.

Tabel 8.1 Geschatte output bij de winning van biogas uit het afvalwater bij de verwerking van tapioca.

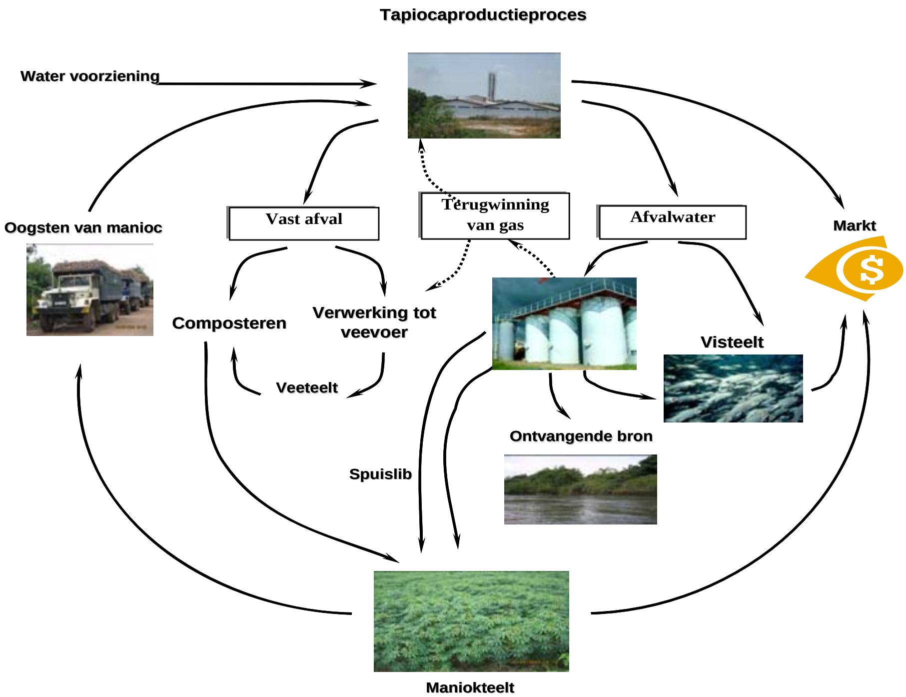
	Variabele	Instroom in UASB	Uitstroom uit UASB
1.	Doorstroomsnelheid	2000 m^3/d	2000 m^3/d
2.	COD-concentratie in afvalwater	10–15 kg/m^3	3,0–4,5 kg/m^3
3.	Gemiddelde biogasproductie per m^3 afvalwater (op basis van gegevens over methaangehalte)		2.1–3.1 m^3
4.	Methaangehalte		>60%
5.	Totale hoeveelheid biogas geproduceerd per dag		4200–6200 m^3/d
6.	Totale hoeveelheid energie- equivalent (1 m^3 biogas met 60% CH_4 $\approx$ 26 MJ)		109,200 – 161,200 MJ/d
7.	Totale hoeveelheid FO-equivalent		2600–3838 l/d
8.	Bespaarde energiekosten (USD 0,33 per liter FO)		858 – 1,266 US$/d
9.	Emissieverlaging eCO_2 per dag		34,44–50,78 ton
10.	Emissieverlaging eCO_2 per jaar		12.054–17.773 ton
11.	Winstequivalent (USD 10–20 per ton eCO_2 emissieverlaging)		USD 120.000–355.000/jaar

De schatting laat zien dat een installatie met een capaciteit van 2000 m^3/d aan biogas 4200–6200 m^3/dag zal produceren (>60 % methaangas), wat overeenkomst met 2600–3800 liter FO per dag. Besparingen aan energiekosten voor de fabriek worden geschat op USD 850–1260 per dag. Als 1 m^3 biogas (met 50% methaan) gelijkstaat aan 1.7 kWh aan elektriciteit (gegevens van de energiecentrale die biogas gebruik van het Go Cat stortterrein, HCMC, Vietnam), kan de energiecentrale 7100–10.500 kWh per dag genereren.

Het voorgestelde systeem voor de behandeling van afvalwater in combinatie met terugwinning van energie kan ook voordeel hebben bij de internationale handel in emissierechten en de financiering van projecten helpen ondersteunen via het Clean Development Mechanism (CDM). Het project kan ook rechten inzake gecertificeerde energiereductie verkopen onder het CDM dat is voorgesteld in het Kyoto Protocol. In dit project – dat is gebaseerd op het omzetten van afvalwater in energie en winst – zijn zowel de technologie als het businessmodel absoluut uitstekend levensvatbaar.

Deze oplossing, die de implementatie betekent van de AnWT-technologie in combinatie met aërobe nabehandeling, laat duidelijk het enorme voordeel zien van energiebesparing en natuurbescherming met bovendien het vermogen aan de werkelijk buitensporig strenge lozingsnormen van afvalwater te voldoen. De oplossing laat ook zien dat het zeer winstgevend is voor investeerders als CDM.

8.5 AANBEVELING VOOR DUURZAME ONTWIKKELING IN DE TAPIOCAVERWERKINGSINDUSTRIE



Figuur 8.2 Aanbevolen systeem voor een duurzame ontwikkeling van de tapiocaverwerkingsindustrie.

Op basis van onze onderzoeksresultaten kunnen wij een bijna volmaakt systeem voor de behandeling van afvalwater aanbevelen voor de tapioca-industrie in Vietnam, overigens niet alleen voor de tapiocaproductie onder Vietnamese omstandigheden. De voorgestelde behandeling combineert een vermindering van de vervuiling met de herwinning van energie uit afvalstoffen en bescherming van natuurlijke bronnen. Met dit geïntegreerde behandelingssysteem, dat een minimalisering van de afval productie en hergebruik van waardevolle stoffen uit het 'afval' impliceert, kan een duurzame ontwikkeling van de tapioca-industrie worden bereikt, waarbij afval en afvalwater de bron voor productie van waardevolle hulpbronnen betekenen. Het behandelde afvalwater kan worden hergebruikt in hydrocultuur of voor irrigatie in de streek. Afval uit het pellen kan worden gecomposteerd en de compost kan worden gebruikt voor het verbouwen van maniok of andere industriële gewassen. Vezelrijke reststoffen kunnen worden gebruikt voor de productie van veevoer. Zo kan een industrieel systeem zonder afval worden gecreëerd (zie figuur 8.2).

