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Assessment of anaerobic domestic wastewater treatment: Case study of Ciudad de la Costa WWTP in Uruguay

Sarah Dominguez Ciejanowiecki

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Assessment of anaerobic domestic wastewater treatment: Case study of Ciudad de la Costa WWTP in Uruguay

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by

Sarah Dominguez Ciejanowiecki

Supervisors

Carlos Madera, MSc. PhD, Universidad del Valle

Mentors

Héctor García, MSc. PhD, UNESCO-IHE

Tineke Hooijmans, MSc. PhD, UNESCO-IHE

Diana Miguez, MSc. PhD, LATU

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Abstract

In Uruguay, sanitation and water supply provision is responsibility of the governmental company OSE (Spanish acronym for State waterworks), as well as the operation of WWTPs. Most of the plants use biological treatment to remove organic matter and nutrients, as activated sludge, aerobic ponds for small villages, and anaerobic treatment.

The Ciudad de la Costa WWTP was designed for biological removal of organic matter using up-flow anaerobic sludge blanket (UASB) and chlorination as post-treatment to remove the pathogens, with a maximum capacity of 344.000 P.E. Nowadays, this unique plant using anaerobic treatment for domestic wastewaters, and is in operation since July of 2015. The plant that was being operated by the contractor, and in July of 2016, passes into the hands of the state company OSE. Due to this, most of the problems of the plant, are related to the protocols of operation, and the learning of the personal to handle it. Hence, the aim of this work is evaluate the performance of the plant in this stage.

The average inflow of this period is 3780 m³/d, receiving wastewater from Pando, and Ciudad de la Costa city. This last one is conveyed by trucks, because the sewer system it is being constructed. The average composition of the influent is 899 mgCOD/L, and 361 mgBOD/L, and the efficiency in terms of removal of BOD is 75%, and TSS is 147 mg/L. Also, the average temperature of the influent is 20oC, reaching a minimum value of 9oC. The loading rate is high compared with the low SMA reported in January of 2016, but this value depends of the quality of the sludge, and varies with the time, so is recommended to do another analysis. Besides of this, the alkalinity indexes were analysed, and are according to a stable process.

For determine the current situation, two sampling campaigns for the physiochemical parameters, were necessary to determine the characteristic of the wastewater, including sulphates, sulphides and iron. The objective is to analyse the impact of iron chloride, dosed at the pumping station, in the anaerobic reactors. As well as, the relation with the production of H₂S in the reactors, that can lead to the inhibition of methanogenic activity. From the data measured, the sulphate is in the range of 30 to 40 mgSO₄/L, and the total iron from 2 to 11 mgFe/L. However, the relation between COD/SO₄ is high so the inhibition of methanogenics is not expected.

Regarding the mass balance of sulphates, the efficiency in the removal is in average 43%. The sulphate removed is reduced to H₂S, it is dissolved in the effluent, and released in the discharge structures, due the high turbulence generated. As well as, is accumulated in the sludge as FeS.

Due the lack of information related to the biogas production, this value is estimated from the COD balance. The methane yield estimated is between 0.10 - 0.17 Nm³CH₄/kgCODremoved, an average production of 500Nm³/d of biogas, assuming 70% of methane.

Finally, a model is implemented using a PetWin™, simulator from EnviroSim Ltda., developed for industrial effluents, which includes the sulphate reduction in the process. Based in the data of November, the model is implemented, and calibrated. But to have an accurate model, measurements of the biogas production are required. The parameters more sensitive were the methanogens yields, while the yields of the SRB don't affect the model, due the low concentration, all the sulphate was reduced into H₂S, the results shows values less than 1% of H₂S in the biogas composition. Although, the validation of the model is not achieved with the data of February, the model fits with the average values of the plant. Due to this, for an accurate model, information of biogas production and composition is required.

Keywords: domestic wastewater, anaerobic digestion, UASB, iron chloride, sulphur reduction, PetWin

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Abbreviations

ADM1	Anaerobic digestion model 1
Alk	Alkalinity
ASM	Activated sludge Model
ASDM	Activated Sludge/Anaerobic Digestion Model
BSM	Benchmark Simulation Model
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DINAMA	Spanish acronym for Environmental National Direction (Uruguay)
EC	Emerging Contaminants
ED	Endocrine Disruptors
FSA	Free and saline ammonia
GLSS	Gas liquid sludge separator
GFRP	Glass-Fiber Reinforced Plastic
HRT	Hydraulic retention time
IWA	International Water Association
LATU	Spanish acronym for Technologic Laboratory of Uruguay
OSE	Spanish acronym for State Waterworks (Uruguay)
OLR	Organic loading rate
PS	Pump Station
SCADA	Supervisory control and data acquisition
SMA	Specific Methanogenic Activity
SLR	Sludge Loading Rate
SRB	Sulphate reduction bacteria
SRT	Sludge retention time
SS	Settable solids
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TS	Total Sulphur
TSS	Total suspended solids
TVS	Total Volatile Solids
VFA	Volatile fatty acids
VSS	Volatile suspended solids
UASB	Up-flow anaerobic sludge blanket
UdlaR	Spanish acronym for University of the Republic of Uruguay
WWTP	Wastewater Treatment Plant

CHAPTER 1

Introduction

In this chapter, will be exposed the description of the waste treatment plant and their issues. Also, the problems whose are being assessed in this work. Finally, will be defined the objectives of this research.

1.1. Background

There is an increasing awareness in Uruguay about the impacts on the fauna and flora due to the discharge of raw wastewater into the water bodies, resulting in a master plan to solve the problems of sewerage in different locations. The performance of wastewater plants, regarding nutrient removal, is being studied after some algae blooms events were seen in rivers and lakes. The evaluation and optimization of the treatment plants reduce this kind of impacts in the aquatic environment.

In Uruguay, sanitation and water supply provision is responsibility of the governmental company OSE (Spanish acronym for State waterworks), as well as the operation of WWTPs. Most of the plants use biological treatment to remove organic matter (and sometimes nutrients), as activated sludge, aerobic ponds for small villages, and anaerobic treatment. At the present moment, one plant is using anaerobic digesters, such as UASB. Due to this, there is a lack of knowledge on anaerobic digestion in the company

Anaerobic reactors for treatment of domestic effluents are used mainly in countries with high temperatures (tropical climate), but also experiences with full scale systems in places with moderate to low temperatures. (Uemura and Harada 2000; O'Reilly et al. 2009; Turkdogan-Aydinol et al. 2010; Elmitwalli 2013; Chernicharo et al. 2015). The formation of granular sludge is a characteristic of this type of high loading reactors, mainly in tropical countries. Authors reported also the formation of granular sludge in UASB reactors treating domestic wastewater under low temperature.(Seghezzeo 2004; Elmitwalli 2013).

In addition, mathematical modelling of the anaerobic process has been developed in the last decades, and the use of those models in computer tools is increasing. These tools could be used for different purposes, such as to optimize the performance of the anaerobic reactors, reducing the lab test time, calculating the biogas production or for trying different scenarios (van Lier, *et al.*, 2015). This could reduce the time of start-up or prove strategies to solve particular problems.

1.2. Ciudad de la Costa WWTP

The Ciudad de la Costa WWTP was designed for biological removal of organic matter using up-flow anaerobic sludge blanket (UASB) and chlorination as post-treatment to remove the pathogens. A subaquatic emissary of 1000 m to the coastal line discharges the final effluent of the plant into the estuary “Río de la Plata”. The first experience of OSE, in anaerobic treatment of domestic wastewater, was the WWTP of Pando town (located a 10 km of the actual WWTP), with two small UASB reactors of 600 m³ each one. Nowadays, this plant is out of order, due to several problems in the structure of the reactors, and the construction of Ciudad de la Costa WWTP. Hence, this is the only one plant using anaerobic treatment for domestic wastewaters.

Ciudad de la Costa WWTP is operating since 2015, designed to treat a maximum inflow of 120.000 m³/d (344.000 P.E in 2035). However, based on the data of the company, the average inflow of the plant is less than 5% of the maximum design flow (4280 m³/d). There are two streams to the plant, 60% of the influent comes from the pumping station in Pando town (10 km of pipeline) and the remaining is conveyed by vacuum trucks from septic tanks of householders of Ciudad de la Costa, on average 100 per day between 8:00 to 17:00, representing 40% of the average daily inflow. In Figure 1-1 the average influent per month during 2016 is represented, as well as the average inflow of 2016.

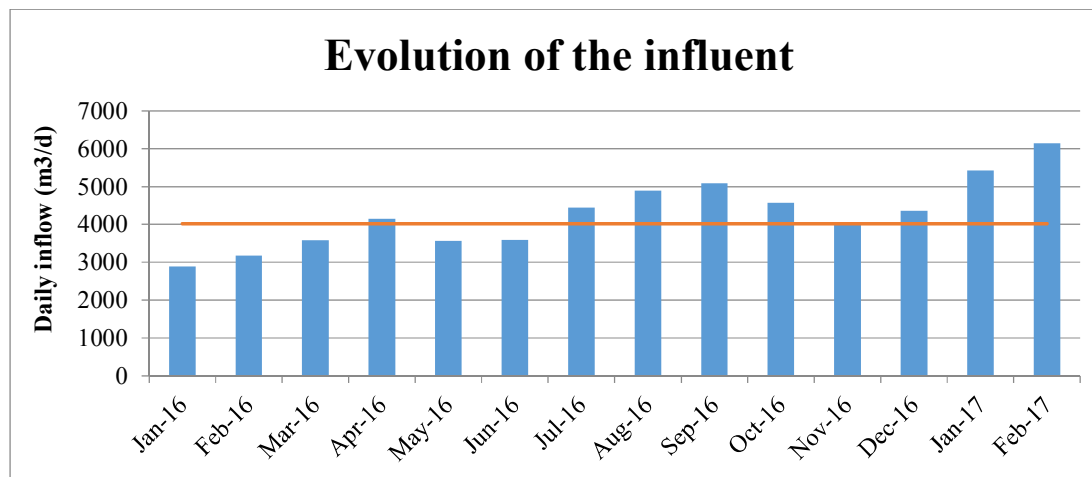


Figure 1-1: Evolution of the influent during 2016 (Based on data given from OSE)

The National Environmental Agency (DINAMA) regulates and controls the discharge in natural water bodies of wastewaters. Depending on the quality base of it, and the related uses, is how stringent is the standard (National Regulation 253/79). Regarding the quality and uses of the estuary “Río de la Plata” (Class 2b: Water bodies intended for recreation by direct contact with the human body) the standards for direct discharge are: pH between 6 and 9, BOD₅ max 60 mg/L, TSS max 150mg/L, Oil and grease max 50mg/L, Sulphur max 1mg/L, TP max 5mgP/L, Faecal coliforms max 5000UFC/100mL, and ammonium max 5mgN/L. In this case the underwater emissary was designed so that the effluent of the same, complies with these standards, considering that the effluent of the plant will have the following

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characteristics: BOD₅ <130 mg/L, TSS< 150mg/L, TP < 6mg/L, Oil and grease< 50 mg/L, and Faecal Coliforms< 1000 UFC/100m, as is referenced in the executive project. These parameters are the reference for the authorities to control the plant. Also, is monitored the zone of the discharge to evaluate the performance of the emissary.

Once per month samples of the effluent are analysed by the central Laboratory of OSE, and once per year these values are reported to DINAMA. In terms of BOD, the plant was designed to have at least 50% of removal in terms of BOD, 65-70% in terms of TSS and 99.99% of pathogens. In the evaluation period, the plant achieves removal around 75% reaching values of 90% of BOD. In terms of TSS, during this period the average was near the maximum value, but in the reports presented to DINAMA, the plant reaches the values expected.

1.2.1. Coastal Sewer system

Ciudad de la Costa is a city of Uruguay, located on the margin of the estuary “Río de la Plata” (see Figure 1-2), next to the capital, Montevideo. Is a coastal city developed in parallel, the south of the country and represents one of the main axes of urban expansion of the capital.

The coastal sewer system is formed by 5 different towns, located near the plant, being Ciudad de la Costa, the biggest one, in area and population, as can be seen in Figure 1-3. At the present time, these towns have separate sewer systems, using ponds as treatment for wastewater, except Ciudad de la Costa city. In this case, the sewer system is being constructed, and most of the houses have septic tanks, emptied and delivered by vacuum trucks to the plant. Pando city is connected to the WWTP but the other towns will be progressively connected prior to 2035.



Figure 1-2: Location of Ciudad de la Costa, Canelones, Uruguay. Source: Google Earth

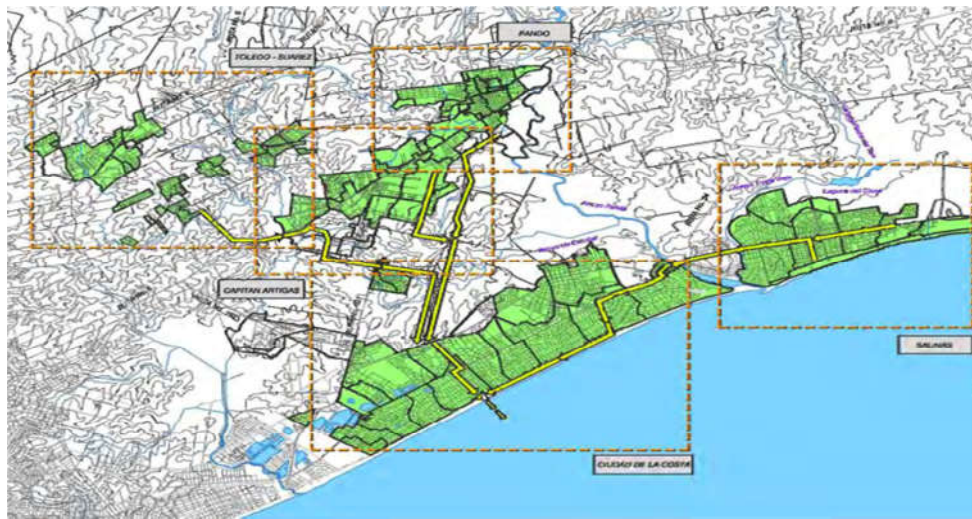


Figure 1-3: Coastal sewer system projected for 2035

In the master plan of OSE, the wastewater generated in all these towns will be treated in WWTP of Ciudad de la Costa. Therefore it was required to design and construct pipelines and pump stations to convey the wastewater to the plant. For these reasons the design of the plant considered a population served from 344,000 to 2035.

The different stages of this project can be seen in Figure 1-3 where the first phase covers Ciudad de la Costa city (in red) and will be finished at 2020, while the system for the other towns will be finalized at 2035. Also at this time the expansion of the WWTP is projected, with the construction of another module of 8 UASB reactors as the existent module.

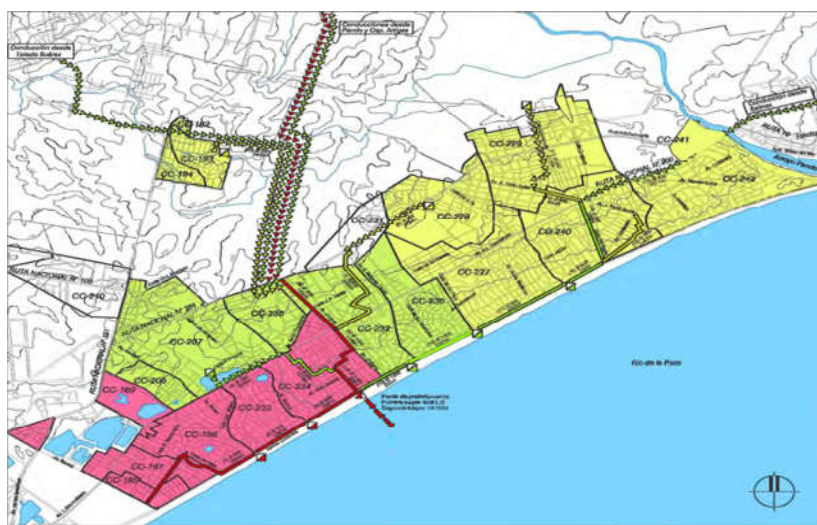


Figure 1-4: Phases of the project, in red the sewer system of Ciudad de la Costa city for 2020, in green the second phase.

This WWTP has been designed to mainly to remove organic matter by anaerobic reactors and pathogens by chlorination. The pre-treatment consists on fine screens (6 mm) and a grit chamber. The secondary treatment consists of 8 Up-flow Anaerobic Sludge Blankets (UASB) in parallel, to remove the organic matter. The effluent of the reactors is directed to the disinfection step with chlorine, followed by dechlorination. The final effluent is discharged in the coast of the estuary “Río de la Plata” through a subaquatic emissary 1 km from the coastal line.

1.2.2. Design capacity and operation parameters

The final design of the plant consist of 4 modules (named A, B, C and D) with 4 reactors each of 2363 m³ of volume, but at the present day 2 modules are constructed (A and B). Module A has reactors 201 to 204, while modules B are the reactors 205 to 208. The plant is designed for a loading rate of 38.000 kgCOD/d and total average flow rate of 74.131 m³/d. This full capacity will be achieve at 2035.

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Table 1-1: Design parameters for different stages

Parameter	Operation condition	
	2015	2035
Operating reactors (units)	8	16
Volume of each reactor	2363	2363
Retention Time (h)	16	12
Flow rate for each UASB (m ³ /h)	150	197
Up flow velocity (m/h)	0.32	0.42
Loading rate (kgCOD/d)	16.882	38.081

1.2.3. Current situation and issues

One of the problems reported, are related with the removal of the scum from the reactors. The channel inside the reactors used to convey the scum, by gravity, to the tank, is not working properly. Due to that, it is removed manually from the top of the reactors, firstly was done every day, but nowadays is twice a week. However, this operation was until December, nowadays the process of cleaning is done once per week.

Another relevant issue is the change in reactors that are operative, this procedure produces certain instabilities in the process and the biomass. For instance, the reactor 201 was operative the first six months (201), in 2016 two different reactors were operative (203,204), and at present reactors 201 and 202 are in operation. In these cases the operators identify gases escaping from the effluent of reactors 203 and 204. Also the gasmeters are not calibrated, and the biogas production can't be measured in the plant.

In addition, the consumption of alkalizing products in the plant is quite high, and the analyses of the plant in terms of VFA are not accurate. There is a lack of information to do a complete analysis of the plant, using the historical data. Also to determine the efficiency of the plant in the coldest months is impossible.