8

Tóm Tắt, Kết Luận và Kiến Nghị

8.1 SỰ CẦN THIẾT CỦA NGHIÊN CỨU

Ngành công nghiệp chế biến nông sản thực phẩm (công-nông nghiệp) đóng vai trò quan trọng đối với nền kinh tế Việt Nam và thế giới. Tuy nhiên, ngành công nghiệp này cũng có thể gây ra rất nhiều vấn đề ô nhiễm môi trường trên toàn cầu, đặc biệt tại các nước Châu Á. Nguồn nguyên liệu sử dụng cho ngành công-nông nghiệp rất phong phú. Do đó, lượng nước thải sinh ra từ quá trình chế biến các nguyên liệu này thay đổi rất lớn trong năm, kể cả về lưu lượng lẫn tính chất nước thải. Trong khuôn khổ của luận án này, công nghiệp chế biến tinh bột khoai mì đã được chọn để nghiên cứu. Các nguồn nước thải chính sinh ra trong quá trình chế biến tinh bột là từ công đoạn lắng và ly tâm tách bột. Lưu lượng đặc trưng dao động từ 3 – 5 m^3 nước thải cho 1 tấn củ mì tươi. Với tỉ lệ khoảng 3,5 – 4,0 tấn củ mì tươi ban đầu sẽ sản xuất được 1 tấn tinh bột khoai mì. Nếu nhà máy có công suất 100 tấn tinh bột/ngày sẽ thải ra khoảng 1.200 – 2.000 m^3 nước thải mỗi ngày. Hầu hết toàn bộ nước thải sinh ra từ các nhà máy có qui mô sản xuất nhỏ (qui mô hộ gia đình) được thải trực tiếp ra sông hay kênh rạch xung quanh mà không hề được xử lý, trong khi đó ở các nhà máy sản xuất có qui mô lớn hơn thì nước thải được xử lý bằng một chuỗi hệ thống hồ sinh học tự nhiên. Tuy nhiên, nếu chỉ áp dụng công nghệ xử lý như vậy thì nước thải sau xử lý không thể đạt tiêu chuẩn xả thải tại địa phương. Chỉ tính riêng cho tỉnh Tây Ninh, với tổng công suất của các cơ sở khoảng 6.580 tấn củ mì tươi/ngày (tại thời điểm mùa vụ) thì tổng lượng nước thải sinh ra ước tính khoảng 30.000 m^3 mỗi ngày. Đây là nguyên nhân dẫn đến sự ô nhiễm môi trường nghiêm trọng tại địa phương. Do đó, kiểm soát việc xử lý nước thải trước khi xả thải vào nguồn tiếp nhận đang là mối quan tâm hàng đầu của các nhà quản lý hiện nay.

8.2 KẾT QUẢ ĐẠT ĐƯỢC

Kết quả nghiên cứu cho thấy nước thải sinh ra từ các nhà máy chế biến tinh bột khoai mì có hàm lượng chất hữu cơ cao, COD (7.000-41.500 mg/L), BOD (6.200-23.000 mg/L) và SS (500-8.600 mg/L), pH thấp, dao động trong khoảng 4,2 – 5,7. Bên cạnh đó hàm lượng độc tố CN^- khá cao (19 - 96 mg/l). Khả năng phân hủy sinh học kỵ khí của nước thải tinh bột khoai mì rất cao có thể đạt đến 92,3 – 93,3 % đối với nước thải nguyên thủy, và đạt đến 94,6 – 94,7 % đối với nước thải sau lắng sơ bộ. Vì vậy, phương pháp xử lý sinh học được lựa chọn cho nghiên cứu. Đầu tiên nước thải được xử lý tại bể lọc kỵ khí dòng chảy ngược – còn gọi là thiết bị UAF (Upflow Anaerobic Filter) – đây là giai đoạn tiền xử lý để giảm bớt hàm lượng cặn lơ lửng (SS) có trong nước thải. Quá trình xử lý chính xảy ra tại hệ thống kỵ khí cao tải – sử dụng hệ thống UASB (Upflow Anaerobic Sludge Blanket), tại đây một lượng đáng kể chất hữu cơ được xử lý. Cuối cùng, quá trình xử lý triệt để bằng hệ thống xử lý hiếu khí kết hợp hệ thống hồ sinh học sẽ được áp dụng để loại bỏ hoàn toàn hàm lượng chất hữu cơ còn lại, cùng với các hợp chất nitơ và photpho. Kết quả nghiên cứu được trình bày trong các phần tiếp theo.

8.2.1 Nghiên Cứu Công Nghệ Xử Lý Thích Hợp

Dựa vào kết quả đã trình bày trong Chương 3, Chương 4 và Chương 5 có thể chứng minh rằng công nghệ được đề xuất là công nghệ khả thi, phù hợp để xử lý nước thải công nghiệp chế biến tinh bột khoai mì.