Finally, the sludge of the reactors has a high amount of sulphates and iron, so is not possible to send to an appropriate land field. At present day it is disposed in the plant, waiting for a final solution.

1.2.4. Treatment line

As is shown in Figure 1-5, the influent comes from three sources, the town of Pando and from the septic tanks of Ciudad de la Costa. The sludge from the trucks is discharged in three pit chambers, goes to an equalization tank with grease trap, and pumped to the loading chamber

of the plant, where is discharged Pando sewer system. All the pump stations have screens of 25 mm, to protect the electromechanical equipment.

Pre-treatment has three parallel lines, with fine screens controlled by three Parshall flume and circular grit chamber, also is added the alkalizing in the Parshall flume.

The effluent of the grit chamber goes to UASB modules, and after there to disinfection with liquid chlorine and after minimum contact time of 30 minutes, residual chlorine is dechlorinated by sodium metabisulfite. The effluent goes to the pipeline, by gravity that ends in the estuary at 1 km of the coast.

The sludge digested in UASBs are regularly extracted and conducted by a pumping station to two sludge concentrating tanks, after which they are pumped to the two centrifuges to dewatering. Rejected water from thickening and dewatering of sludge are conducted by pumping to the entrance chamber to the UASB reactors.

The supernatant foams produced in the UASB are regularly extracted by a gravity extraction system and taken to two separation and pumping chambers. The separated and concentrated foams are homogenized and pumped into the sludge collection tank to be dehydrated in the centrifuges. The residual liquids from the separation of the foams are conducted by pumping into the loading chamber at the pre-treatment entrance.

The drained sludge is conditioned as bio solids for agricultural use through a vermicomposting process or alternatively sent to landfill.

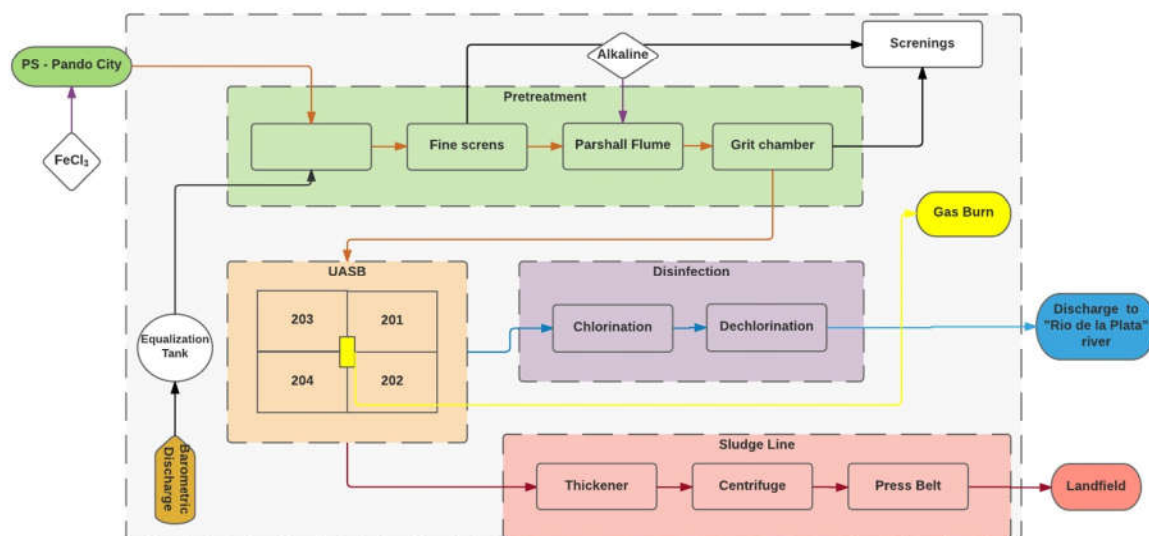


Figure 1-5: Scheme of WWTP

Excess of sludge removed from the UASB goes to the thickener, mechanical dewatering and then is disposed in a landfill. Also, scums removed from UASB and grease from the septic trucks, goes to a decanter tank, where the solids go to thickener and water to pre-treatment.

The plant has odour control treatment for the covered units; the biogas produced in the anaerobic reactors is expected to be burned using flare device. In addition, the plant has an

Introduction

automatized control system (SCADA Figure 1-6) but not all the sensors are working due to the lack of calibration.

For monitoring the process, water samples from influent, effluent and biomass in the reactors are grabbed once a month from the sampling points. These procedure was done in this way until June 2016, from there the monitoring was only in the reactors once a week (mostly) and for the effluent once per month.

Parameters measured in the effluent are: BOD₅, TSS, SS, pH, and Alkalinity (carbonaceous), due to the standards of discharge that the plant has to achieve.

In case of the operation of the reactors, VSS, TSS, pH, alkalinity and the solids profile from the blanket of the reactor. This last point only was until June 2016, after that were measured only the VSS and TSS of a representative sample of the reactor.

The flow from the pumping stations is monitored by the SCADA and the total inflow is measured by a Parshall flume located after the grit chamber. Daily and monthly reports are done automatically by the SCADA.

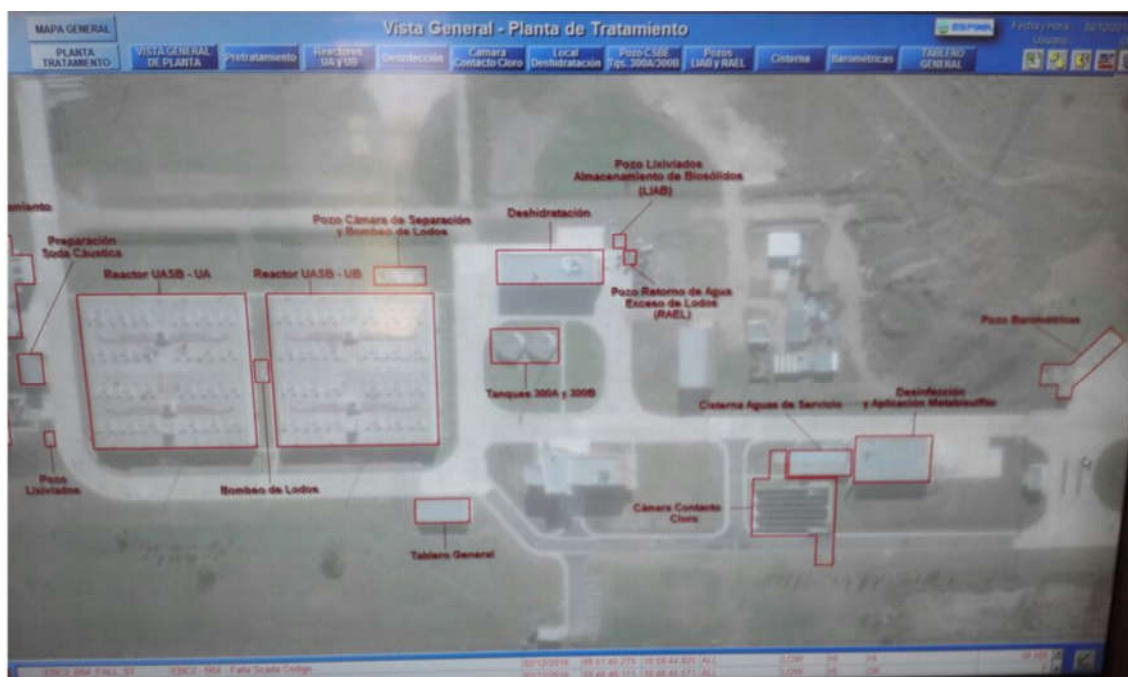


Figure 1-6: General layout view of the plant in the SCADA

1.2.5. Influent sources

The sources of the WWTP are the sewer system from Pando city, located at 10 km from the plant, and from Ciudad de la Costa. The wastewater from Pando is pumped through a pipeline GFRP (Glass-Fiber Reinforced Plastic) with a nominal diameter of 500 mm, and an average of 2700 m³/d. To avoid odours in the intermediate pumping station (“La Tahona”), is dosed Introduction

Iron Chloride in the pump station of Pando, in average 120 kg/d of FeCl_3 with 40% of concentration in weight.

From “Ciudad de la Costa” city comes the 30% of the total influent mostly is delivered by vacuum trucks. Near of 100 trucks with 15 m³ discharge in the plant between 8 am to 17 pm, maximum three trucks at the same time. In addition, there is a pump station for the sewer system, for the 400 households connected, with an estimated of 30 l/s.

The content of the vacuum trucks is delivered to small equalization tank, of 26 m³, designed to take out the scums, oil and grease coming from the trucks, and with a HRT between 9 and 15 minutes. From these tank is pumped to the head of the plant, to pre-treatment and the scums goes to a dewatering tank for the scums.

The septic wastewater conveyed by the trucks, mostly are from kitchens and bathrooms of the households, but also some industries. The control of these trucks depends in the departmental authority, and the WWTP can deny the discharge, due to the high pH, colour or suspicious origin. Also, due to the high content of sand in the wastewater from septic tanks, minimum once a week is required to clean the equalization tank.

1.2.6. Pre-treatment

All the influents are pumped to the head of the plant, the pipelines of the pumping stations and from the vacuum trucks. The water from the thickening of sludge and the scums, go to the pre-treatment, as well. The wastewater from the sewer systems passes through a pump station, with a screen of 25 mm. Also the tank of the vacuum trucks has a deflector to avoid the larger particles. Due to that, the first step of pre-treatment are two mechanized fine screens (6mm). After that, in the Parshall flumes, is measured the flow is measured, and the alkalinizing is added. Last step is in the girt chambers, and after that goes to the UASB. To prevent the acidification in the reactors, sodium hydroxide is dosed as alkalinize in average is used 125 kg to 300 kg per day. The sand and screenings are cleaned once or twice a week, and goes to landfill.

1.2.7. Sludge line

At the present day sludge the sludge is dewatered by a centrifuge and deposit in the field of the WWTP. The original project considered using composting for later use as soil improver, but the results were not satisfactory. From OSE was assessed to send them to landfills, but due to the high content of sulphates and metals (iron) have not been accepted. Currently they are being gathered in the field of the plant, while a feasible option for this sludge is being studied.

1.3. Problem statement

The design of the plant was performed for a higher flow and organic load than it currently receives. The scenario established for this moment, is far away, given the backlog in the construction works of the sewer and pumping stations planned for this time. Almost two years after its start the operation, the average flow of the tributary to the plant is 30% of the average design flow, a difference of 20% with respect to the estimated flow for 2017. Due to this the configuration established in the project does not correspond with the current scenario,

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generating operational problems. In turn, the operators and technicians of the company O.S.E have little experience in this type of treatment, as this is the second anaerobic wastewater plant, the only operand, but with a treatment capacity 10 times greater.

In the other hand, starting an anaerobic reactor requires more time than traditional systems, due to the multiple factors that can affect the process. This can be reduced by having qualified operators, as well as good frequency in the monitoring the process, and control key factors such as SRT, accumulation of inert solids and scums in the reactors, favouring the conditions required for mass transfer between the sludge and substrate.(Chernicharo 2007)

Therefore, within the evaluation of the plant to be performed, it should be analysed whether the process is stable, in terms of efficiencies and yields, or whether actions should be taken to complete the start-up process.

Hence, is necessary to evaluate the operation of the plant, determinate the state of the process, focusing on the operating parameters of UASB reactors, their efficiency of removal of organic matter and optimum operating range, in the current scenario of low flow and high loads.

In addition, vacuum trucks convey the wastewaters from the zones without sewer system, mainly from Ciudad de la Costa city, but also from other near towns. The amount of trucks estimated by the WWTP is 100 per day, while in the design were 60 trucks per day. The content of the trucks is mostly domestic wastewater, but with high contents of sand. Due to this, the influent to the plant increases 40% from the average inflow without trucks discharge, concentrated between 8:00 to 17:00, from Monday to Friday. So, the impact of these discharges should be assessed, in the overall process of the plant.

On the other hand, to minimize odours in the plant, ferric chloride is dosed in the pumping stations, which reduces the formation of H_2S , precipitating the sulphate present as FeS . Due to this, the reduction of sulphate inside the reactors in the presence of ferric chloride should be analysed, as well as the optimal dosage. (Hvitved-Jacobsen et al. 2013)

One of the advantages of anaerobic treatment is the production of biogas, which can be used as fuel. Moreover, the production of biogas is used as a control parameter of methanogenic activity in anaerobic reactors. (Chernicharo et al. 2015) However, in this WWTP, the gas meters are not calibrated, so a theoretical production of biogas in the plant is estimated, and compared with results obtained in similar plants.

Finally, mathematical modelling of the anaerobic plant can be used to analyse the performance of the anaerobic reactors, also to estimate the biogas production, and analyse the impact of the discharge of vacuum trucks. Additionally, if a validate model is achieved, can be used to explore different scenarios (van Lier, *et al.*, 2015).

1.4. Research objective

The aim of this study is to assess the performance of the WWTP of Ciudad de la Costa, during the first year of operation, by determining the efficiency of the anaerobic reactors in terms of BOD, COD and TSS, regarding the intermittent discharges, and the impact of dosed

chemicals (iron chloride) on the process of sulphide reduction. Additionally, estimate the biogas produced and the formation of hydrogen sulphide.

1.4.1. Specific research objectives

- Evaluate the efficiency of the UASB in terms of COD, BOD and TSS, from February to June 2016,
- to determinate the state of the process in the UASB reactors,
- Evaluate the impact of the iron chloride in the production of sulphide in the reactor,
- Estimate the production of biogas in the plant,
- Implement a computational model of the plant to analyse the production of hydrogen sulphide and methane.

CHAPTER 2

Literature review

In this section, the current state of relevant literature for this research is summarized, mostly for the assessment of the anaerobic reactor, modelling of UASB and the fate of endocrine disruptors in sewerage treatment plants.

2.1. Anaerobic Treatment of wastewaters

Anaerobic digestion is a biological process that involves different communities of microorganisms, who perform the degradation of organic matter and produce biogas (methane and carbon dioxide mainly). This process occurs in different places (sediments, soils, digestive organs ruminants), without presence of oxygen (low redox potential) (van Lier, *et al.*, 2008) where each community consumes what is produced in the previous step.

This process usually is presented as two main stages, the decomposition of the organic matter (acid forming step) and the gas-forming step. This is done by facultative and strictly anaerobic microorganisms that produce volatile fatty acids (VFA), carbon dioxide, hydrogen gas and other simpler organic materials from the organic compounds (carbohydrates, proteins and lipids). In the second stage, these compounds are transformed in methane and carbon dioxide by the methanogenic microorganisms (archaea) in a strictly anaerobic environment, using the substrate produced by the acid forming bacteria. Also the presence of other electron donors as SO_4^{2-} and NO_3^- other group of bacteria could be developed to compete for the substrate as denitrifiers and sulphate-reductor groups.

2.1.1. Description of the process

The anaerobic digestion could be divided in four metabolic pathways: hydrolysis, acidogenesis, acetogenesis and methanogenesis, in each one there are different microorganisms involved and is represented in Figure 2-1. In this process, the products of each step are used as substrate in the next that means a complex consortium of microorganism and biochemical process to achieve this.

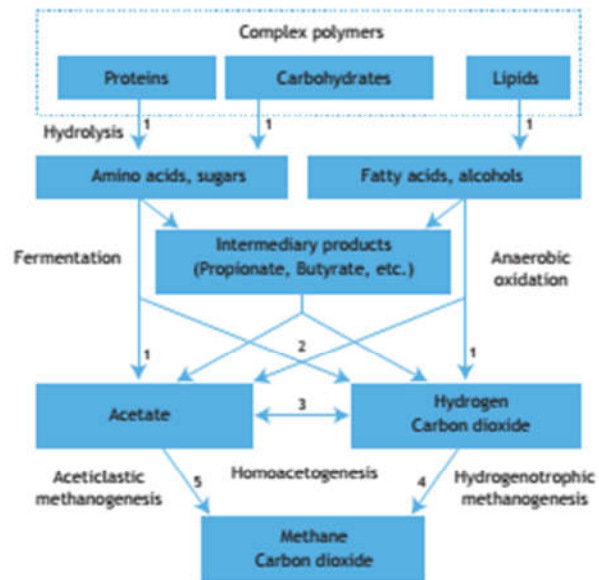


Figure 2-1: Metabolic pathways and microorganisms involved.

Source: (van Lier, et al., 2008)

Degradation and Hydrolysis

The particulate material (polymers) from the substrate has to be dissolved in to smaller compounds, to allow pass through the cell wall of the fermentative bacteria. This is done by enzymes excreted by fermentative bacteria (acetogenic bacteria), called exo-enzymes. Due to be a surface phenomenon, this process is slow inasmuch as has several factors that affect the rate and the degree of the degradation. For example, pH, temperature, size of the particles, and biodegradability of the substrate. Domestic wastewaters has high content of SS (45 to 75%), low temperatures and organic load, also high percentage of proteins, carbohydrates and lipids, so this step is the rate limiting for the overall process. (van Lier, et al., 2008)

Acidogenesis

Hydrolysis products are anaerobically oxidized or fermented inside the cells and excreted as VFA's (mainly acetate, propionate, and butyrate), alcohols, lactic acid, carbon dioxide, hydrogen, ammonia and hydrogen sulphide also as new cells. The species related with this process are large group of hydrolytic and non-hydrolytic bacteria, clostridia group and the family of *Bacteroidaceae*. (Chernicharo 2007; van Lier et al. 2008)

In addition, acidogenic bacteria have the highest yield and conversion rates, being the quickest reaction of all the processes, as is shown in Table 2-1. Due to this, if the microbial population is not equilibrated, methanogenic cannot consume the VFA as the same rate is produced, due to overloading the reactor or presence of toxic compounds. In this case, these acids accumulate in the reactor, consuming the alkalinity of the system and dropping pH, which leads to the inhibition of the methanogenic bacteria. This situation is called souring of the reactor, for the odour emitted. (van Lier et al. 2008)

Literature review

For this reason, the identification of short chain volatile acids (formic, acetic, propionic, butyric, valeric and isovaleric acids) presents in the reactor is used to check the equilibrium of the species. Short chain volatile acids are characterized for the low molecular weight, and at atmospheric pressure can be distilled. The most important precursors of methane formation are acetic and propionic acids, mostly acetic acid because it is formed from all the organic compounds while propionic acid only by fermentation of carbohydrates and proteins. Other acids such as ethanol and lactate are reported but in low concentrations and quickly degraded to acetate. These ones appear in substrates with high concentration of glucose, or in reactors with pH lower than 5. (Batstone et al. 2002)

Table 2-1: Average kinetics parameters of acidifiers and methanogens

Process	Conversion rate gCOD/gVSS.d	Yield gVSS/gCOD	K _s mgCOD/L	μ _m 1/d
Acidogenesis	13	0.15	200	2
Methanogenesis	3	0.03	30	0.12
Overall	2	0.03-0.08	-	0.12

Source:(van Lier et al. 2008)

Acetogenesis

Digestion products of acidogenesis are converted into acetate, H₂ and CO₂ by the acetogenic bacteria, and from H₂ and CO₂ by homoacetogenic bacteria, in this case is called homoacetogenesis. Acetogenic microorganisms are sensible to the concentration of hydrogen, so they require the H₂-consumers as the methanogenics to maintain the hydrogen under certain concentrations. Other way to decrease the amount of hydrogen produced during this process, is through the formation of organic acids (propionic and butyric acids) from hydrogen, carbon dioxide and acetic acid, by fermentative bacteria.