Kết quả nghiên cứu tiền xử lý với thiết bị UAF đã cho thấy rằng cơ chế chính để loại bỏ cặn lơ lửng trong bể UAF là quá trình lắng, giữ và hấp phụ nhờ vào lớp vật liệu lọc. Các nghiên cứu trong Chương 3 đã chứng tỏ rằng các quá trình xử lý bằng hệ thống UAF sử dụng các loại vật liệu lọc khác nhau RPF, PPF, và PW đều đạt hiệu quả xử lý cặn lơ lửng (SS) khá cao, với hiệu quả xử lý tương ứng là 68-85%, 64-74%, 75-83%; do đó làm giảm đáng kể hàm lượng cặn lơ lửng trong nước thải đầu vào từ 900-1.183 mg/L xuống còn 180-352 mg/L. Trong điều kiện Việt Nam, loại vật liệu lọc PW được xem là thích hợp nhất do giá thành thấp và rất phổ biến.

Kết quả nghiên cứu trong Chương 4 cho thấy rằng vận hành hệ thống UASB hiệu quả nhất khi các thông số đầu vào được kiểm soát thích hợp. Với hàm lượng COD đầu vào là 1.500mg/L và thời gian lưu nước dao động từ 8-10 giờ, hiệu quả xử lý COD đạt được rất cao, lên đến 93-96%. Và chỉ trong vòng 13 tuần, tải trọng hữu cơ đã tăng lên đến 13-25 kg COD/m^3.ngđ. Tiếp tục vận hành, tải trọng hữu cơ có thể áp dụng lên đến 56 kgCOD/m^3.ngđ (đặc biệt lên đến 80 kgCOD/m^3.ngđ) với hiệu quả xử lý đạt 82-93%. Các kết quả nghiên cứu cũng chứng minh rằng bùn bể tự hoại được xem là loại bùn thích hợp cho quá trình khởi động hệ thống trong điều kiện Việt Nam. Bùn hạt có thể xuất hiện và quan sát rõ ràng trong các mô hình vào ngày vận hành thứ 20 đến 26, tương ứng tại tải trọng hữu cơ 6 kgCOD/m^3.ngđ. Sau 300 ngày vận hành, không phát hiện sự khác biệt về hiệu quả xử lý COD của hệ thống UASB vận hành với nước thải nguyên thủy và hệ thống UASB vận hành với nước thải đã tách cặn lơ lửng (nước thải sau hệ thống UAF). Kết quả này đã chứng minh rằng ảnh hưởng của cặn lơ lửng trong quá trình vận hành hệ thống UASB đối với nước thải chế biến tinh bột khoai mì là không đáng kể, khi hàm lượng cặn lơ lửng đầu vào lên đến 1.100-1.800 mg/L. Do đó, thiết bị UAF có thể chỉ được áp dụng khi thành phần nước thải đầu vào chứa hàm lượng cặn lơ lửng quá cao.

Mặc dù hệ thống UASB cho hiệu quả xử lý chất hữu cơ rất cao, nhưng hàm lượng COD đầu ra thấp hơn 300 mg/L vẫn không thể đạt đến trong trường hợp áp dụng cho nước thải chế biến tinh bột khoai mì. Để đạt được tiêu chuẩn xả thải Việt Nam, nước thải sau xử lý bằng hệ thống UASB cần phải phải được xử lý triệt để trước khi xả vào nguồn tiếp nhận. Quá trình xử lý triệt để bao gồm hệ thống bùn hoạt tính hiếu khí và hệ thống hồ sinh học tự nhiên cho thấy rằng đây là phương pháp kết hợp tốt nhất để xử lý các loại nước thải có nồng độ chất ô nhiễm cao như nước thải chế biến tinh bột khoai mì.

Áp dụng quá trình bùn hoạt tính hiếu khí – sau khi xử lý với hệ thống UASB – sẽ cho hiệu quả xử lý COD khá cao, đạt đến 96,4 - 97,4% và như vậy hiệu quả xử lý của toàn bộ hệ thống cũng rất cao. Tuy nhiên, với kết quả này, chất lượng nước thải sau xử lý vẫn chưa đạt tiêu chuẩn xả thải vào môi trường. Do đó, bước xử lý triệt để kế tiếp là áp dụng hệ thống hồ sinh học tự nhiên, gồm có hồ tảo, theo sau đó là hồ lục bình. Hệ thống hồ kết hợp này được sử dụng để loại bỏ hoàn toàn COD, SS và chất dinh dưỡng. Với tổng thời gian lưu nước trong hệ thống hồ sinh học là 13 - 15 ngày, với tải trọng bề mặt là 111 - 265 kg COD/ha.ngđ, nồng độ COD đầu ra đạt đến 36 - 58 mg/l. Hệ thống này không chỉ mang lại hiệu quả khử COD cao mà còn làm giảm đáng kể hàm lượng nitơ và photpho. Như vậy nước thải sau xử lý sẽ đạt tiêu chuẩn xả thải của Việt Nam đối với nước thải công nghiệp - nguồn loại B.

8.2.2 Các Yếu Tố ảnh Hưởng Đến Hoạt Động Của Hệ Thống UASB

Kết quả nghiên cứu trình bày trong Chương 6 cho thấy hệ thống UASB chịu ảnh hưởng rất lớn bởi sự thay đổi của nhiều yếu tố bên ngoài như nhiệt độ, pH, hàm lượng chất dinh dưỡng đa lượng và vi lượng, tải trọng hữu cơ và sốc tải trọng. Khi thay đổi điều kiện vận hành hệ thống

UASB có thể gây ra quá trình mêtan hóa không hoàn toàn; kết quả là pH giảm, quá trình sinh khí biogas giảm và hiệu quả xử lý COD cũng giảm.

Giá trị pH đầu vào thấp có thể ảnh hưởng đáng kể đến hoạt động của quần thể vi sinh vật trong hệ thống UASB, do quá trình mêtan hóa chỉ xảy ra với pH tối ưu trong khoảng 6,5-7,5. Ảnh hưởng này cũng có thể xảy ra ngay khi pH không quá thấp – khoảng 6,10. Kết quả nghiên cứu chỉ ra rằng với giá trị pH 6,10, cũng gây ảnh hưởng bất lợi trong quá trình vận hành hệ thống, kết quả là hiệu quả xử lý COD và quá trình sinh khí biogas giảm mạnh, ngay cả khi vận hành với pH như trên chỉ kéo dài trong vòng 4h. Đây là một kết quả hoàn toàn mới mẻ và đáng chú ý.