This process takes relevance in the hydrogen oxidation under 20°C (psychrophilic conditions), due to the low activity of the methanogenic organism. For this reason, homoacetogenesis is not included in the model of the anaerobic digestion. (Batstone et al. 2002)

Thermodynamically, some reactions to convert the intermediate acids to acetate in standard conditions (25 C°, 1 atm) are unfavourable ($\Delta G^{\circ} > 0$), like propionate, butyrate and ethanol, In Table 2-2 standard free energy for this reactions are showed assuming, neutral pH, the activity for soluble compounds is 1mol/kg and the liquid as pure water.

If the concentration of hydrogen is maintained low, the acids will be degraded and the acetate will be produced. This happens when microbial population is equilibrated; the production of H₂ by acetogenics is consumed at the same rate by methanogenic bacteria, conserving the partial pressure of H₂ between 10⁻⁴ to 10⁻⁶ atm, allowing the production of acetate by propionate, butyrate and ethanol.

Table 2-2: Stoichiometry and standard free energy of Gibbs for the acetogenic reactions regarding 25C°, 1 atm, neutral pH, water as pure liquid, and all the soluble compounds with activity on 1 mole/kg

Intermediate acid	Reaction	ΔG^0 (kJ/mol)
Propionate	$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$	+76.1
Butyrate	$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+48.1
Ethanol	$CH_3CH_2OH + H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+9.6
Lactate	$CH_3CHOHCOO^- + 2H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 2H_2$	-4.3

Methanogenesis

Methanogenesis is the last step where the substrate is transformed in to CO₂ and CH₄, using as substrate acetate, methanol, methylamines, formate, H₂, CO₂ and CO, but in general, 70% of the methane is produced from acetate. There are two main groups of anaerobic microorganisms involved both archaea: aceticlastic methanogens (acetate users) and hydrogenotrophic methanogens (hydrogen users). Aceticlastic methanogens grow rate is very low (doubling time 1 to 6 days), comparing with the hydrogenotrophic that have doubling times of 4 to 12 hours. (van Lier, *et al.*, 2008).

These process consumes the hydrogen produced in the previous phases, controlling the partial pressure of hydrogen, to allow the acidogenesis and acetogenesis process. This microbial association between the acetogenic and the hydrogenotrophic bacteria (hydrogen produced – consumed) to maintain the partial hydrogen pressure in optimal conditions (10⁻⁴ atm) is called syntrophic association, and the equilibrium between this species are clue to the process. (Batstone et al. 2002)

Table 2-3: Reaction characteristics in Methanogenesis

Methanogen group	Reaction	ΔG^0
Aceticlastic	$CH_3^-COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	-31
Hydrogenotrophic	$CO_2 + 4H_2 \rightarrow CH_4 + H_2O$	-131

Aceticlastic methanogens are composing of two different genres: Methanosarcina spp. (coccus shape) uses different type of substrate as acetate, H₂, CO₂, methylamines, methanol and formate and Methanosaeta spp. are developed in filamentous form and uses only acetate as substrate. Also has high affinity than Methanosarcina spp. so could develop under low concentrations of substrate (10⁻³ M of acetate), but there are more sensitive to pH and has lower growth rate yield. These characteristics are summarized in Table 2-4. (van Lier et al. 2008)

Literature review

Table 2-4: Kinetic characteristics of the different functional groups Source:(van Lier et al. 2008)

Functional step	μ_{\max} (1/d)	Td (d)	K_s (mgCOD/L)
Methanosarcina spp	0.12	5.8	30
Methanosaeta spp	0.71	1.0	300
Hydrogenotrophic methanogens	2.85	0.2	0.06

In reactors with high solid retention times, as sludge bed systems and anaerobic filters, the substrate inside the granules or flocks are near zero, with low concentrations of the influent. That allows the growth of the *Methanosaeta spp*, than *Methanosarcina spp*. producing an effluent with low concentrations of acetate. (Chernicharo 2007; van Lier et al. 2008)

In other hand, practically all hydrogenotrophic methanogens uses hydrogen and carbon dioxide to produce methane. *Methanobacterium*, *Methanospirillum* and *Methanobrevibacter* are the more frequently isolated in anaerobic reactors (Chernicharo 2007; van Lier et al. 2008)

Sulphate reduction

If the wastewater contains sulphate or sulphite, the process includes a new group of microorganism, called sulphate reducing bacteria (SRB) that can use these compounds as electron acceptor to produce hydrogen sulphide.

(Chernicharo 2007; van Lier et al. 2008) divide in groups of SRB regarding the pathways, ones that oxidise organics acids or H_2 . One group uses organic acids oxidise to acetate, meanwhile the other uses acetate and organics substrates to carbon dioxide. The interest in sulphate reduction is increasing as the identification of the different types of microorganism involved as is showed in (Hao et al. 2014)

As is shown in Figure 2-2, the SRB can use as substrate the intermediate products of the acidogenesis, also acetate and H_2 , and compete with the fermentative, acidogenic, acetogenic and methanogenic bacteria, decreasing the production of methane. In Table 2-5 some reactions of SRB are shown.

Table 2-5 Sulphate reduction reactions

Substrate	Reaction
Propionate	$4C_2H_5 COOH + 7H_2SO_4 \rightarrow 12CO_2 + 12H_2 O + 7H_2 S$
Acetate	$CH_3 COOH + H_2SO_4 \rightarrow 2CO_2 + 2H_2 O + H_2 S$
Hydrogen	$4H_2 + H_2SO_4 \rightarrow 4H_2 O + H_2 S$

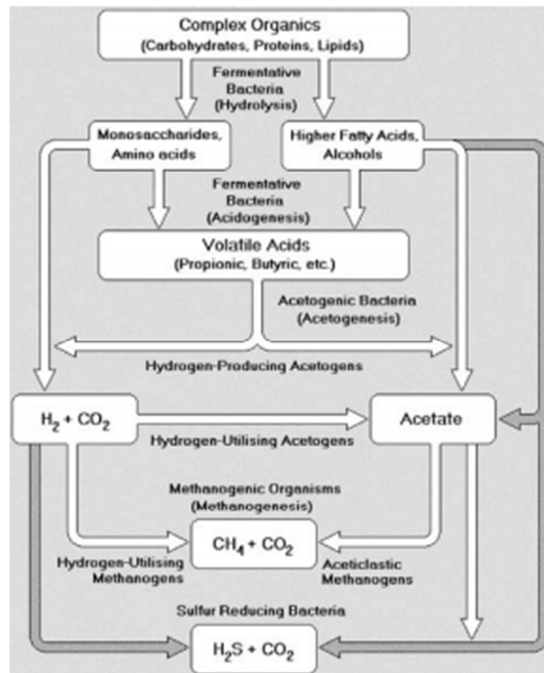


Figure 2-2: Metabolic pathways when sulphate reduction bacteria are presents

Source:(Chernicharo 2007)

Depending on the pH and temperature of the reactor, sulphur can found as H_2S , HS^- or S^{2-} , at low pH mainly present as hydrogen sulphide, a gas with solubility higher than methane in water. In sewage temperature (25°) and neutral pH it is not expected to find free sulphide (S^{2-}) as is shown in Figure 2-3, where the concentration of the different species are plot vs. pH of the medium.

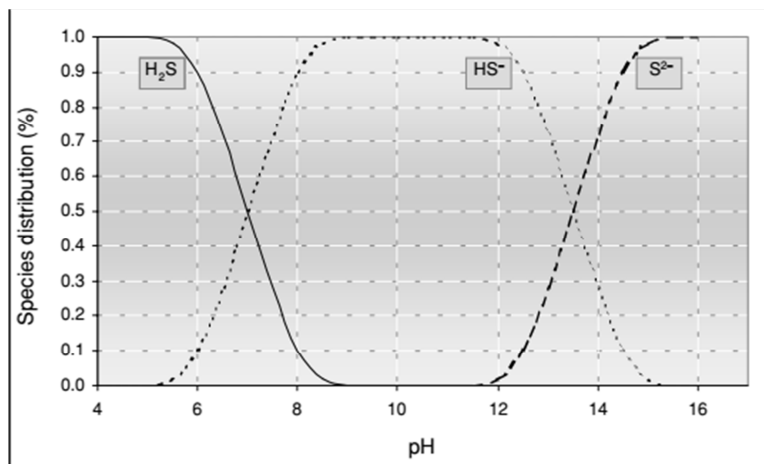


Figure 2-3: Sulphate system

The main problem is that at pH 7, H₂S and HS⁻ are present in the same proportion, and H₂S is toxic to methanogenic, acetogenic bacteria and also for SRB, decreasing the yield of growth and the quality of biogas. For instance, the average concentration of inhibition for methanogenic bacteria is around 30 to 250 mg S-H₂S/L. In addition, it is toxic for humans at concentrations higher than 10 ppm and dead risk at 300 ppm, also lower detection threshold 0.00047 ppm. Besides of these, the reactor itself, can be affected by sulphuric acid, produced by oxidation (chemical or by sulphide oxidizing bacteria) as well as in sewer pipes and manholes. For instance, in Table 2-6 are presented typical concentrations of H₂S in gas phase, in different points of the sewer system (Chernicharo et al, 2015)

Table 2-6: Reported ranges of presence of H₂S in different units

System Unit	Range reported of H ₂ S	
	mg/m ³	ppm
Sewerage	0-417	0-300
	70-556	50-400
Pumping station	0.57	0.7
	1-3	0.7-2
	4.8	3.3
Pre-treatment	2.8-51.5	2-37
	3.5	2.4
Dewatering	6.5	4.5
Waste gas from settled zone UASB	0-73	0-50
Waste gas downstream UASB	146-730	100-500

Source:(Chernicharo et al. 2015)

Besides, the biogas produced has H₂S, resulting in a decrease in the quality, depending the final use, and needs to be removed. Other nuisance associated with it is the formation of metal compounds, as FeSO₄. The concentration of H₂S removed from the water phase, increases with the biogas production, so the effect of sulphide in anaerobic reactors depends of the pH and COD/SO₄⁻² ratio. If that ratio is over ten, the H₂S will be release from the water, decreasing the effect in the biomass but generating other issues.

Besides of the production of H₂S, the methane production decreases, due to the consumption of organic matter by SRB, because per mol of SO₄⁻² oxidized to sulphide, 2 moles of O₂ are required, that means 0.67 g COD per mol of sulphate oxidised. (Chernicharo 2007; van Lier et al. 2008)

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Sulphate reduction will occur even with low concentrations of sulphates, as is present in domestic wastewaters. Most of the solutions focus on an aerobic post treatment of effluent with recirculation (stripping H₂S, absorption, biological removal), treating biogas or pre-acidification of the effluent, to remove the sulphate, by physiochemical process.

2.1.2. Relevant factors for the anaerobic digestion

Temperature

Temperature is an environmental factor that affects the overall process in the reactor. Most of the kinetic behaviour and thermodynamic rates are temperature depending, also the solubility and other physiochemical parameters of the medium. Temperature affects the net growth rate, is expressed in terms of this two competitive process, bacterial synthesis and decay, both of them represented by Arrhenius equation as is shows in the follow equation:

$$K = k_s e^{\left(\frac{-E1}{RT_{abs}}\right)} - k_d e^{\left(\frac{-E2}{RT_{abs}}\right)}$$

Where

K_s= bacterial synthesis rate

K_d= bacterial decay rate

E1, E2= activation energy of each process (cal/mole)

T_{abs}= absolute temperature (K)

R= gas constant (1.98 cal/mole*K)

The growth rate increases exponentially to reach the optimum temperature, after that decreases rapidly to zero, giving the maximum temperature possible.

Regarding the operational temperature, anaerobic microorganisms can be divided in three groups, regarding the operational temperature: psychrophilic (4–15°C), mesophilic (20–40°C), and thermophilic (45–70°C). For mesophilic and thermophilic organism's optimal temperature is 30°- 35° and 50°-55° respectively. Most of the experience in anaerobic digestion is under mesophilic conditions. According to (Batstone et al. 2002), temperature changes the disintegration rates and the first order hydrolysis rate, both described by an Arrhenius equation.

Under psychrophilic conditions, methanogenic activity decreases therefore a lower production of methane occurs, mostly for the lower hydrolytic rate. Due to these, is necessary to increase the solids retention time and decrease the loading rate, to prevent acidification in the reactor, particularly in case of substrate with high content of suspended solids (Van Lier et al. 1997). According to (Batstone et al. 2002; Dhaked et al. 2010) the main pathways for methane production is from acetate and aceticlastic methanogenic activity, hence the Homoacetogens and Methanosaeta out-compete hydrogenotrophic methanogens. In addition, mesophilic methanogens are shown as psychrotolerant instead of psychrophilic organism, the activity rates decreases, but the community structure is the same. Although, there are in nature psychrophilic methanogens, in anaerobic reactors they are rarely found.

Literature review

In other hand, at higher temperatures like thermophilic conditions, the sludge retention time is shorter and the loading rate can increase, resulting in a higher methane production. Some of the advantages are related to the inactivation of pathogens; the release of toxic compounds to the gas phase, as well as the biogas produced could be used in the process to heat the influent. However, the operational disadvantage might be poor quality of the effluent and the instability of the process. (Van Lier et al. 1997; Chernicharo 2007)

Nutrients

Nutrient requirement is based on empirical composition of the microbial cell, regarding the similar composition and proportions for all the cells, and assuming the same nutritional needs. In order of relevance, the compounds are: nitrogen, phosphorus, sulphur, iron, cobalt, nickel, molybdenum, selenium, riboflavin and vitamin B12. Some of them are macronutrients regarding the concentration required, while for the others a low concentration is required. In case of domestic wastewaters these compounds are present in the concentration and the variety or the required nutrients.

pH, alkalinity and VFA

Anaerobic microorganisms are a complex community affected by pH fluctuations, the optimum pH for all processes is around 7. For methanogenic microorganism the optimum is between 6.6 and 7.4, a pH below 6 and above 8.3 could inhibit them. For SRB optimal pH ranges are similar to methanogens, but at a pH lower than 7 they have higher growth rate.

The decrease of pH is related to a low alkalinity of the medium and disequilibrium in the production-consumption of VFA. As was explained in 2.1.1, methanogenic activity decreases with the pH, increasing the concentration of acids. Acidogenic microorganism can work at pH 5 to 6, strengthening the accumulation of acids in the reactor until the complete inhibition of methanogenics.

The buffer capacity of the system can prevent problems pH fluctuations, and is conditioned by the alkalinity. In anaerobic digestion, carbonic acid and volatile acids are the main factors. At pH 6 to 7.5 the buffer capacity depends of carbonate and VFA concentrations.

During the digestion of organic compounds the alkalinity formed by the conversions of VFA and amino acids, neutralizing the acid formed in the process and buffering the accumulation of them. To prevent the acidification of the reactor, other sources of alkalinity are required.

For instance: hydrated lime ($\text{Ca}(\text{OH})_2$), quicklime (CaO), sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3), sodium hydroxide (NaOH), and ammonia bicarbonate (NH_4HCO_3) are used as external sources. These compounds can provide bicarbonate alkalinity directly (NaOH , NaHCO_3 , NH_4HCO_3) or by reacting to form bicarbonate (CaO , $\text{Ca}(\text{OH})_2$, NH_3). The cheapest solution is lime, reacting with CO_2 , but has associated accumulation of solids inside the reactors, due to the low solubility. Also the use in closed reactors could increase the pH values higher than the optimum range, due to the lack of CO_2 available in the reactor. In other hand, sodium bicarbonate is highly soluble, and the reaction is without dioxide, but is more expensive.

However, for operational purposes, the portion of alkalinity of volatile acid at pH 4.3 is 85% of the total at this end point. So the relation between Bicarbonate alkalinity (BA), total alkalinity (TA) and partial alkalinity or intermediate alkalinity (IA) is showed in the next equation:

$$\text{Equation 2-1: } BA = TA - 0.85 * 0.83 * VFA$$

Where:

BA = bicarbonate alkalinity (as mgCaCO₃/L)

TA = total alkalinity (as mgCaCO₃/L)

VFA = concentration of volatile fatty acids (as mg Hac/L)

0.85 = corresponds to the factor of ionisation of the acids to the titration point

0.83 = conversion factor from acetic acid into alkalinity

According to (Ripley et al. 1986) to determine these values, a titration process in two stages can be performed, until pH 5.75 to determine the bicarbonate alkalinity (partial alkalinity PA) and to pH 4.3 related to the alkalinity of VFA (intermediate alkalinity IA). To evaluate the stability of anaerobic reactors, the most used is ratio alkalinity due to VFA/bicarbonate alkalinity (IA/PA), values higher than 0.30 means disturbances in the process, and needs correction. Moreover, values higher than 0.8 implies complete inhibition of methanogenic activity and the acidification of the system. (Chernicharo 2007) But this value depends of the type of wastewater analysed. (Sun et al. 2016)

Other index used to estimate the buffer capacity are Buffer index, ratio between alkalinity of VFA (IA) and total alkalinity (TA) and related to the acidic condition of the reactor is the Alfa factor, ratio between bicarbonate alkalinity and total alkalinity (PA/TA). Buffer index range is 0.20 to 0.40, implies 60 % of total alkalinity is due to the bicarbonate system, values under 0.20 are related to low load, while values over 0.35 indicates souring of the reactor. In case of the Alfa factor, during start up values are near 0.5, and under stable conditions 0.7. Due to this, is recommended to use these indexes together to have a good estimation of the process inside the reactor. (Pérez and Torres 2008; Li et al. 2014; Sun et al. 2016)

Toxics and inhibitors

Anaerobic systems depend of an equilibrated medium for the microorganism. This equilibrium could be affected by the presence of different compounds in the influent or generated in the process. Compound concentrations above a certain level could be toxic, affecting the rate of the biological process, until complete inhibition. This level could be change due to the acclimatisation of the biomass to a certain compound, so the ranges are not absolute. For instance, for the anaerobic process the most relevant are: oxygen, cations (salts), heavy metals, sulphuric acid, sulphate, ammonia, fatty acids.