Trong quá trình xử lý kỵ khí, các chất dinh dưỡng đa lượng và vi lượng là những thành phần cần thiết cho hoạt động trao đổi chất và tăng trưởng của vi sinh vật. Kết quả nghiên cứu cũng cho thấy đối với quá trình xử lý nước thải tinh bột khoai mì, chất dinh dưỡng đa lượng như nitơ và photpho; các nguyên tố vi lượng như Fe, Zn, Mn, Mo, Co, Ni, Se… cần được cung cấp, nhưng chỉ trong giai đoạn vận hành ban đầu của hệ thống UASB để làm tăng hiệu quả xử lý và cải thiện quá trình sinh khí biogas.

Tải trọng hữu cơ đóng vai trò quan trọng trong quá trình vận hành hệ thống UASB. Kết quả nghiên cứu chỉ ra rằng khi tăng dần dần từng bước một đối với tải trọng hữu cơ, thì hiệu quả xử lý chất hữu cơ khá tốt và hệ thống hoạt động rất ổn định với tải trọng hữu cơ lên đến 56 kgCOD/m^3.ngđ.

Các kết quả nghiên cứu về sốc tải trọng với tải trọng cao hơn gấp 2 – 3 lần so với tải trọng bình thường (thời gian sốc – ngắn hạn: 24 h và dài hạn: 5 ngày) chứng tỏ rằng hệ thống xử lý nước thải cao tải như UASB thực sự là hệ thống khá ổn định; nghĩa là hệ thống có thể phục hồi sau khi sốc tải (như trường hợp hệ thống UASB-3, sốc tải trọng với COD đầu vào cao gấp 3 lần so với bình thường, trong thời gian 5 ngày – với nồng độ COD đầu vào tăng từ 4.884 mg/L đến 14.330 mg/L – và sau 5 ngày, duy trì nồng độ COD đầu vào trong khoảng 9.400-11.800 mg/L), mặc dù trong suốt thời gian hệ thống chịu sốc tải thì hiệu quả xử lý cũng có thể giảm mạnh và thời gian cần thiết để khôi phục lại toàn bộ hệ thống khá dài và phụ thuộc vào khoảng thời gian hệ thống gặp sự cố.

8.2.3 Ảnh Hưởng Của Độc Tính Xyanua Trong Quá Trình Thủy Phân Và Axít Hóa Các Hạt Tinh Bột Khoai Mì

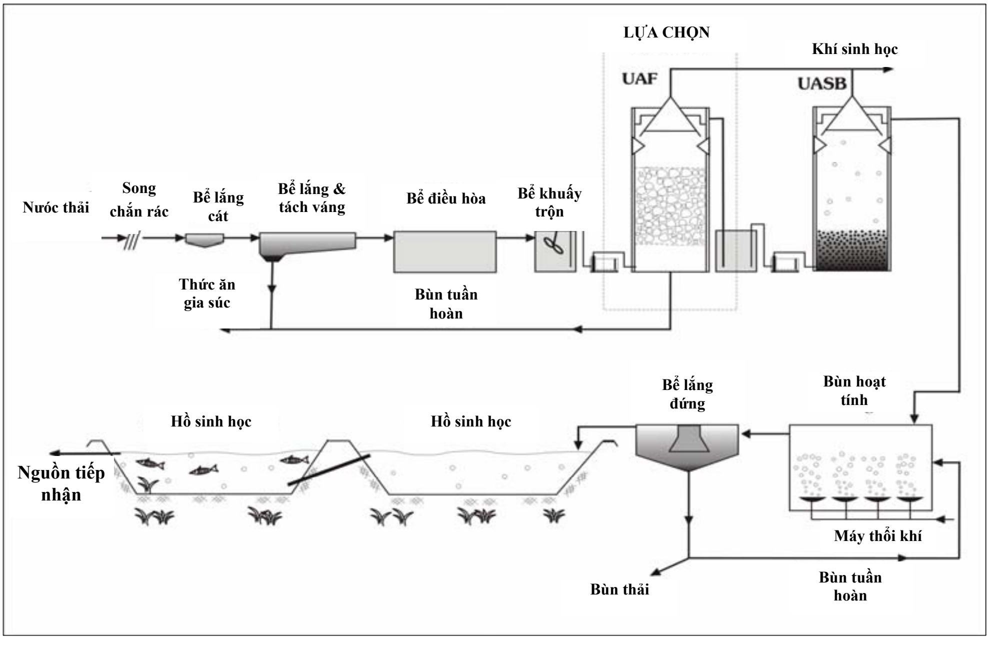
Nồng độ xyanua trong nước thải chế biến tinh bột khoai mì dao động trong khoảng 19 – 96 mg/L, với giá đặc trưng dao động trong khoảng 22 – 34 mg/L. Tuy nhiên, khá may mắn là các hợp chất xyanua này rất dễ tự phân hủy. Do đó, khi vận hành hệ thống UASB trong dãy giá trị nồng độ xyanua trong nước thải thì không quan sát thấy bất kỳ ảnh hưởng bất lợi nào đến hệ thống, và nồng độ xyanua đầu ra luôn thấp hơn 1 mgCN^-/L.

Kết quả nghiên cứu ảnh hưởng của độc tính xyanua lên quá trình thủy phân các hạt tinh bột khoai mì cho thấy độc tính đặc trưng của xyanua. Trong thí nghiệm trắng (thí nghiệm kiểm chứng – không có xyanya) thực hiện với 2 g tinh bột mì và 2 gVSS/L, ở nhiệt độ 30^oC, quá trình thủy phân hoàn toàn xảy ra trong vòng 2 ngày. Trong khi đó thí nghiệm tương tự nhưng thực hiện ở nồng độ xyanua 120 mgCN^-/L thì quá trình thủy phân hoàn toàn phải mất 6 ngày. Quá trình thích nghi của vi sinh vật ở nồng độ xyanua 20 mg/L là khá tốt ở lần nạp liệu (feed) thứ 2. Tuy nhiên sự thích nghi này là rất kém ở nồng độ xyanua lên đến 60 mg/L. Sự trễ pha của quá trình này phụ thuộc vào sự thích nghi của vi khuẩn cũng như quá trình phân hủy xyanua, và tùy thuộc nồng độ của xyanua trong dung dịch.

Kết quả nghiên cứu chỉ ra rằng các ion $[SO_3]^-$ – với nồng độ thấp hơn 64 mg/L – không làm giảm độc tính của xyanua (do hình thành thio-cyanate) mà thay vào đó còn làm tăng thêm độc tính của nó. Tuy nhiên, sự có mặt Fe^{2+} sẽ làm giảm đáng kể độc tính của xyanua cả trong quá trình thủy phân lẫn trong quá trình mêtan hóa do có sự hình thành phức chất fero-cyanide. Dù vậy, sự giảm độc tính này cũng không thể kích thích quá trình phân hủy xyanua nhanh hơn.

8.3 CÔNG NGHỆ THÍCH HỢP XỬ LÝ NƯỚC THẢI TINH BỘT KHOAI MÌ

Những công nghệ truyền thống đơn giản không đáp ứng được nhu cầu xử lý và quản lý nước thải phục vụ cho phát triển bền vững, điển hình là ngành chế biến tinh bột khoai mì tại Việt Nam. Dựa vào các kết quả nghiên cứu đạt được ở qui mô phòng thí nghiệm, công nghệ thích hợp để xử lý nước thải tinh bột khoai mì được đề xuất như Hình 8.1



Hình 8.1 Công nghệ thích hợp xử lý nước thải chế biến tinh bột khoai mì.

Đây là công nghệ xử lý với nhiều ưu điểm như không đòi hỏi quá nhiều năng lượng, có thể tái sinh năng lượng từ nguồn khí biogas thu được, giảm thiểu đáng kể nhu cầu sử dụng đất rộng lớn cho hệ thống hồ sinh học. Mặt khác – thực tế đã cho thấy rằng – hệ thống xử lý kỵ khí cao tải thực sự có hiệu quả đối với những loại nước thải chứa hàm lượng chất hữu cơ cao. Tuy nhiên, sau hệ thống xử lý kị khí bao giờ cũng cần bước xử lý triệt để tiếp theo. Đó cũng là lý do tại sao cần phải áp dụng quá trình xử lý triệt để với hệ thống bùn hoạt tính hiếu khí và sau đó là hệ thống hồ sinh học tự nhiên, để giảm thiểu nồng độ chất hữu cơ và chất dinh dưỡng đến mức thấp nhất, đạt tiêu chuẩn xả thải nước thải công nghiệp hiện hành tại Việt Nam (nguồn loại B). Giai đoạn tiền xử lý với thiết bị UAF được đề cập đến ở phần trên có thể được xem là sự lựa chọn không bắt buộc, bởi vì kết quả thực nghiệm đã cho thấy rất rõ rằng không xảy ra bất kỳ tác hại nghiêm trọng nào do chất rắn lơ lửng gây ra trong suốt 300 ngày vận hành hệ thống UASB với hàm lượng chất rắn lơ lửng nhỏ hơn 1.800 mg/L.

Hiện tại, một hệ thống xử lý thí điểm, công suất 10 m^3/ngđ đã được thiết kế và lắp đặt (bỏ qua thiết bị UAF). Hệ thống xử lý này đã được khởi động và vận hành vào giữa tháng 2 năm 2006 tại nhà máy tinh bột khoai mì KMC, tỉnh Bình Phước. Sau 73 ngày vận hành, hệ thống UASB đang được vận hành với tải trọng hữu cơ trong khoảng 6,2 – 7,4 kgCOD/m^3.ngđ, hiệu quả xử lý đạt được khá tốt. Hàm lượng COD đầu vào giảm từ 3.020 – 3.660 mg/L giảm còn 620 – 1.040 mg/L ở đầu ra, hiệu quả xử lý COD dao động trong khoảng 72 – 82%. Kết quả vận hành cho thấy lượng khí sinh ra dao động trong khoảng 260 – 350 L khí biogas (> 60% mêtan) cho 1kg COD bị khử. Lượng khí biogas đo được sau khi cho toàn bộ khí sinh ra đi qua dung dịch kiềm để loại bỏ CO_2 và H_2S. Thành phần của hỗn hợp khí sinh ra chưa được phân tích chính xác. Việc ứng dụng thành công công nghệ xử lý này có thể góp phần đáng kể đến sự phát triển bền vững cho ngành chế biến tinh bột khoai mì tại Việt Nam.

8.4 LỢI ÍCH CỦA VIỆC THU HỒI KHÍ BIOGAS (KHÍ SINH HỌC)

Như đã đề cập ở Chương 1, hiện tại ở Việt Nam hầu hết các nhà máy chế biến tinh bột khoai mì áp dụng hệ thống hồ sinh học để xử lý nước thải. Tuy nhiên, hệ thống hồ sinh học luôn luôn chiếm một diện tích đất rộng lớn và nếu chỉ áp dụng phương pháp này sẽ bỏ phí nguồn năng lượng có giá trị. Trên thực tế, mặc dù hồ sinh học đã được áp dụng từ rất lâu – song đây là kỹ thuật lỗi thời và sự hiểu biết để vận hành tốt hệ thống còn quá hạn chế. Rất nhiều hệ thống được xây dựng trước đây đã trở thành hồ kị khí và giải phóng ra một lượng lớn khí sinh học, góp phần làm gia tăng nồng độ khí nhà kính trong khí quyển. Bên cạnh đó, những hồ kị khí thường có mùi hôi và chúng tiềm ẩn nguy cơ gây ô nhiễm nguồn nước ngầm. Hơn thế nữa, khi chỉ áp dụng hệ thống hồ sinh học thì đầu ra sau xử lý thường không đáp ứng được tiêu chuẩn xả thải nghiêm ngặt của Việt Nam.