In case of cations, the most relevant are sodium, ammonia, potassium, calcium and magnesium and the inhibiting concentrations are shown in Table 2-7. But these concentrations could be higher in case of acclimatisation. One way to solve the inhibiting effects is adding an antagonist salt to the influent.

The presence of ammonia bicarbonate was discussed as beneficial to maintain the buffer capacity, in concentrations of 50 to 200 mg N/L are beneficial to the process. But concentrations of free ammonia (NH₃) high than 1500 mg/L and ammonium (NH₄⁺) higher Literature review

than 3000 mg/L could inhibit the methanogens. Depending on the pH, the inhibition could be caused by the presence of the ammonium ion (pH lower 7.2) or free ammonia. Also under thermophilic conditions fermentation of high ammonia waters is more difficult than mesophilic conditions. (Chen et al. 2014)

Table 2-7: Inhibiting concentrations of different ions in anaerobic digesters

Cation	Moderately inhibiting (mg/L)	Strongly inhibiting (mg/L)
Calcium	2500 -4500	8000
Magnesium	1000-1500	3000
Potassium	2500-4500	12000
Sodium	3500-5500	8000

Source: (Chernicharo 2007)

As was mentioned above, the concentration of sulphide in the reactor depends on the COD/SO₄⁻² ratio of the influent, pH and temperature, the predominance between SRB and methanogenics, all relevant to determine the maximum concentration of H₂S allowed in the reactor. For UASB and reactors with biomass retention capacity, the level reported was 170 mg H₂S/L, but levels higher than 200 mg H₂S/L, can be toxic without an acclimatisation phase. (Chen et al. 2015)

Other compounds present in wastewaters are heavy metals such as copper, zinc, lead, mercury, chromium, cadmium, iron, nickel, cobalt and aluminium, most of them required as micronutrient in different concentrations, but excessive amount of them could inhibit the process. These concentrations could be tolerated due to the presence of sulphates; in order to precipitate 1.8 to 2.0 mg/l of metal 1.0 mg S/L of free sulphide is required. Other removal mechanisms are sorption and chelation using organic and inorganic ligands. (van Lier et al. 2008; Chen et al. 2014)

Sludge retention time

Sludge retention time or solids retention time (SRT) is the average time of the biomass in the system, measured as volatile suspended solids in reactor. In anaerobic digestion, the growth rate of the biomass is low; due to this the SRT has to be higher than aerobic systems. As an empirical rule the SRT has to be 3 times higher than the doubling time (Td) of the rate limiting step, in this case methanogenesis. As the growing rate depends on the temperature, the SRT increases when the temperature decreases, as is shown in Figure 2-4. In case of subtropical conditions (under 20 °C) the SRT is above 100 days, but under regular conditions the SRT is around 30 days, due to the doubling time (Td) of methanogens at 25°C is 10 days. (van Lier et al. 2008)

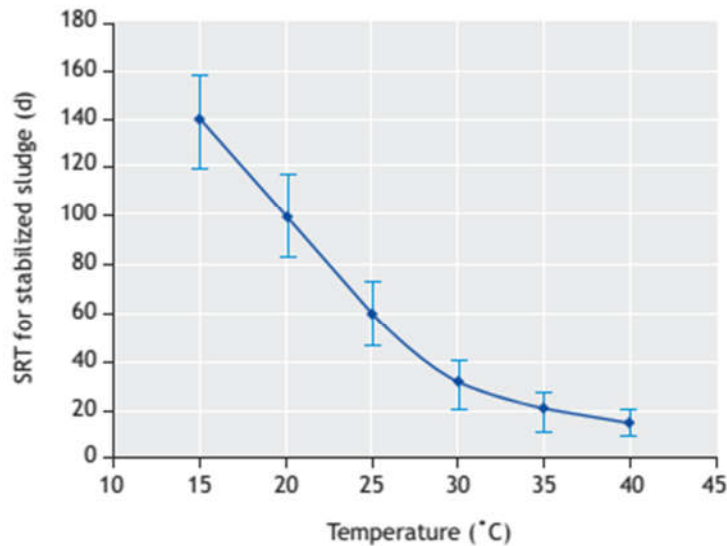


Figure 2-4: Required SRT for domestic sewage treatment vs. temperature

Source: (van Lier et al. 2008)

Internal Mixing

Another aspect relevant to obtain good efficiencies in removal of organic matter is optimizing the internal mixing inside the reactor. To remove the organic matter, the biomass needs to be in continuous contact with the substrate, and dead zones or preferential ways. Complete mixing in the reactor, also maintains the temperature and pH homogenised. The scums formation is avoided, allowing a gas-liquid clean interphase. The mixing could be done by a mechanical mixer or using the biogas produced.

Specific Methanogenic Activity (SMA)

The Specific Methanogenic Activity (SMA) is the measure of the activity of methanogenic sludge under ideal conditions, and measures the maximum capacity of the sludge to produce methane and carbon dioxide from organic substrate. To perform the test, the biomass (gVSS) and substrate (gCOD) are required, and the production rate of methane can be evaluated during test period, controlling conditions, as temperature and mixing. The SMA is reported in terms of $\frac{kg\ COD-CH_4}{kgVSS.d}$ and values of reference can be seen in Table 2-8

Table 2-8: SMA for different types of sludges

Sludge type	Activity at 30°C (kgCOD kg ⁻¹ VSS.d ⁻¹)
Granular Sludge	0.8-1.5
Sludge or other anaerobic reactors	0.4-1.2
Digested sewage sludge	0.02-0.15
Digested manure	0.02-0.08
Sludge from a septic tank	0.01-0.02
Cow manure	0.001-0.006
Primary domestic sludge	0.001-0.003
River sludge	0.002-0.005

Source: UNESCO-IHE notes from van Lier, 2016, (Seghezzeo 2004)

The evaluation of these parameters can be used as routine analysis to quantify the methanogenic activity, for determine the maximum organic load that can be applied, and to determine the toxicity and the degradability of several compounds, also substrates.

Organic Loading Rate

According to (Chernicharo 2007) Organic loading rate (OLR) is the load of organic matter applied per unit of volume of the reactor (Equation 2-2) is a design parameter for different reactors, and allows the comparison of different anaerobic systems. Also, can be calculated based in Monod, from the biomass in the reactors, SMA and a contact factor (fc: 0 to 1) depending the distribution of the substrate in the reactor.

$$\text{Equation 2-2} \quad OLR = \frac{Q * S_0}{V}$$

Where:

OLR: organic loading rate in kgBDO/m³.d or kgCOD/m³.d

Q: average influent flowrate in m³/d

S₀: influent BOD or COD concentration in kgBDO/m³ or kgCOD/m³

V: total volume of bioreactor (m³)

The OLR depends on the type of influent, in case of industrial wastewater there are larger organic loads applied but for full scale design, the load is lower than 15 kgCOD/m³.d, for domestic wastewaters (low concentration) it is **2.5 to 3.5 kgCOD/m³.d**. Also, this value depends in the content of SS, VFA and temperatures of the process, as is presented Table 2-9.

Sludge Loading rate

Biological or sludge loading rate is the mass of organic matter applied to the reactor per unit biomass in the reactor.

$$\text{Equation 2-3} \quad SLR = \frac{Q * S_0}{V * X_{VS}}$$

Where:

SLR: sludge loading rate in kgBDO/kgVSS.d or kgCOD/kgVSS.d

Q: average influent flow rate in m³/d

S₀: influent BOD or COD concentration in kgBDO/m³ or kgCOD/m³

X_{VS}: biomass in bioreactor (kgVSS/m³)

V: total volume of bioreactor (m³)

In case of UASB reactors, the difference between suspended solids and total solids is insignificant, so is used to represent biomass (usually as VSS) instead VS.

(Chernicharo 2007)) recommends SLR between 0.05 to 0.15 kgCOD/kgVSS.d during the start-up of anaerobic reactors, which can gradually be increased until the maximum value, depends of the SMA, so depends in the type of substrates. In case of domestic wastewater the maximum value is between 0.3 to 0.4 kgCOD/kgVSS.d. In case of high rate reactors, these values can be increased.

2.1.3. UASB Reactors

One of the most developed anaerobic reactors is the UASB reactor (Up flow Anaerobic Sludge Blanket reactor). It is a robust and compact technology, with a good efficiency in COD and BOD removal, and also produces stabilized sludge. One of the principles of the UASB is the combination of two units, the anaerobic digester and clarifier. In the bottom a dense flocculent sludge bed or granular sludge is formed and in the top is the settling area, resulting in an uncoupling of the hydraulics and biomass retention, increasing the sludge retention time, while the hydraulic retention time (HRT) is really low. Beside of that, the incorporation of the three phase separator (gas-liquid-sludge separator, GLSS) allows to maintain the different phases and recover the biogas. In the Figure 2-5 is showed a typical scheme of a UASB reactor for sewage wastewater.(van Lier, *et al.*, 2008)

This reactor has an easy design and does not require sophisticated implements to attach the biomass. Due to the low concentrations of the influent, the volume is defined for the hydraulics (HRT), and the biomass is attached to the sludge. (Chernicharo, 2007, van Lier, *et al.*, 2008) However, due to the high content of suspended solids in this type of influent, and in case of low temperature, the overall process is limited by hydrolysis step.

The UASB reactor is fed from the bottom of the reactor, and passes through the *sludge bed*, where the sludge accumulates and is more density. The sludge has good settling properties and can be flocculent or granular, depends on the seed sludge, the characteristics of the influent and the operation of the system. While the influent is passing, the organic matter is converted into biogas and sludge by the biomass in the sludge bed, by the different process described in Table 2-9. The bubbles of the gas rise to the top, providing the mixing required

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between the sludge and the influent. The sludge is dragged with the gas and the water flow, but in the three phase separator, the gas is entrapped by an inverted cone or similar, the sludge settles and comes back to the bottom. There are baffles between the three phase separator and the walls to avoid the escape of biogas, and the water flow carrying some sludge pass through. The outside of the GLSS, works as clarifier, allowing the sedimentation and return of the sludge to the bottom, while the water is collected by overflow weirs.

To achieve that and avoid a high concentration of suspended solids in the effluent, the velocities of up flow in the cross sectional area have to be in a range, depending the type of sludge could be higher. Besides of that, the upward velocity of the biogas has to avoid the turbulence in the GLSS, for conventionally designed devices the maximum is between 2-3 m/h. (van Lier, *et al.*, 2008)

The granular sludge has better settling characteristics, a higher density, and higher fraction of methanogenic bacteria than flocculent sludge. Also the removal efficiency of COD, BOD and TSS is in the range of 50-90%, 40-95% and 50-97% respectively, as is shown in Table 2-9.

Table 2-9: Removal efficiencies in different countries and different temperatures.

Country	Volume (m ³)	T (°C)	HRT (h)	OLR (kg COD/m ³ d)	Influent concentration		Removal Efficiency	
					COD (mg/L)	TSS (mg/L)	COD (%)	TSS (%)
Italy	336	7 - 27	14	0,35	205-326	100-250	31-56	55-80
Netherlands	205	16 - 19	1.5-5.8	2,35	391	-	30	-
Colombia	3360	24	5	1,82	380	240	45-60	60
India	6000	18 - 32	8	1,21	404	362	62-72	70-80
Brazil	120	18 - 28	5 to 15	0.6	188 - 459	67-236	60	70
Colombia	6600	25	5,2	1,75	380	-	60-80	-
India	1200	20-30	6	1,69	563	-	74	-

Source: Adapted from (Seghezzo 2004; van Lier *et al.* 2008))

The UASB is a high rate reactor proven to treat different types of substrates, mostly industrial, with high and complex loads, but also low or diluted influents as sewer or domestic wastewater. In tropical and subtropical countries the number of these reactors has been increased, due to the easy operation, and the simple design, also the reduction of the footprint, compared with other systems, climate conditions also stimulate or favour the UASB. Also the production of biogas, reducing the gas emissions and the stabilized sludge produced, make the UASB an interesting option in domestic wastewater treatment. The major constraint is related to the smell in case of influents with high concentrations of sulphate, or the scum in the reactor. (Chernicharo, *et al.*, 2015)

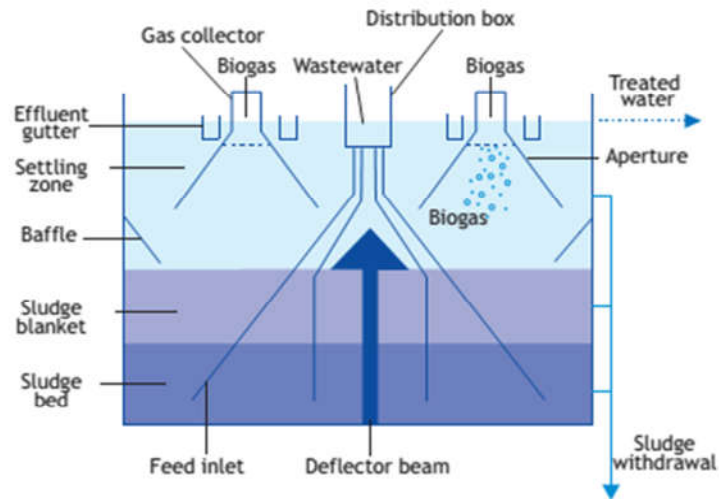


Figure 2-5: Typical UASB reactor for treating sewerage wastewater

Source: (van Lier, et al., 2008)

There are some constraints in the design and operation of the reactors, mostly in the productions of scums and release of odours. This last is related with the presence of sulphide in the influent. That means a reduction of the production of methane and could be problematic if the methanogens are inhibited. Besides of that, the start-up of these reactors is critical and depends of the selected seed and the loading rate steps. If the inoculum is granular sludge the reactor can start up quickly, but it can also take 3 or 4 months.(van Lier, et al., 2008)

However, this technology is being studied and applied in different countries, with different conditions, contributing to the development, searching improvements and solutions to existing problems.

Design guidelines of UASB

The UASB requires fine screenings as pre-treatment to reduce the suspended solids in the reactor, and also depending on the standards of discharge, a post treatment is required, to decrease the phosphorus, ammonia and the pathogens.

The design of an UASB is based on optimizing the high activity of the biomass in the reactor, achieving high removal efficiencies in terms of organic matter (COD, BOD) and stabilised sludge. For this reason, the design criteria are a function of the maximum hydraulic surface loading related to SMA and the biomass in the reactor, the SRT that depends of the temperature, and the hydraulics inside.

The volume of the reactor is limited to the hydraulic or the organic loading rate. In case of domestic wastewaters, the volume of the reactor is defined by the hydraulic surface loading, due to the low concentration. In Table 2-10, the recommended HRT is shown as function of the temperature for domestic wastewaters.

Table 2-10: Recommend hydraulic retention times for domestic wastewater

Sewage temperature (°C)	Average HRT (hours)	Minimum HRT (hours) (max inflow)
16 to 19	10 to 14	7 to 9
20 to 26	6 to 9	4 to 6
> 26	> 6	> 4

Source: Chernicharo 2007

The up flow velocity (V_{upflow}) is the ratio between average flow and cross sectional area of the reactor (Equation 2-4). This value depends on the type of sludge to allow the mixing in the reactor and avoid the scape of solids in the effluent. In case of flocculent sludge, the maximum velocity is 1 m/h, while for granular sludge's are in ranges of 2 up to 6 m/h. When the up flow velocity is set and with the average flow, the minimum area required or the surface loading rate can be calculated from the maximum up flow velocity allowed, some recommended values are shown in Table 2-11. Also is V_{upflow} related to the reactor height and HRT as is shown in Equation 2-5, for HRT and up flow velocities recommended the height of UASB are between 3 to 6 m.

$$\text{Equation 2-4 } A_{min} = \frac{Q}{v_{upflow}}$$

Where:

Q is average flow in m³/h

V_{upflow} is the up flow velocity in m/h

A_{min} is the minimum area required in m²

$$\text{Equation 2-5 } v_{upflow} = \frac{Q \cdot H}{V} = \frac{H}{HRT}$$

Table 2-11: Up flow velocity range for different flowrates

Influent flowrate	Up flow velocity (m/h)
Average flow	0.5 to 0.7
Maximum flow	<0.9 to 1.1
Peak flows (2 to 4 hours)	<1.5

Source: Chernicharo 2007

Another design recommendation is the area per feed point, to have a good distribution of the influent in the base of the reactor, the angle of the GLSS (above 50 degrees) and channel weirs for scum removal, inside the GLSS.

For sludge wasting one discharge point per 100 m² of bottom area is recommended, from two different heights, close to the bottom and around 1 m, with a pipe line of at least 100 mm. In case of biogas, pipe lines of 50 mm, with velocities lower than 5 m/s are recommended. (Chernicharo et al 2015)

Biogas production

The biogas composition in case of domestic wastewater is in the following ranges: 70–80 %CH₄, 10–25 %N₂, 5–10 % CO₂, also 0 to 50 ppm of H₂S was reported. The recovered methane in gaseous phase is calculated as 0.35 Nm³ per kgCOD removed at standard pressure and temperature (STP 1 atm and 273K), due to the high fraction that escapes dissolved with the effluent, and the suspended COD that goes to the sludge.

The theoretical production of methane gas can be determinate using stoichiometry (Buswell equation), if the exact composition of the compound in terms of C, H, O and N is known. In this case the compound is assumed to be biodegradable. (van Lier et al, 2008)

(Lobato et al, 2012) developed a model to estimate the methane losses, biogas production and energy potential in an UASB, taking in account the COD used in the conversion of sulphates to H₂S. In this case the load converted into methane ($COD_{CH_4-converted}$) can be calculated as follows:

$$\text{Equation 2-6: } COD_{CH_4-converted} = COD_{removed} - COD_{sludge} - COD_{SO_4-converted}$$

Where

$COD_{CH_4-converted}$ = COD mass converted into methane in kgCOD_{CH₄}/d

$COD_{removed}$ = COD mass removed from system in kgCOD/d

COD_{sludge} = COD mass converted into biomass in kgCOD_{sludge}/d

$COD_{SO_4-converted}$ = COD used by SRB for sulphate reduction

Each term is determined as following equations:

$$\text{Equation 2-7: } COD_{removed} = Q * Eff_{COD}$$

Where:

Q = average inflow in m³/d

Eff_{COD} = efficiency in terms of COD

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$$\text{Equation 2-8: } COD_{sludge} = COD_{removed} * Y_{sludge\ COD} = COD_{removed} * Y_{sludge} * 1.42$$

Where:

$Y_{sludge\ COD}$ = sludge yield in terms of COD (kgCOD_{sludge}/kgCOD_{removed}) usually between 0.11 to 0.23

Y_{sludge} = sludge yield in terms of TVS

1.42 = conversion factor kg TVS/kgCOD_{removed}

$$\text{Equation 2-9: } C_{SO_4\text{-converted}} = SO_{4,INF} * Q * Eff_{rem\ SO_4} * k_{COD-SO_4}$$

Where:

$SO_{4,INF}$ = sulphate concentration in the influent in kgSO₄/m³

$Eff_{rem\ SO_4}$ = efficiency of sulphate reduction, (70-80 %)

k_{COD-SO_4} = COD consumed in sulphate reduction $\left(0.667 \text{ kgCOD} - SO_4 / \text{kgSO}_4\right)$

Daily production of methane in terms of m³/d can be determined using a correction factor for temperature.

$$\text{Equation 2-10: } Q_{CH_4} = COD_{CH_4\text{-converted}} * \frac{R*(T+273)}{1000 * P * K}$$

Where:

R = gas constant 0.08206 atm Lmol⁻¹K⁻¹

T = operational temperature of the reactor in °C

K = 0.064 kgCOD per mole of CH₄

Q_{CH_4} = theoretical volumetric production of methane

Knowing this value, and regarding the percentage of methane in the biogas (70 – 80%), the biogas produced can be determined. From there the biogas upward velocity could be checked, dividing the production of biogas between the liquid-gas interphase areas. For conventional GLSS designed the maximum allowed velocity is between 2 to 3 m/h.

Operational constraints

The problems related to the operation of these plants are summarized in (Chernicharo et al. 2015)

- Low skilled personal: problems related to the maintenance of the units,
- Odour nuisance: due to the release of sulphide hydrogen,
- Failures in the pre-treatment: related to the design and bad operation,
- Fluctuations of the flow: by pass for rainy stations, low connections,
- Inadequate materials or coatings : cause corrosion in concrete and metal structures,

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- Inadequate sludge dewatering systems: impact in the sludge management,
- Lack or inadequate scum removal devices: accumulation inside GLSS,
- Inadequate hydraulic profiles: dissolved gases released to the atmosphere, preferential flows, risk for sludge bed by pass,
- Unlevelled collection weirs: preferential fluxes inside the settler compartment and scum accumulation near the weirs,
- Lack of process control and data acquisition instruments: such gas analysers and on line flow meters for wastewater and biogas production.

In case of scum accumulation different coefficients have been reported, as is shown in Table 2-12. Different solutions were proposed, based on control of the water level in the GLSS, but requiring control of the pressure inside the GLSS. In addition, lack of trained operators, is pointed as the main problem assessed in developing countries, increasing the problems of the operation mentioned before. (Chernicharo et al. 2015)

Table 2-12: Scum accumulation in UASB reactors

Type of scum	Accumulation coefficient	
	Value	Unit
Settler	100	mL/d
	4-8	cm/year
GLSS	0.22	L/m ³ _{sewage}
	0.16	L/kgCOD _{applied}
	0.32	L/kgTSS _{applied}
	3	cm/month
	12.5	cm/year
	15.8	cm/year
	0.11-1.26	gTS/kgCOD _{applied}
	0.11-4.0	gTS/kgCOD _{applied}
6.79-10.33	mL _{scums} /kgCOD _{applied}	

Source: (Chernicharo et al., 2015)

2.2. Mathematical models applied in anaerobic digestion

Regarding the objectives of the model, three different approaches could be applied. White box or mechanistical models, describes physically all the process involved, using mass balances, kinetics rates, etc., requiring a wide and deep knowledge of the system and the calibration of a high number of parameters. These models are used in design and optimization of systems.

In grey box or semi empirical models, some process are simplified and groped to decrease the number of parameters, combining simultaneous process, hindering the individual

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identification. Regarding the description of the phenomenon, could be more empirical or mechanical.

Black box or empirical models are based in statistical information without considering the process in the model, fitting the parameters to the data. So the number of parameters to use is low, but is limited to the initial conditions of the problem, presenting problems to represents different scenarios.

Actually the best approach to do an optimization of a plant is to use the mechanistical model or grey box model. (Lauwers, *et al.*, 2013) Also, could be done for a punctual set of values (steady state) or dynamic state, and depending the definition of the process.

Several mathematical models were developed since 1960, but in 2002 the Anaerobic Digestion Model 1 (ADM1) was developed by (Batstone, *et al.*, 2002) in the IWA task group on Anaerobic Digestion, to unify these models. Since that the ADM1 is the most used model and has been applied to different influents, including domestic wastewater and the digestion of primary and secondary sludge. In particular there are applications and modifications for anaerobic biofilms reactors (Saravanan and Sreekrishnan, 2006, Tartakovsky, *et al.*, 2008). This model is implemented in computational environments as Matlab and also in simulation software as SIMBA, BioWin, West and Aquasim.

2.2.1. ADM1 applied for domestic wastewater

ADM1 was published in 2002, by the Anaerobic Digestion group of IWA. They gather works and presented a unified model. ADM1 assumes a complete mixing condition in the reactor, and components are described in terms of COD. There are two types of reactions: biochemical (irreversible process) and physiochemical reactions. The biochemical processes are represented in Figure 2-6 and refer to the anaerobic metabolic pathways (hydrolysis, acidogenesis, acetogenesis and methanogenesis), including the biomass growth and decay. While physiochemical equations describe the ion association/dissociation and gas-liquid transfer. In this model the precipitation of solids is not included.

As is shown in Figure 2-6, seven biochemical processes are included in ADM1, each related to a microorganism group: acidogenesis from sugars, aminoacids (acidogenic bacteria) acetogenesis from LCFA, also acetogenesis from propionate, butyrate and valerate (same group for the last ones), aceticlastic methanogenesis and hydrogenotrophic methanogenesis. The hydrolysis step as extracellular process is assumed to be first order as well as decay, including this one in the particular matter. For intracellular processes, for the growth Monod type kinetics for substrate uptake is used.

The physiochemical processes are included to determine the inhibition of biological activity by pH, and also for the determination of dissolved gases and dissociate acids, estimation of biogas and alkalinity. These processes are grouped in the different phases: liquid-liquid reactions (equilibriums of basic acid), gas-liquid exchanges (gas transfers), liquid solids transformations (precipitation and solubilisation), but this one is not included in ADM1. Three main process gas components are modelled: CO₂ (medium solubility), CH₄ (low solubility) and H₂ (low solubility)

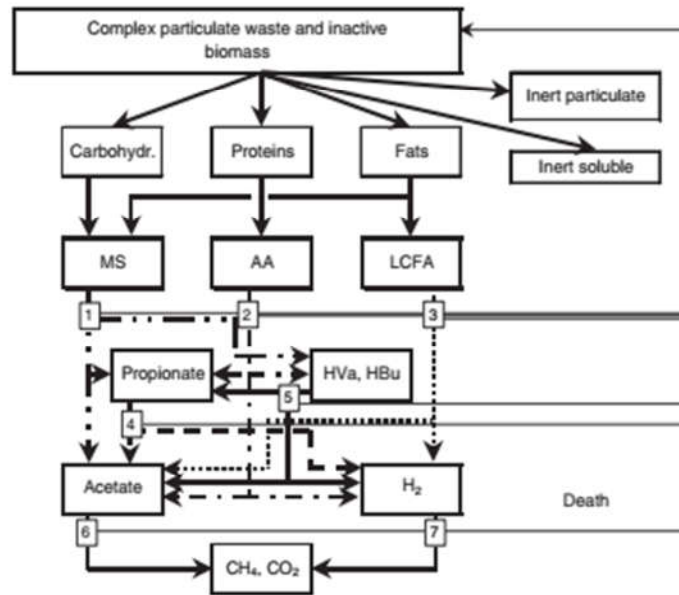


Figure 2-6: Biochemical process implemented in ADM1

The implementation includes 19 processes, represented by differential equations from the mass balances, 26 for dynamic state concentration variables, and 8 implicit algebraic variables per element. According with (Batstone, 2006) this model is suitable for optimization of the reactor stability, and the prediction of biogas, including the sulphide reduction in the model.

2.2.2. Mathematical models of anaerobic digestion including sulphate reduction

(Kalyuzhnyi and Fedorovich 1998; Fedorovich et al. 2003; Batstone 2006) developed extension to ADM1 on sulphate reduction, including competition for hydrogen or include also competition with acetogens.

Therefore, a further extension was implemented to consider the processes of sulphate reduction, from (Batstone et al. 2002). This approach is valid to S:COD ratios lower than 0.1 gS/gCOD and only includes sulphate reduction by oxidation of available hydrogen (Batstone, 2006). In addition, an inhibition function for the parameter H_2S was introduced. This model is effective in predicting the behaviour with an influent ratio S:COD lower than 0.06 gSgCOD^{-1} , while for higher values of sulphate the SRB use VFAS as electron donors, requiring updating the model with this pathway. (Batstone et al. 2015; Flores-Alsina et al. 2016)

Sulphate reduction could be added to the Gujer matrix of ADM1, including the hydrogen and bicarbonate as separate variables. Also the addition of two processes is required: growth and decay of HSRB, three state variables: total reduced sulphides (S_{IS}), sulphates (S_{SO_4}) and sulphate reducing bacteria (X_{HSRB}), presented in Figure 2-7.

Component →		i	8	8a	10	11	12a	23a	Rate (ρ_j , kg COD.m ⁻³ .d ⁻¹)
j	Process ↓		S _{h2}	S _{IS}	S _{IC}	S _{IN}	S _{SO4}	X _{SO4}	
12a	Sulfate reduction		-1	(1-Y _{SO4})	-(Y _{SO4}) C _{bac}	-(Y _{SO4}) N _{bac}	-(1-Y _{SO4})/64	Y _{SO4}	$k_{m,SO4} \frac{S_{SO4}}{K_{S,SO4} + S_{SO4}} \frac{S_{h2}}{K_{S,Sh2} + S_{h2}} X_{SO4} I_1$
			Hydrogen gas (kgCOD m ⁻³)	Sulfides (kgCOD m ⁻³)	Inorganic carbon (M)	Inorganic nitrogen (M)	Sulfates (M)	Sulfate reducers (kgCOD m ⁻³)	Parameters: k _{m,SO4} : 50 CODS CODX ⁻¹ d ⁻¹ K _{S,SO4} : 0.0001 M K _{S,SH} : 4×10 ⁻⁶ kgCOD m ⁻³ Y _{SO4} : 0.08 CODX CODS ⁻¹ Inhibition factors: I ₁ : See Batstone <i>et al.</i> (2002)

Figure 2-7: Process and components added to ADM1 Source: (Batstone 2006)

In addition, inhibitions functions for H₂S to hydrogen degrading organism and pH of HSRB has to be included. Physiochemical model includes H₂S/HS⁻/S²⁻ acid base equilibrium and SO₄²⁻ in the charge balance. Also gas stripping of H₂S is put into the calculation of the total gas pressure.

Another extension of ADM1 is presented in (Kalyuzhnyi and Fedorovich 1998; Fedorovich et al. 2003), with the inclusion of four groups of SRB: hydrogenotrophic (HSRB, X_{HSRB}), propionate degrading (X_{PSRB} PSRB), butyrate degrading (X_{BSRB}) and acetotrophic sulphate reducing bacteria (X_{ASRB}). In addition, two soluble components are included: sulphate (S_{SO4}) and sulphur S_S.

This extension adds eight new processes, corresponding to the growth and decay of each one of the SRB added, and an inhibition term for H₂S in the kinetics rates of growth of the 11 microorganism groups. In the same way has to be added the acid base equilibriums of H₂S/HS⁻/S²⁻ and H₂SO₄/HSO₄⁻/SO₄²⁻, and the H₂S in the gas-liquid transfer.

Component →	i	4	5	6	7	8	13	14	15	16	24	30	31	32	33	34	35	
j	Process ↓	S _{va}	S _{bu}	S _{pro}	S _{ac}	S _{h2}	S ₁	X _{ch}	X _{pr}	X _{li}	X _i	S _{SO4}	S _{IS}	X _{HSRB}	X _{ASRB}	X _{PSRB}	X _{CSRB}	
26	Growth of X _{HSRB} on S _{h2}					-1						$-\frac{(1-Y_{HSRB})}{64}$	(1 - Y _{HSRB})	Y _{HSRB}				
27	Decay of X _{HSRB}						f _{sl,xb}	f _{ch,xb}	f _{pr,xb}	f _{li,xb}	f _{sl,xb}			-1				
28	Growth of X _{ASRB} on S _{ac}				-1							$-\frac{(1-Y_{ASRB})}{64}$	(1 - Y _{ASRB})		Y _{ASRB}			
29	Decay of X _{ASRB}						f _{sl,xb}	f _{ch,xb}	f _{pr,xb}	f _{li,xb}	f _{sl,xb}				-1			
30	Growth of X _{PSRB} on S _{pro}			-1	0.57 (1 - Y _{PSRB})							$-\frac{0.43(1-Y_{PSRB})}{64}$	0.43 (1 - Y _{PSRB})			Y _{PSRB}		
31	Decay of X _{PSRB}						f _{sl,xb}	f _{ch,xb}	f _{pr,xb}	f _{li,xb}	f _{sl,xb}						-1	
32	Growth of X _{CSRB} on S _{bu}		-1		0.8 (1 - Y _{CSRB})							$-\frac{0.2(1-Y_{CSRB})}{64}$	0.2 (1 - Y _{CSRB})				Y _{CSRB}	
33	Growth of X _{CSRB} on S _{va}	-1		0.54 (1 - Y _{CSRB})	0.31 (1 - Y _{CSRB})							$-\frac{0.15(1-Y_{CSRB})}{64}$	0.15 (1 - Y _{CSRB})				Y _{CSRB}	
34	Decay of X _{CSRB}						f _{sl,xb}	f _{ch,xb}	f _{pr,xb}	f _{li,xb}	f _{sl,xb}							-1
			Total valerate (kg COD.m ⁻³)	Total butyrate (kg COD.m ⁻³)	Total propionate (kg COD.m ⁻³)	Total acetate (kg COD.m ⁻³)	Hydrogen (kg COD.m ⁻³)	Soluble parts (kg COD.m ⁻³)	Carbohydrates (kg COD.m ⁻³)	Proteins (kg COD.m ⁻³)	Lipids (kg COD.m ⁻³)	Particulate inert (kg COD.m ⁻³)	Sulfate (kmol S.m ⁻³)	Hydrogen sulfide (kg COD.m ⁻³)	H ₂ -degrading SRB (kg COD.m ⁻³)	ac-degrading SRB (kg COD.m ⁻³)	pro-degrading SRB (kg COD.m ⁻³)	Ca-degrading SRB (kg COD.m ⁻³)

Figure 2-8: Biochemical rate coefficients added for S model extension components

Source: Supplementary data (Flores-Alsina et al. 2016)

This model extension was calibrated using experimental data from literature, predicting sulphate removal, concentrations of butyrate, propionate and acetates, also methane and biogas production.

2.2.3. Modelling chemical iron transformations in anaerobic digesters

The iron cycle in anaerobic digestion is a complex interaction with sulphur and phosphate cycles, affecting all the water process.(Batstone et al. 2015). Interaction of sulphides and iron in sewer systems were studied by (Nielsen et al. 2005) and an extension for ADM1 to evaluate the impact of ferric ion in sulphate reduction is presented in (Liu et al. 2015). In addition, an extension of ADM1 including phosphorus, sulphate and iron interaction was presented in (Flores-Alsina et al. 2016). The extension includes the description of chemical iron (III) reduction to iron (II) using hydrogen and sulphides as electron donors.

Iron chloride is used in sewer systems to control the odour in the pipes, increasing the iron concentrations in the wastewater. Under anaerobic conditions Fe (III) is rapidly converted in Fe (II), using a range of electron donors as H₂, VFAs, H₂S or NO₃⁻. Fe (II) can precipitate as iron sulphide or iron phosphate compounds. But under anaerobic conditions, the sulphate is reduced to sulphide, and bound with iron. When the molar ratio Fe:S is higher than 1, almost all sulphide is precipitated, decreasing the production of H₂S.(Batstone et al. 2015; Flores-Alsina et al. 2016)

2.2.4. Plant-wide Modelling

According to (Grau et al. 2009) the most used approaches of plant-wide modelling are: connecting the different models used for each unit, and conversion factors to unify the components of them (“Interfaces” approach), as the interfaces developed for ASM1 and ADM1 (Benchmark Simulation Model No.2) or using only one mathematical model (super model) based on a common component vector including only relevant biochemical and physiochemical process for whole the plant.

The advantage to use an Interface approach is the wide knowledge of using standard models, but when new models are developed the complexity of the interface increases. Also, dynamic conditions sometimes require re definitions of the mass composition, to achieve the total elemental mass continuity in the standard models. In the Benchmark simulation Model No. 2 (BSM2) the objective is providing a representation of a real activated sludge, where the control strategies can be evaluated, an interface between ASM and ADM was developed. Also a Continuity-Based Interfacing Methodology (CBIM) was proposed, as a methodology to construct model interfaces between two standard models, ensured the elemental mass and charge continuity.

In case of supermodels all the reactions describing the relevant reactions in all the units of the plant are based in a unique model. All the processes are active (as a common vector of state variables) in all the streams of the plant, due to that the operation of the unit determines the biomass, not the model. For describing the state variable vector two types of supermodels are developed “standard supermodel” or “tailored supermodels”.

Standard supermodel could be used in all the WWTP, describing the relevant processes, and using the same state variables in all the streams. Examples of these are Biological Nutrient Removal Model No 1 (BNRM1), ASDM and BNRM2.