Theo công nghệ đã đề xuất ở mục 8.3 ở trên, ưu điểm nổi bật là năng lượng có thể được thu hồi ở dạng khí biogas và có thể tái sử dụng ngay tại chỗ. Đối với nhà máy có công suất 100 – 120 tấn tinh bột, lưu lượng nước thải khoảng 2.000 m^3/ngày và nồng độ COD dao động trong khoảng 10.000 – 15.000 mg/L, lượng khí biogas thu hồi được ước lượng và trình bày tóm tắt trong Bảng 8.1. Trung bình một nhà máy sản xuất tinh bột với công suất như trên tiêu thụ một lượng năng lượng trung bình khoảng 53.000 MJ (tương ứng khoảng 25% - cho năng lượng điện – dùng để vận hành thiết bị, động cơ) và 160.000 MJ (chiếm khoảng 75% - cho năng lượng nhiệt – dùng để sấy khô bột), lượng năng lượng này tương đương với 3.000 - 3.600 L dầu FO mỗi ngày.

Bảng 8.1 Lượng khí biogas ước tính thu hồi từ HTXL nước thải chế biến tinh bột khoai mì

Thông số	Đầu vào UASB	Đầu ra UASB
1. Lưu lượng	2.000 m^3/ngđ	2.000 m^3/ngđ
2. Nồng độ COD của nước thải	10 – 15 kg/m^3	3,0 – 4,5 kg/m^3
3. Lượng khí biogas trung bình sinh ra tính trên 1 m^3 nước thải		2,1 – 3,1 m^3
4. Hàm lượng khí mêtan		> 60%
5. Tổng lượng khí biogas sinh ra mỗi ngày		4.200 – 6.200 m^3/ngày
6. Tổng năng lượng tương đương đương [1 m^3 khí biogas (>60% CH_4) # 26 MJ]		109.200 – 161.200 MJ/ngày
7. Tổng lượng dầu FO tương đương		2.600 – 3.838 L FO/ngày
8. Tiết kiệm chi phí năng lượng (0.33 US$/L FO)		858 – 1.266 US$/ngày
9. Giảm phát thải khí CO_2 mỗi ngày		34.44 – 50.78 tấn/ngày
10. Giảm phát thải khí CO_2 mỗi năm		12.054 – 17.773 tấn/năm
11. Cân bằng lợi ích (10-20 US$/tấn khí CO_2 giảm phát thải)		120.000 – 355.000 US$/năm

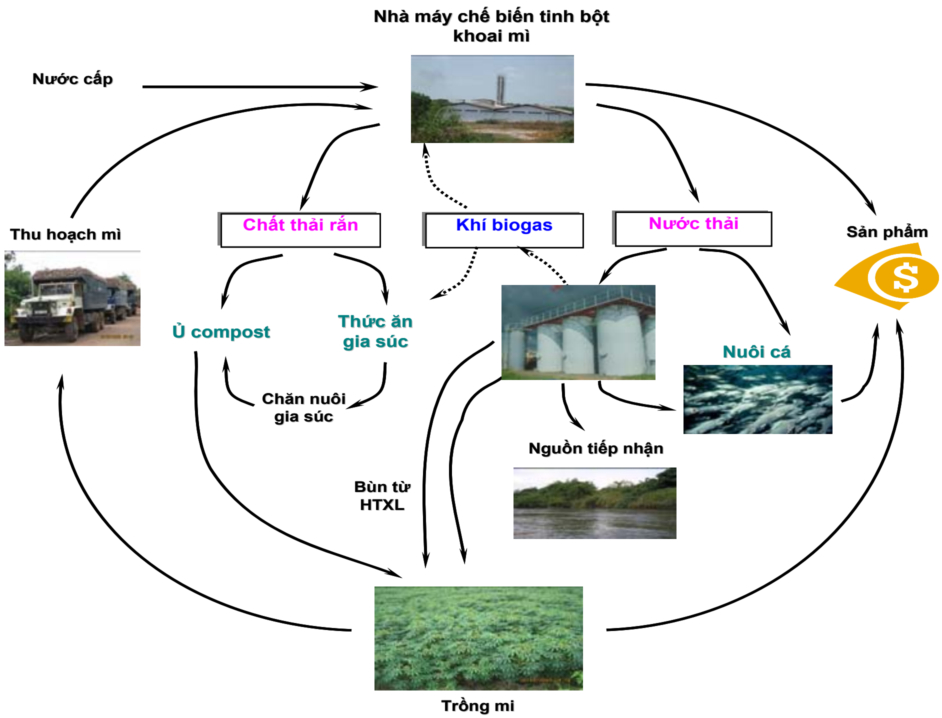
Bảng ước tính trên chỉ ra rằng hệ thống xử lý với công suất 2.000 m^3/ngày sẽ tạo ra 4.200-6.200 m^3 khí biogas/ngày (> 60% khí mêtan), lượng khí này nếu sử dụng cho lò đốt sẽ sinh ra năng lượng tương đương với 2.600-3.838 lít dầu FO/ngày. Tiết kiệm chi phí năng lượng cho nhà máy ước tính khoảng 850-1.266 US$/ngày. Nếu 1 m^3 khí biogas (chứa 50% khí mêtan) có thể sản xuất 1,7 kWh điện (số liệu từ nhà máy điện sử dụng khí biogas của bãi chôn lấp Gò Cát, HCMC, Việt Nam), thì từ lượng khí biogas thu được từ nhà máy xử lý nước thải, nhà máy điện có thể sản xuất 7.100 - 10.500 kWh/ngày.