Tailored supermodels are based on a construction of a biochemical model for the studied plant that means each process of this particular plant is included. In this case, the complexity and the components are adapted to this situation.

2.2.5. Calibration of anaerobic models

The models described above, have a high number of parameters, regarding the variables that can be measured directly on a WWTP. Due to that, most of the parameters have to be experimentally calibrated, using mathematical algorithms to adjust the model results with the experimental data.

Different methodologies were used for calibration, such as steady state calibration, using average data of the WWTP analysed, dynamic calibration, more frequency measurements related with the process is required, and off line calibration, by laboratory essays.

However, one of the major issues, is the diversity of approaches to estimate the parameters, particularly kinetic, which make it difficult to compare results, even when they are performed under the same conditions (Donoso-Bravo, *et al.*, 2011). Most of the parameters are calibrated by trial and error, and using dynamic calibrations.

Validation is first made directly with the data used, and after that has to be validated with a different set of measurements (cross validation), where the difference between the prediction and the measured is referred to terms of R^2 . For model prediction and when the cross validation is not possible, it is recommended to study the confidence intervals of the parameters estimated.

Another issue on the application of the ADM1 is the characterization required of the wastewater, regarding the concentrations of amino acids, carbohydrates and lipids. (Kleerebezem and Van Loosdrecht, 2006), made an approximation using practical data as well as COD, VSS, TOC, nitrogen compounds, and alkalinity (carbonaceous and VFA). Also they proposed a methodology estimating the rest of the parameters required. For instance, from the total alkalinity the initial concentrations of inorganic carbon can be derived, as well as fatty acids and cations. Also a general composition of amino acids is assumed, and the oxidation state of the organic carbon is directly related to the COD/TOC ratio.

2.3. Simulation software PetWin™

BioWin™ is a wastewater treatment process simulator, developed by EnviroSim Associates of Canada, used for design, control and optimizations of whole plants, mostly based in traditional systems as activated sludge. According the manual of BioWin™, the model used includes Activated Sludge and Anaerobic Digestion models, integrated in a general model.

Literature review

Also includes the model of settling, pH, chemical precipitation and gas transfer process, including 45 state variables and 58 processes. According with (Jones and Takacs 2004) in each unit the processes are dependant of the global process such as dissolved oxygen, nitrite concentration, SRT, temperature and ph. According to the User manual, the modules included are activated sludge bioreactors, anaerobic and aerobic digesters, settling tank modules. It is also possible to define different types of input elements, and other processes as holding or equalization tanks, dewatering units, flow splitters and combiners.

In addition, two modules are presented: a steady state module based on constant influent loading and/or flow weighted averages on time varying inputs, and interactive dynamic simulator, used to analysing system response of time varying inputs or changes in operation

PetWin™ is computational software from EnviroSim developed to simulate the behaviour of wastewater treatment plants configurations, designed for petrochemical and other industrial wastewater inputs. As BioWin, PetWin™ is a COD based simulation, using a general ASDM model, with more than 60 state variables, and 100 process expressions. The difference is the inclusion of sulphur reduction in the process model.

In PetWin™ model the anaerobic degradation is based on four population models presented in (Mosey, 1983) and showed in Figure 2-9. The following functional categories are included in the process:

- Heterotrophic growth through fermentation, for VFA generation (ordinary heterotrophic organisms ,OHO)
- Growth and decay of propionic acetogens (acetogens)
This process describes the conversion or propionate to acetate, CO₂ and hydrogen.
- Growth and decay of methanogens (acetoclastics and hydrogenotrophic)
- Growth and decay of sulphur reducing biomass (propionate degrading SRB, acetotrophic SRB, hydrogenotrophic SRB)
- pH and alkalinity model
- chemical precipitation of phosphorus
- sulphur modelling

Sulphur reduction is based on three microorganism groups related to the electron donor; hydrogen, acetic acid and propionic acid substrates. Also Sulphur oxidation is modelled using a single population (sulphur oxidizing organisms), oxidizing H₂S to H₂SO₄, in presence of oxygen or nitrate.

For anaerobic digestion processes the modules included are the heterotrophic growth through fermentation, growth and decay of propionic acetogens, of methanogens and of SRB. Each module includes the switching and inhibition functions.

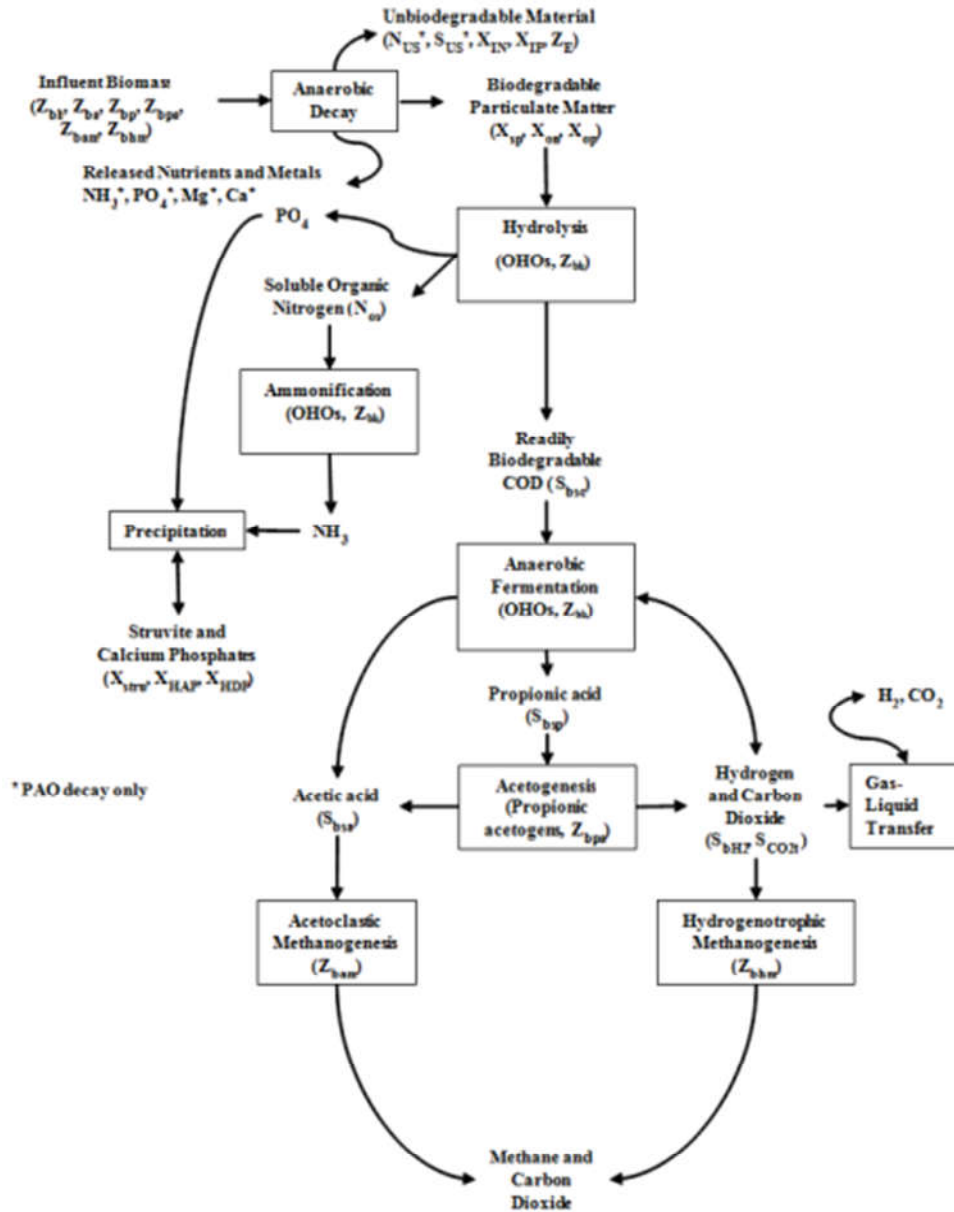


Figure 2-9: Conceptual schematic for anaerobic degradation model. Source: (EnviroSim Associates Ltd)

CHAPTER 3

Methodology and Methods

In this chapter the parameters and methods used for the analyses done from the sampling campaigns are described.

3.1. Sampling and analytical procedures

The sampling routine of WWTP is based in weekly analysis of pH, TS, VS, VFA and Bicarbonate Alkalinity of the reactors. Once per month a grab sample is taken from the effluent and send to Laboratory of OSE to made a complete analysis (COD, BOD, TN, FSA, Nitrates, TP, Oil and grease, TSS, VSS, FC) to present once a year to the Environmental Agency (DINAMA). Hence, it was required to do a sampling campaign to have a complete characterisation of the different streams of the plant. Also, is required the measurements of the effluent, for the mass balances of COD and sulphur in the reactors.

The first campaign was done at 22-23 of November, with the technicians of LATU. Grab samples were taken from: septic equalization tank (Q1), Pando PS influent (Q2), effluent (Q4) before it enters the chlorination tank (Q3), Reactor 203 (V203) and 204 (V204), as is shown in Figure 3-1. A telescopic grab was used to measure in the reactors.

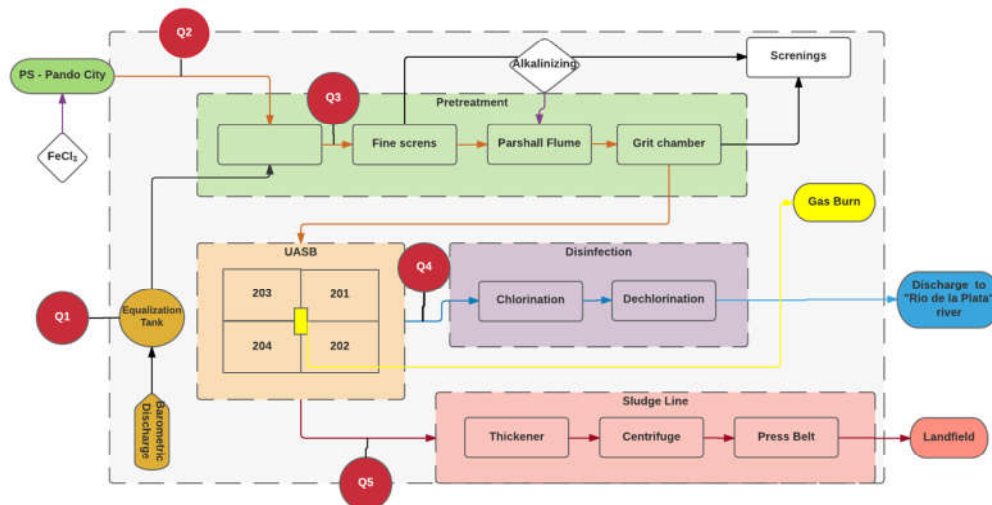


Figure 3-1: In red are indicated the sampling points from the plant

A 24 hours composite sample was taken from the head chamber of the plant before the screens, where the influent flows are mixed. An Avalanche® Multi-Bottle Transportable Refrigerated was used, which is a multi-function sampler that took samples every 2 hours and cooled them to about 4°C, to preserve the wastewater characteristics.

Most of the analyses were made in LATU using APHA standards. In case of the VFA, the samples were analysed at INIA, by gas chromatography. For alkalinity and VFA, titration method was used with H₂SO₄ 0.02N until first until pH 5.75 to determine Bicarbonate alkalinity and then pH 4.3 to determine VFA, as is described in (Pérez and Torres 2008; Sun et al. 2016). The first sampling campaign was done by the technicians of LATU. In addition, the biogas composition was performed in situ, using Dräger X-AM 7000, equipment configured with 5 sensors, two infrared to measure CH₄ and CO₂ and three electro chemical to measure CO, O₂, and H₂S, in different points of the reactors.



Figure 3-2: Equipment used for the sampling campaigns

The second sampling campaign was done from 15 to 22 of February of 2017, following the recommendations of (Chernicharo 2007) To analyse the performance of the reactors, and only relevant parameters as COD, BOD, sulphide, sulphate, TSS, VSS, and VFA, were analysed. Most of them were done at the laboratory located in the plant, except sulphide, sulphate and VFA. For sulphide and sulphate the analysis was done at LATU, and VFA analysis was performed at the laboratory of the INIA (Spanish acronym for National Institute of Agricultural Research) using gas chromatography. The titration technique was used to analyse the alkalinity indexes, such as Alfa factor, Buffer index and VFA/BA (Pérez and Torres 2008; Sun et al. 2016), and for COD test Spectroquant® COD cell test was used using a colorimetric method based on APHA 5220D. For TS, TSS, VS, VSS the APHA 2540 B, 2540 D, 2540 E was used. In Table 3-1 the analysis done and the frequency is summarized.

For the 24hs composite sampler, the equipment provided by OSE HACH SIGMA SD 900 was used, and samples were taken by flow, one sample per 40 m³. To do that the sampler was connected to the flow meters inside the Parshall flume. For the other points, 4 grab samples per point were taken each 4 hours from 9 to 18, to have a composite sample of the different streams. This procedure was done by the operators of the plant. During this time, the samples were refrigerated at 4°C, to preserve the samples. After the last sampling, the composite analysis was done. This procedure was applied for the septic tank (Q1), Pando PS (Q2) influent and for the effluent of the plant (Q4). Temperature and pH as well as the flows required were taken from SCADA system.

3.2. Monitoring UASB reactors

To analyse the quality of the sludge in the reactor, the total volatile solids and total solids have to be done at different heights of the reactor, in order to make a profile of the sludge blanket. In Figure 3-3, the points to take the samples of the sludge bed are shown, located from the bottom of the reactor at: 30 cm, 80 cm, 130 cm, 180 cm, and 230 cm. The parameters and the frequency are summarized in Table 3-1. The laboratory of the plant does the VS and TS of the sludge. In addition, total iron was analysed in dewatered the sludge.



Figure 3-3: Sampling points of sludge bed profile

Table 3-1: Operational monitoring of the UASB reactor, parameters and frequency (Chenicharo, 2007)

Parameter	Unit	Frequency of the sampling in the point		
		Influent UASB	Effluent UASB	Sludge blanket
COD total	mg/L	3xweek	3xweek	
BOD ₅ total	mg/L	Once per week	Once per week	
VFA	mg/L	3xweek	3xweek	
Alkalinity	mg/L	3xweek	3xweek	
VSS (VS)	mg/L	3xweek	3xweek	Once per week
TSS (TS)	mg/L	3xweek	3xweek	Once per week
Sulphate	mg/L	Once per week	Once per week	Once per week
Sulphide	mg/L	Once per week	Once per week	Once per week

CHAPTER 4

Results and Discussion

The information of the WWTP of 2016 is not complete; reports from February to June are used to determine the current situation of the UASB reactors. In July 2016 the plant passes from the contractor company, to the state water company O.S.E. During that period, the procedures for operating and surveying the information were being adjusted. Due to that, the rest of the year, the information is based weekly analysis of the TSS, VSS and alkalinity indexes of the UASB reactors, from the analysis of BOD, TSS, TKN, COD in the effluent once per month. The rest of the information is collected during the visits to the plant, from the operators and technical personnel. Then, the complete information was from February to June, and based in this, was done a primary characterization of the influent and the performance of the UASB reactors as well.

Secondly, with the results of the sampling campaign, the different sources of the plant can be described. The biogas production is determined from the mass balance of COD. As well as the H_2S produced, and the impact of the chemicals dosed. From these analyses, will be check optimal parameters and dosages. In addition, with the characterization of the influent, a computational model, using PetWin™ is implemented. For calibration and validation, data sets from sampling campaigns are used, but for an accurate model, is required more information, such as biogas production. Finally, a dynamic simulation is used to analyse the impact of the vacuum trucks into the plant.

4.1. Analysis of historical data of Ciudad de la Costa WWTP

The average composition during February to June 2016 of the influent is presented in Table 4-1, from 18 composite samples, every 10 days from the Parshall flume. The values presented are monthly averages and in brackets the standard deviation is presented. The flowrate of the plant since the operation started can be seen in Figure 4-1. The flowrate, temperature and pH are measured on-line, due to this the information is available, but the other parameters are measured off-line, and laboratory analyses are required.

During the first months of 2017, the average summer temperatures were higher than normal ($35^{\circ}C$), increasing water consumption, and therefore the affluent to the plant. In turn from December to March, it is the season of summer, increasing the population in the coastal cities, as well as the influent to the plant. In Figure 4-1 is represented the flowrate to the plant since June 2015 until February 2017, and between the vertical lines is the period referred above.

Table 4-1: Characteristics of the influent from February to June 2016

Month	Daily inflow	COD	BOD ₅	pH	Loading rate	Temperature
	(m ³ /d)	(mg/l)	(mg/l)		(kgCOD/d)	Influent (°C)
February	3172 (519)	847 (300)	300 (141)	7.3 (0.2)	2780 (1098)	23 (0.51)
March	3585 (590)	840 (208)	413 (133)	7.3 (0.2)	3029 (979)	24 (1.02)
April	4148 (709)	744 (261)	174 (58)	7.5 (0.3)	3098 (904)	23 (0.79)
May	3570 (553)	1215 (189)	416 (233)	7.4 (0.2)	4626 (1015)	21 (0.87)
June	3592 (530)	731 (188)	433 (45)	7.4 (0.2)	3228 (926)	18 (1.93)
Average (SD)	3780 (623)	899 (264)	361 (162)	7.4 (0.2)	3387 (1109)	20 (0.92)

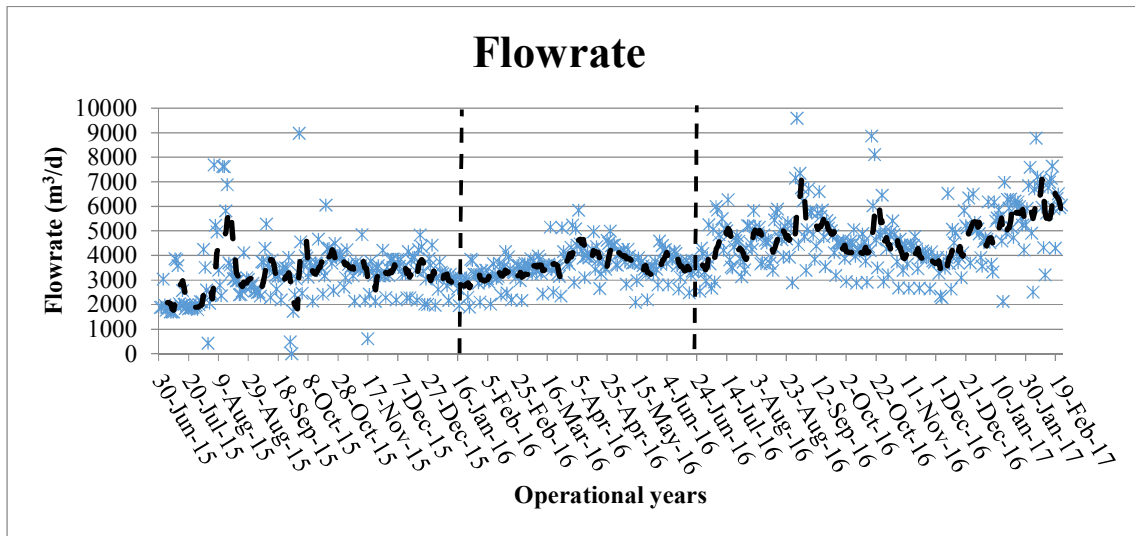


Figure 4-1: Daily flowrate from June 2015 to February 2017

The daily influent has variations and during the discharge of the vacuum trucks the flow increases with 40% of the average inflow. In Figure 4-2, is shown the average hourly inflow (from Monday to Friday) of February to June of 2016, where the inflow as well as COD, increases during this period (8:00 to 17:00). As was mentioned, these peaks will decrease when

all the cities will be connected to the plant. Meanwhile, the plant has to handle these daily variations.

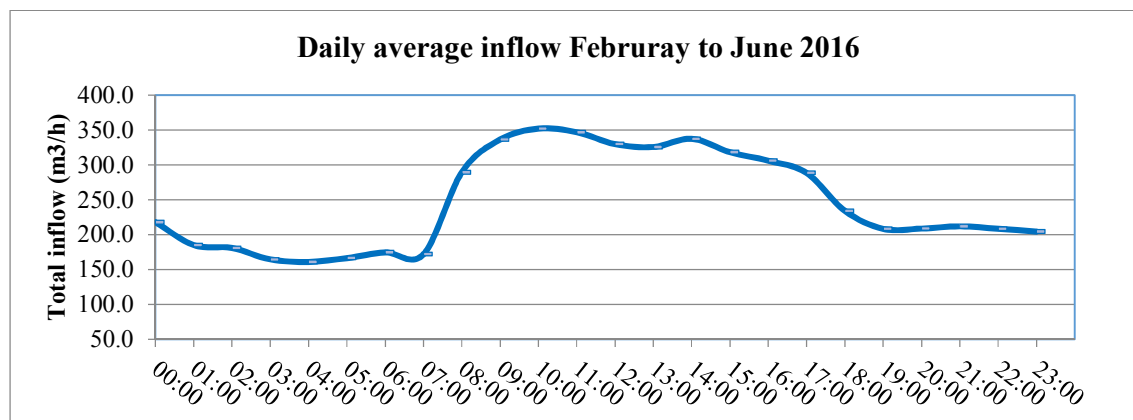


Figure 4-2: Daily fluctuation of the influent to the plant

The efficiency of the plant in terms of BOD was over 60%, also when the temperature of the influent started to decrease; reaching values lower than 20°C, during May and June, see Table 4.3. Despite the low efficiency, the effluent standard for this plant was most of the time reached, achieving less than 130 mg/L in terms of BOD, the results are presented in Figure 4-4. In case of TSS, most of the times the TSS concentrations were under the standard of 150 mg/L, only 3 times higher values were measured, as can be seen in Table 4-3.

Table 4-3: Summary of the effluent data from January 2016 to June 2016

Month	pH	BOD ₅ (mg/L)	Efficiency (%)	TSS (mg/L)	COD (mg/L)
January	7.3	117	61%	257	565
February	7.4 (0.3)	93 (31)	69%	185 (127)	-
March	7.2 (0.2)	61 (13)	85%	70 (40)	194
April	7.2 (0.2)	56 (11)	68%	59 (17)	241
May	7.2 (0.1)	97 (7)	77%	177 (57)	-
June	7.4 (0.2)	90 (32)	79%	102 (26)	318
Average	7.3	86	76%	142	330
Number of data	182	18	18	25	5

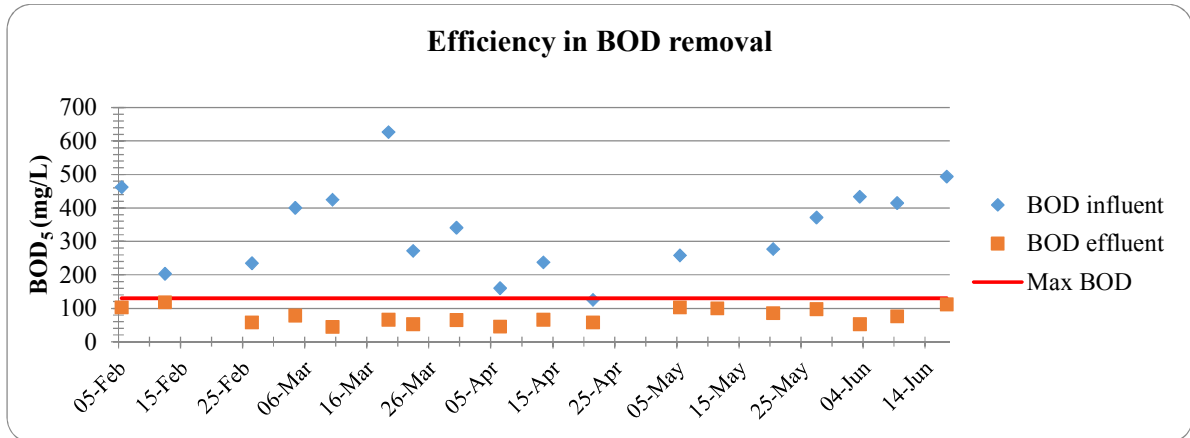


Figure 4-4: Evolution of the concentration of BOD from February to June 2016

Design HRT for this inflow was 12 hours, but due to the high TSS in the effluent (near 300 mg/L), the HRT was increased up to 30 hours in February 2016, increasing the number of reactors in operation from 1 to 2, to decrease the upflow velocity from 0.4 to 0.2 m/. The recommendations for HRT, regarding the temperatures of the influent, are higher than 12 hours for low temperatures, and in average the HRT is 36 hours. (Chernicharo 2007) The fluctuation during the first months of 2016 can be seen in Figure 4-5 as well as in Figure 4-6, the TSS in the effluent, where the concentration of TSS in the effluent was less than 100mg/L after the increasing of HRT.

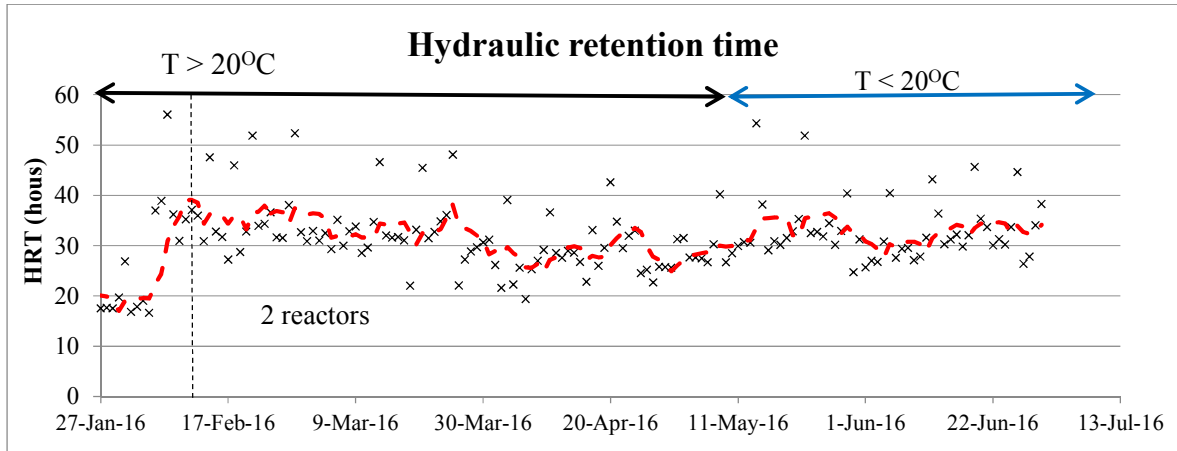


Figure 4-5: HRT fluctuation during the first six month of 2016

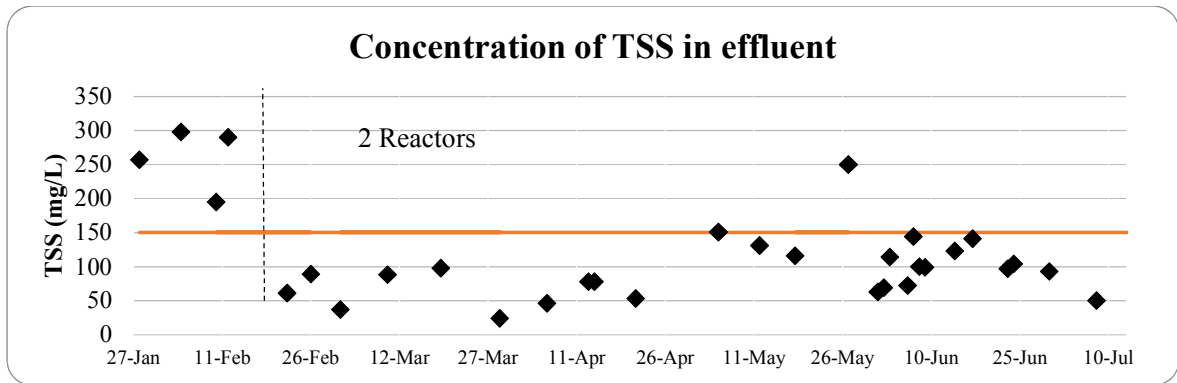


Figure 4-6: Concentration of TSS in the effluent during the first six month of 2016

From February to June of 2016, the efficiency of the treatment in terms of BOD was in average 75%, acceptable compared with the 55% to 75% of removal efficiency reported (Chernicharo 2007). From the data provided, is not possible to determine a relation between HRT and TSS in the effluent. Even when the TSS were in high ranges (150-250 mg/L), the maximum up flow velocity was 0.6 to 0.8 m/h. Due to this, the increase of TSS might be related to the sludge accumulation in the UASB reactors, more than the volumetric loading rate. In addition, the loading rate to the plant is not a control variable, so a proper wastage of sludge has to be done.

4.1.1. Evaluation of the performance of the UASB reactors

One of the main issues was the changes in the number and the reactors used, as is shown in Table 4-2. As was mentioned, of the 2 modules (Modulo A and B), only A is used. Module A has reactors 201 to 204, while module B has reactors 205 to 208. The plant started using reactor 201 since July 2015 to first days of February 2016 (6 months), afterwards started using 203 and 204 from February to January 2017, during finals days of December 2011 started to

work again, and in February 2017, 202 started to operate. While the reactors 201 and 202 are operative, 203 and 204 are used to stabilize the sludge.

Table 4-2: Reactors operative since July 2015 to March 2017

Reactor	2015						2016												2017			
	Jul	Ago	Set	Oct	Nov	Dic	Ene	Feb	Mar	Abr	May	Jun	Jul	Ago	Set	Oct	Nov	Dic	Ene	Feb	Mar	
201	■	■	■	■	■	■	■									■	■	■	■	■	■	■
202																					■	■
203								■	■	■	■	■	■	■	■	■	■	■	■	■		
204								■	■	■	■	■	■	■	■	■	■	■	■			

Start-up of Reactors 203 and 204

Reactors 203 and 204 started to operate in February 2016, while reactor 201 was in operation since June 2015. The sludge of 201 was used to start the other reactors. Hereby, during the first months of 2016, the 203 and 204 reactors were in the start-up phase. Due to that, SLR is a relevant parameter to follow during this phase. The maximum organic loading in the reactors can be determined through the SMA and monitoring the mass of TSS and VSS in the reactor.

The SMA was done in January 2016 by specialist in Anaerobic Reactors, from the group of BIOPROA of the Faculty of Engineering, UdelaR. The value reported was $0.05 \frac{kg\ COD-CH_4}{kg\ VSS.d}$, and is in the range of digested sewage sludge ($0.02-0.15 \frac{kg\ COD-CH_4}{kg\ VSS.d}$). (Seghezzi 2004)

The minimum mass in the reactors can be calculated dividing the loading rate per reactor by the SMA. (Chernicharo 2007; Rosa et al. 2012). From February to June of 2016, the average loading rate is 1751 kgCOD/d per reactor, and dividing by the SMA, the minimum mass is 35000 kgVSS (15 gVSS/L) per reactor. Regarding the ratio of VSS/TSS of 0.51, the minimum mass in terms of TSS, is 67 935 kgTSS (29 gTSS/L). Although, with values lower than this minimum, the TSS in the effluent, were higher than the standard (150 mg/L). Hence the value estimated as minimum mass rate cannot be used.

Another reason for the low difference between the SMA measured and the activity observed in the reactor, can be related to the low VSS/TSS ratio. According with (Chernicharo 2007) the accumulation of inert particles in the reactors, can lead to lower values of the SMA. This accumulation can be related to the low upflow velocities in the reactors (0.2 m/h with peaks of 1m/h) and the solids due to the use of sodium carbonate as alkalinizing, with low solubility. Then, to reduce the solids in the reactors, as the velocity cannot be increased, can be increased the frequency of wasting sludge from the bottom. In addition, is recommended to analyse the SMA once per month to monitor the performance of the sludge. (Chernicharo 2007)

Alkalinity indexes

Results and Discussion

Other parameters relevant to monitor the reactor, are the alkalinity indexes, as the Alfa factor, the Buffer index, pH and alkalinity, to evaluate the relation VFA/alkalinity, and prevent the acidification of the reactor. For instance, during the February 2016, was required to add sodium carbonate (Na_2CO_3) to increase the buffer capacity of the reactors and prevent the souring was started to add, using near of 25 to 50 kg of Na_2CO_3 per day. Commercial sodium carbonate has a concentration of 90% w/w and a density of 2.54g/mL. Thus the maximum alkalinity dosed is calculated in 121 mg CaCO_3 /L per day. According to (Van Haandel 1994) based in the COD removed, and an optimal pH of 7, the dose can be estimated between 150 to 200 mg CaCO_3 /L.

Based on the reference values for the Alfa factor, and the Buffer Index, after addition of Na_2CO_3 , the measured parameters showed stable values. For instance, a Buffer index between 0.2-0.4 means that at least 60% of the total alkalinity is in the form of bicarbonates. Also, the Alfa factor is in average 0.7, which is related to a reactor stable situation, while for start-up reactors the values has to be higher than 0.5. In concordance, the Buffer Index is between 0.2 -0.4, that means the alkalinity of VFA is near 60% of the total alkalinity, which is good indication of the buffer capacity of the reactor. (Li et al. 2014; Sun et al. 2016)

However, the ratio VFA/BA is larger than 0.3, that can represent souring problems in reactor, but this value depends on the type of wastewater. Regarding the stable pH inside the reactors at 7, and the other indexes, it can be concluded that the values obtained are not representative, or the uncertainty in the procedures in determining these values are bigger than the value itself.

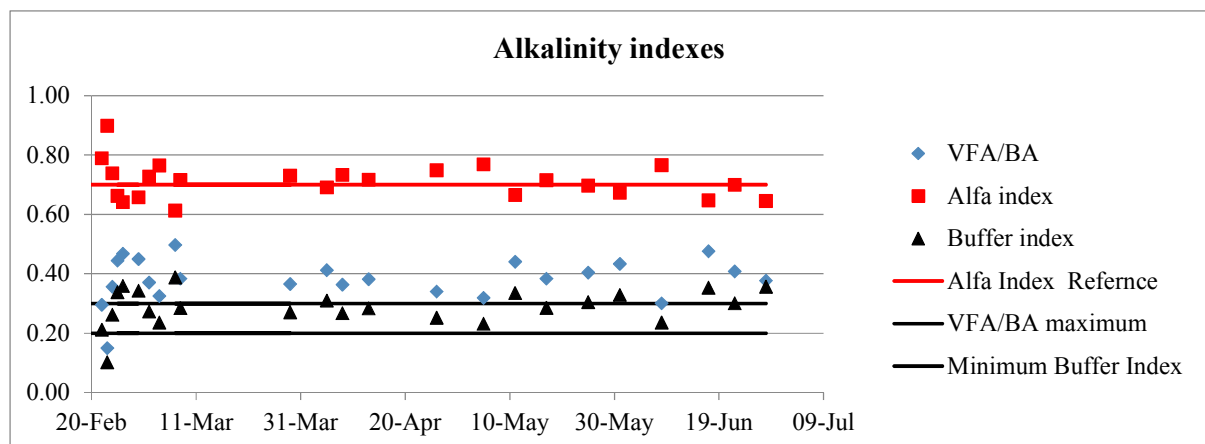


Figure 4-7: Alkalinity indexes from the reactors

Sludge wasting

The first wastage of sludge was in March, around 30 m³ of sludge from reactor 203. After that, once per month an average of 1000kgTSS was wasted from each reactor. From these the mass in the reactors was maintained until the TSS achieved 15 g/L. During April and May, the

TSS in the reactor reached up to 19 g/L, but the VSS/TSS ratio was really low: 0.4. Hence, the majority of sludge was inert mass accumulated inside the reactors, possibly due to application of high amount of sodium carbonate used and the low upflow velocity.(Chernicharo 2007). Due to this the sludge wasting frequency increases from 20 m³ per month up to 20 m³ per week. Due to this, the SRT of the sludge increases from 45 days to 60.

Solids profile

In a UASB reactor it is expected that the suspended solids profile will be concentrated in the lower layers of the sludge bed and that the concentration of the solids will decrease with height. But that depends in general on the type of sludge, the velocities inside the reactor and the organic load. During the first two months of operation, the solids profile shows a higher concentration of solids at lower points and low concentrations at high points.

From April to May the accumulation of inert solids was critical, reaching 60% of the TSS. In addition, the temperature started to decrease as well as the growth of the biomass. According to (Chernicharo 2007) these problems can be solved reducing the loading rate to the reactors, but in these case is no possible. Due to that, flocculent sludge with poor setteability was developed in the reactor, and the sludge was dispersed throughout the reactor volume, as can be seen in the solids profiles shown in Figure 4-8 for Reactor 203 and Figure 4-9 for Reactor 204. Then, to decrease the amount of inerts in the reactors, during these moths, the frequency of the wasting was increased, 20 m³ per week of each reactor, with a concentration of TS higher than 3%. After that, the TSS in the reactors where in average 14 g/L for reactor 203 and 16 g/L for reactor 204.