Hệ thống xử lý kị khí kết hợp với việc thu hồi và tái sinh năng lượng cũng có thể đem lại lợi nhuận từ việc bán tín dụng carbon và hỗ trợ tài chính qua Cơ Chế Phát Triển Sạch (CDM). Hoặc dự án có thể bán sự chứng nhận giảm phát thải đã được công nhận theo Nghị định thư Kyoto qua chương trình CDM. Trong dự án này – công nghệ xử lý nước thải, tái tạo năng lượng và thu lợi nhuận từ chương trình CDM – cả về mặt kỹ thuật và kinh tế đều mang tính khả thi cao.

Giải pháp này, bao gồm việc thực hiện công nghệ xử lý kị khí cao tải UASB, kết hợp với xử lý triệt để, với những bằng chứng rõ ràng và lợi ích to lớn từ việc tiết kiệm chi phí về năng lượng và bảo tồn tài nguyên cùng với tính khả thi để đáp ứng tiêu chuẩn xả thải nghiêm ngặt nhất, là một giải pháp hứa hẹn cho sự phát triển bền vững trong tương lai. Giải pháp cũng chỉ rõ lợi nhuận hấp dẫn cho các nhà đầu tư khi áp dụng Cơ Chế Phát Triển Sạch.

8.5 HƯỚNG ĐẾN PHÁT TRIỂN BỀN VỮNG CHO NGÀNH CÔNG NGHIỆP CHẾ BIẾN TINH BỘT KHOAI MÌ

Như đã trình bày ở trên, một công nghệ xử lý khá hoàn hảo đối với nước thải chế biến tinh bột khoai mì đã được nghiên cứu và đề nghị, công nghệ không chỉ có thể áp dụng tại Việt Nam mà còn có thể áp dụng cho các nước Châu Á khác. Công nghệ xử lý này đã kết hợp được việc giảm thiểu ô nhiễm, thu hồi năng lượng và bảo tồn tài nguyên. Như vậy, công nghệ sẽ giúp giảm lượng chất thải phát sinh và tái sử dụng các hợp chất có giá trị sinh ra từ chất thải trong quá trình chế biến. Từ đó nước thải và chất thải thật sự là nguồn tài nguyên, thay vì là vấn đề nan giải cho các nhà quản lý như hiện nay. Nước thải sau xử lý có thể được tái sử dụng để nuôi trồng thuỷ sản hoặc dùng cho tưới tiêu xung quanh khu vực. Vỏ mì từ quá trình chế biến có thể được sử dụng như nguyên liệu để làm compost, sản phẩm compost có thể áp dụng để trồng khoai mì hay các loại cây công nghiệp khác. Bã mì có thể được sử dụng để sản xuất thức ăn gia súc. Một khu công nghiệp sinh thái (không/rất ít chất thải) cho công nghiệp chế biến tinh bột khoai mì được kiến nghị như Hình 8.2. Bên cạnh đó, việc áp dụng công nghệ còn giúp hạn chế việc sử dụng tài nguyên thiên nhiên, phục vụ phát triển bền vững cho ngành công nghiệp chế biến tinh bột khoai mì trong tương lai.



Hình 8.2 Khu công nghiệp sinh thái, phục vụ phát triển bền vững đối với công nghiệp chế biến tinh bột khoai mì.

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APPENDICES

1. Vietnamese Standard for Industrial Effluents Discharged

2. Pictures of the researches

VIETNAM STANDARD TCVN 5945-1995

STANDARD FOR INDUSTRIAL EFFLUENTS DISCHARGED

1. Scope

1.1 This standard specifies limit value of parameters and concentration of substances in industrial wastewater.

In the standard "industrial waste water" means: liquid water or waste water produced by reason of working or production processes taking place at any industrial, servicing and trading premises, etc.

1.2 This standard is applies to control of quality of industrial wastewater before being discharged into a water body.

"Water body" means: inland water, include any reservoir, pond, lake, river, stream, canal, drain, spring or well, any part of the sea abutting on the foreshore, and any other body of natural or artificial surface or subsurface water.

2. Limitation values

2.1 Values of parameters and maximum allowable concentrations of substances in industrial wastewater before being discharged into water bodies are shown in the table 1

2.2 Discharge standards applying for waste waters produced by specific industry such as paper; textile or oil industries are specified in a separate standard, respectively.

2.3 Industrial waste waters containing the values of parameters and concentrations of substances which are equal to or lower than the values specified in the column A (table 1) may be discharged into the water bodies using for sources of domestic water supply.

2.4 Industrial waste waters containing the values of parameters and concentration of substances which are lower than or equal to those specified in the column B (table 1) are discharged only into the water bodies using for navigation, irrigation purposes or for bathing, aquatic breeding and cultivation, etc.

2.5 Industrial waste waters containing the values of parameter and concentrations of substances which are greater than those specified in the column B but not exceeding those specified in the column C (table 1) is discharged only into specific water bodies permitted by authority agencies.

2.6 Industrial waste water containing the values of parameters and concentrations of substances which are greater than those specified in the column C (table 1) shall not be discharged into surroundings.

2.7 Standard methods of analysis of parameters and concentration of substances in industrial wastewater are specified in available current TCVNs.

Table 1 Industrial waste water limit values of parameters and maximum allowable concentration of pollutants

No	Parameters and substances	Unit	Limitation values		
			A	B	C
1	Temperature	^oC	40	40	45
2	pH value	-	6 to 9	5,5 to 9	5 to 9
3	BOD_5 (20^oC)	mg/l	20	50	100
4	COD	mg/l	50	100	400
5	Suspended solids	mg/l	50	100	200
6	Arsenic	mg/l	0,05	0,1	0,5
7	Cadmium	mg/l	0,01	0,02	0,5
8	Lead	mg/l	0,1	0,5	1
9	Residual Chlorine	mg/l	1	2	2
10	Chromium (VI)	mg/l	0,05	0,1	0,5
11	Chromium (III)	mg/l	0,2	1	2
12	Mineral oil and fat	mg/l	Not	1	5
13	Animal-vegetable fat and fat	mg/l	5	10	30
14	Copper	mg/l	0,2	1	5
15	Zinc	mg/l	1	2	5
16	Manganese	mg/l	0,2	1	5
17	Nickel	mg/l	0,2	1	2
18	Organic phosphorous	mg/l	0,2	0,5	1
19	Total phosphorous	mg/l	4	6	8
20	Iron	mg/l	0,02	5	10
21	Tetrachlorethylene	mg/l	1	0,1	0,1
22	Tin	mg/l	0,2	1	5
23	Mercury	mg/l	0,005	0,005	0,01
24	Total Nitrogen	mg/l	30	60	60
25	Trichlorethylene	mg/l	0,05	0,3	0,3
26	Ammonia (as N)	mg/l	0,1	1	10
27	Fluoride	mg/l	1	2	5
28	Phenol	mg/l	0,001	0,05	1
29	Sulfide	mg/l	0,2	0,5	1
30	Cyanide	mg/l	0,05	0,1	0,2
31	Coliform	MPN/100ml	5 000	10 000	-
32	Gross α activity	Bq/l	0,1	0,1	-
33	Gross β activity	Bq/l	1,0	1,0	-

Note:
A: using for sources of domestic water supply;
B: using for navigation, irrigation purposes or for bathing, aquatic breeding and cultivation, etc;
C: using for sources specific water bodies permitted by authority agencies.

VIETNAM STANDARD TCVN 6984-2001

WATER QUALITY

STANDARD FOR INDUSTRIAL EFFLUENTS DISCHARGED INTO THE RIVERS USING FOR PROTECTION OF AQUATIC LIFE

1 Scope

1.1 This standard specifies parameter limits and allowable concentrations of pollutants in industrial effluents according to the water current of the receiving water body.
In this standard, industrial effluent is defined as wastewater from production activities of industries. The distance from the effluent to the receiving follows the current regulations.

1.2 This standard is applied in accordance with TCVN 5945:1995 and used to monitor the industrial effluent discharged into the river or lake (called "river") using for protection aquatic life.

2 Quoting standard

TCVN 5945: 1995 Industrial effluent – Discharging standard

3 Limitation values

3.1 The limitation values by parameters, concentrations of the pollutants in the effluent discharged into the different water-current of river is not allowed if exists more than the values in table 2.
The parameters and concentration of pollutant not mentioned in table 1 is applies as TCVN 5945:1995

2.2 Method of sampling, analysis, calculation and determining parameters is stipulated in Vietnam standards or other methods by the environmental organization.

Table 2 Limitation of parameters and concentration of industrial pollutants discharged into the river using for protection aquatic life

Parameter	Q> 200 m^3/S			Q = 50 ÷ 200m^3/s			Q< 50 m^3/S		
	F1	F2	F3	F1	F2	F3	F1	F2	F3
1. Color, Co-Pt (pH=7)	50	50	50	50	50	50	50	50	50
2. Odor, sense	slight	slight	slight	slight	slight	slight	slight	slight	slight
3. Total SS (mg/L)	100	100	100	90	80	80	80	80	80
4. pH	6-8,5	6-8,5	6-8,5	6-8,5	6-8,5	6-8,5	6-8,5	6-8,5	6-8,5
5. BOD_5 (20^oC) mg/L	50	45	40	40	35	30	30	20	20
6. COD mg/L	100	90	80	80	70	60	60	50	50
7. Arsen, As mg/L	0,1	0,1	0,1	0,08	0,08	0,08	0,05	0,05	0,05
8. Cadmi, Cd mg/L	0,02	0,02	0,02	0,01	0,01	0,01	0,01	0,01	0,01
9. Lead, Pb mg/L	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
10. Fe, mg/L	5	5	5	4	4	4	3	3	3
11. CN^-, mg/L	0,1	0,1	0,1	0,05	0,05	0,05	0,05	0,05	0,05
12. Mineral oil and grease mg/L	10	5	5	10	5	5	5	5	5
13. Animal-vegetable fat mg/L	20	20	20	20	10	10	10	10	10
14. Organic P mg/L	1	1	0.8	0.8	0.5	0.5	0.5	0.5	0.5
15. Total P mg/L	10	8	8	6	6	6	5	5	5
16. Surfactant	10	10	10	5	5	5	5	5	5
17. Cl^- mg/L	1000	1000	1000	800	800	800	750	750	750
18. Coliform MPN/100ml	5000	5000	5000	5000	5000	5000	5000	5000	5000
19. PCB mg/L	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01

- Note:

Q: The flow-rate of the river, m^3/S
F: The flow-rate of effluent, m^3/day (24 hours)
F1: From 50 m^3/day to 500 m^3/day
F2: From 500 m^3/day to 5000 m^3/day
F3: = or > 5000 m^3/day

UASB-reactors and UAF-reactors (lab-scale) at the start-up period that are described in the thesis – **CENTEMA laboratory**

The pilot-plant scale version for Tapioca Wastewater Treatment – capacity of 10 m^3/d – at KMC Tapioca Starch Factory, Binh Phuoc. The lower picture showed a group of CENTEMA staffs and students involved in the research.

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