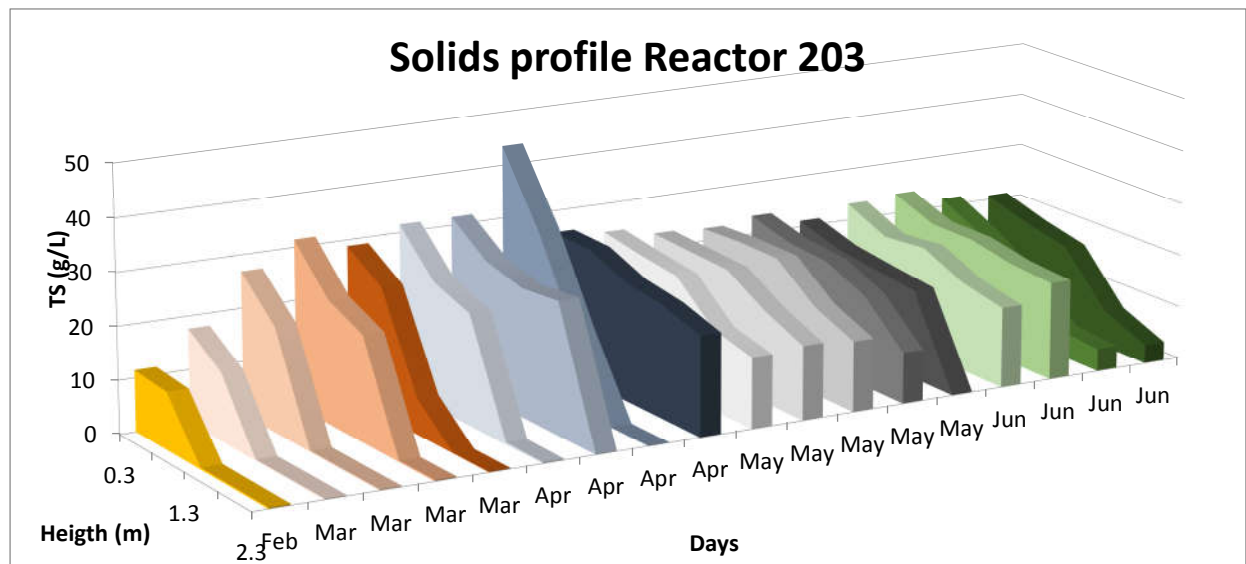


Figure 4-8: Solids profile during first six months of operation reactor 203

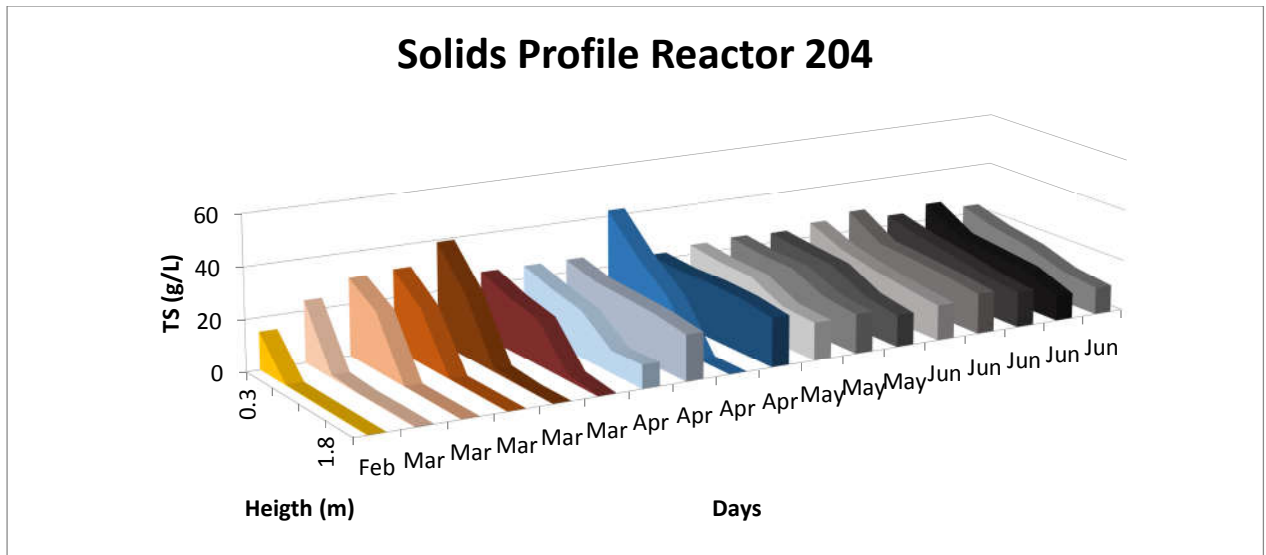


Figure 4-9: Solids profile during the first six months of reactor 204

4.2. Performance of UASB reactors

From the data collected in February of 2017, the efficiency of the plant in balance was 65% in terms of COD, and 70% in TSS. During these weeks, the excess of the sludge of one of the reactors was wasted, due to the high level of the sludge blanket, during this operation the TSS in the effluent increased until 400 mg/L resulting in an efficiency of only around 20%. However, in November the removal efficiencies were 45% in terms of COD, and 87% in TSS. The temperature of the influent was 20°C in November, while in February was 23.5 °C. Also, the average TSS and VSS in the reactors, at 21 November were: 7.39 gTSS/L, and 4.75 VSS, while during 15 and 21 of February were: 15.8 gTSS/L, 9.32 gVSS/L, and 7.76, 4.32 gVSS/L.

4.2.1. Influent characterization

The first sampling campaign was done in November, 2016. 3 reactors were operative. In the Table 4-4, the results and the ranges of the raw influent, measured from a 24 hour composite sample, are shown. Some of the values are out of the normal range reported in (Henze 2008), for domestic wastewaters, as TKN, TP and VFA, and are in bold in Table 4-3. The interference with ferrous chloride was assumed to be responsible for the high concentration of FSA than TKN. Due this, the fraction of TKN and FSA was adjusted, regarding the ratios in (Henze 2008).

The interference with ferrous chloride was assumed to be responsible for the high concentration of FSA than TKN. VFA analysis was done by titration method simplified, giving high values of VFA. Gas chromatography was used, to determine the composition of the VFA, and the concentration of acetate reported is 50 times lower, than the values obtained by titration method. (Li et al. 2014; Sun et al. 2016) From Table 4-3, the VFA/COD ratio is reported in (Henze 2008) is between 0.02 to 0.12, while this case is 0.18. Due to this, the

content of VFA will be used to analyse the alkalinity indexes, and for model purposes, will be used the value from GC analysis.

This technique is used for monitoring the VFA in the reactors. In the report of 25 January 2017, of Faculty of Engineer, the sludge from reactor 201 was conducted for doing the SMA, also determination of TSS, VSS, and VFA, by gas chromatography. VFA was 32.4 mgHAc/L, equal to 34.6 mgCOD/L. According to the results obtained in the plant, the VFA by titration is between 600 to 1000mgHAc/L. As is mentioned in (Sun et al. 2016) in samples with low VFA titration generally is overestimated. One possible reason, is the high content of particulates in the sample, so the requirement of acid is higher, to dissolve the particulates. The samples have to be centrifuged before, at 200 rpm, to avoid losses of VFA. Also, the procedure recommended by the specialists of Faculty of Engineer, UdelaR, is the titration using 5 pH points, 5.75, 4.3, 3, 4, 7, with heating of the sample, to release the CO₂, before measure VFA.

Regarding (Henze 2008) COD/BOD ratio is indicative of the biodegradability of the wastewater, for values lower to 2.5 are recommended in case of biologic treatment, and in this case the average is 2.9. Also, the VSS/TSS ratio is quite high; due to this the volatile component is suitable for anaerobic degradation.

Table 4-3: Wastewater ratios from first sampling campaign

Ratio	22-Nov	15-Feb	21-Feb	Range of value for Raw Domestic wastewater
COD/BOD	2.36	2.63	2.31	Medium (2.0-2.5) ⁽²⁾
VFA/COD	0.18	0.43		Out of range (0.02-0.12)
COD/TN	36.57			Out of range (6-16)
COD/TP	28.01			Low (20-35)
BOD/TN	15.51			Out of range (3-8)
BOD/TP	11.88			Low (20-35)
COD/VSS	1.84	1.45	2.26	High (1.6-2.0)
VSS/TSS	0.75	0.73	0.88	Medium (0.6-0.8)
COD/TSS	1.37	1.06	1.98	High

COD/SO₄	29.1	15.0	5.3
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(In **bold** are the ratios out of range) (Henze 2008)

The ratio of COD/SO₄⁻² in the effluent is 5 to 26, for the first two days, the hydrogen sulphide will not inhibit the methanogens, and 65-100% of the sulphate is expected to be reduced. (Cheremisinoff 2002). Also, the values reported are variable from different places, but the presence of sulphate can be between 0.1 to 10 mgS/L (Henze 2008), or 13 to 25 mgS/L (Cheremisinoff 2002), these last values are taken from countries with moderate to high precipitation rates, as in Uruguay.

For instance, from the results of the biogas in the reactors the concentration of H₂S was between 70 to 244 ppm, while CH₄ was between 12 to 36% of the volume measured. The threshold for H₂S for humans is near 50 ppm, and values higher can cause health problems if the person is continuously exposed. In this case, the gas was concentrated and released to the atmosphere,, and the values are in accordance to the reported concentrations in waste chamber of biogas (0-500 ppm)(Chernicharo et al. 2015). In Table 4-4 are shown the results of the measurements and in Figure 4-10 is detailed the points referenced in the table.

For septic tanks and influent from Pando city, grab samples were taken. The differences are mostly in the total COD, BOD, and VSS, but can be assumed that these values are diluted in a composite sample. From this, the wastewater of the septic tanks has similar characteristics as the other sources.

Table 4-4: Results from the sampling campaign

Description	Unit	Influent	Septic Tanks	Pando city	Reference values
TSS	mg/l	708	824	856	250-600 (1)
VSS	mg/l	528	668	684	200-482 (1)
Total Phosphorus	mg/L	34.6	44.2	42.6	6-25 (1)
PO ₄	mg/L	0.8	5.79	4.54	4-10 (1)
Total COD	mg/L	969	1320	1590	500-1200 (1)
Soluble COD	mg/L	259	406	587	200-480 (1)
BOD	mg/L	411	686	773	230-560 (1)
Soluble BOD	mg/L	166	243	389	
TKN	mg/L	26.5	67.2	133	30-100 (1)
FSA	mg/L	84	108	94	20-75 (1)
Nitrates+ Nitrites	mg/L	0.08	0.07	0.08	0.1-0.5 (1)
Sulphide	mg/l	5.5	-	-	0.1-25 (1)(3)

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Sulphate	mg/L	33.3	14.4	13.8	20-100 (2)
Magnesium	mg/L	14	16	14	
Calcium	mg/L	51	56	49	
Total iron	mg/L	11	-	-	
Alkalinity	mg/L	650*	875	500	100-1000 (2)
VFA	mg/L	245*	302	274	10-80 (1)
pH		7.7	7.35	7.28	6-8 (1)
Temperature	°C	20	20	20	

(1) Henze et al 2011 (2) Chernicharo 2004(3)(Cheremisinoff 2002) (*) Titration method without centrifuge

Table 4-5: Results obtained from the biogas composition

Point	Reactor								
	203				204				201
	1	4	6	7	2	3	8	9	5
CH ₄ (% VOL)	12	30	26	36	19	23	33	34	36
O ₂ (% VOL)	19	17	17	15	20	19	18	18	16
H ₂ S (ppm)	88	92	273	243	92	69	244	115	119

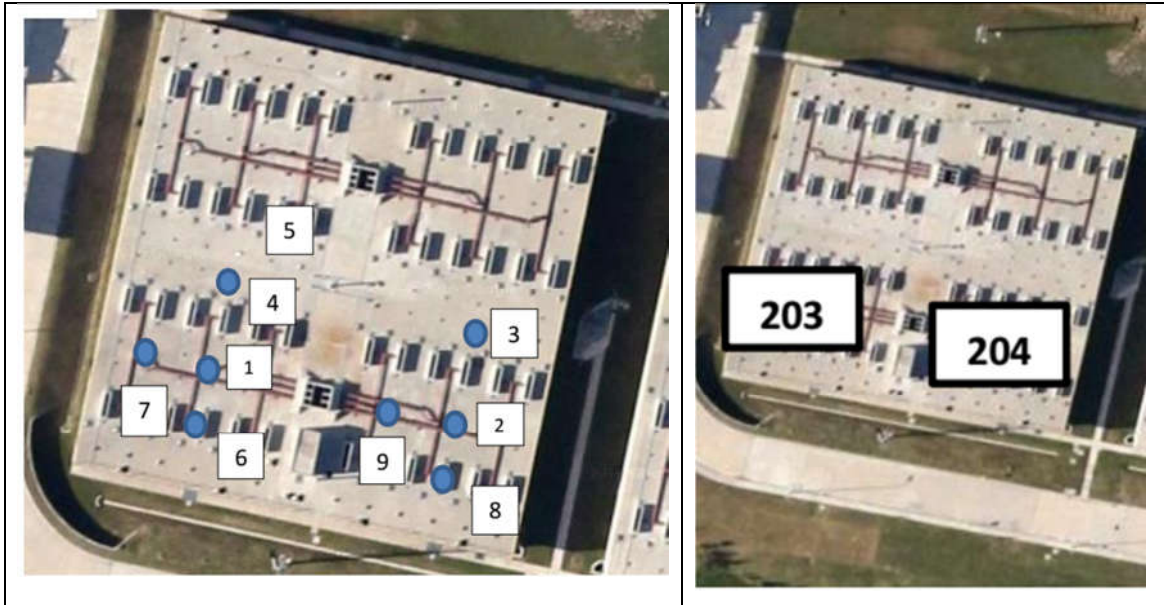


Figure 4-10: Points measured biogas composition

4.2.2. Sludge wasting and SRT

There is no protocol for sludge wasting, so the criteria used is based on the TSS value of the effluent, and an empirical value of TSS in the reactor near of 15 g/L. The sludge is wasted from the bottom of the reactor, so the concentration of TSS is assumed equal to the concentration at point 5, located at the same height. Also, from the first months of the reactors, the sludge was not wasted to increase the biomass inside.

According to (van Lier et al. 2008; Chernicharo et al. 2015) SRT should be higher than the time required to maintain the methanogenic activity. As empirical rule the SRT has to be 3 times higher than the doubling time (T_d) of the rate limiting step, and under tropical conditions are the methanogens, with an estimated T_d of 10 days. Due to that, as is mentioned in (van Lier et al. 2008) at full scale plants SRT is always up to 30 days. Also, from Figure 2-4, for 16°C, SRT should be 140 days. Besides of this, SRT can be by Equation 4-1, resulting in 33 days, quite lower for the coldest months.

Equation 4-1: SRT

$$SRT = \frac{X * V_{reactor}}{Q_{exc} * X_{exc} + Q_{eff} * X_{eff}}$$

For the average COD influent value, and a yield of solids production assumed as 0.15 kgTSS/kgCOD applied (Rosa et al. 2012), the daily sludge production is 508 kgTSS/d. Considering that average concentration in the lowest point of the reactors was 2.6%TSS, the volume produced per day is 19 m³/d. If the mass in the reactor is too high, this is the volume to waste per day. Regarding the admissible flow to the dewatering unit, and the volume of the thickener (100 m³), the operation can be waste 95 m³ each 5 days, and centrifuge during 12

hours (2 works days). Regarding a TSS in the effluent of 100 mg/L, and 18 gTSS/L in the reactors, the SRT calculated as Equation 4-1 is 45 days.

Other approach is considered the accumulation in the reactor, as the difference of the TSS in the effluent, before and after wasting of the sludge. (Chernicharo 2007) The maximum capacity of the sludge to retain the particles, is reached when the TSS in the effluent is in the limit of the standard (150 mg/L), and the optimum can be determined after wasting certain amount of sludge, and the TSS are in an optimal value, for this case, is in average is 90 mg/L, Then, the accumulation is the difference of these two loads, 227 kgTSS/d. Considering the average concentration at the bottom of the reactor, 8.6 m³/d are required to waste. In this case the operation can be done each ten days, and the SRT calculated from Equation 4-1, will be near 100 days. This approach is more feasible and based in the data from the plant, so can be considered more realistic.

In other hand, the average mass in the reactors was 18.262 kgVSS and 34.815 kgTSS, hence the VSS/TSS ratios is 0.51, which means that a high percentage of ISS has accumulated in the reactors. According with (Seghezzo 2004; Chernicharo et al. 2015) the accumulation of solids in the sludge bed of the reactors, takes relevance under lower temperatures (under 18°C), due to the reduce hydrolysis rate. In consequence, the methanogenic activity will be reduced, deteriorating the COD removal efficiency. However, during the coldest months (May and June) the removal efficiency in terms of BOD was higher than the first months, might be for the higher SRT in this months, calculated in 96 days.

4.2.3. COD mass balance

To analyse the mass balance of COD in the reactors the approach presented by (Lobato et al. 2012) was used. The model developed estimates the losses of COD in the reactors, to close the theoretical biogas production to the values obtained in full scale anaerobic digesters. The mass balance include the portion of COD used for sulphate reduction, the COD converted into biomass and the dissolved COD that escapes with the effluent, the COD used for methane and is recovered as biogas, also the fraction that escapes dissolved in the effluent or as waste gas.

Due to the lack of the information on biogas production in the plant analysed, these value is only to check the parameter in a future. The values used for the calculations for the first six months of 2016, are described in Table 4-6, also the percentage for the losses were taken from there, considering at the worst scenario.

Table 4-6: Data used to determine the losses in the model presented in (Lobato et al. 2012)

Parameter	Unit	Worst Case	Best Case
Sulfate concentration	kgSO ₄ /m ³	0.08	0.04
Efficiency of sulfate reduction	%	80	70
COD-CH ₄ lost as waste gas	%	7.5	2.5
Other COD-CH ₄ loses	%	7.5	2.5

Dissolved COD-CH ₄ lost with effluent	kg/m ³	0.025	0.015
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From the COD available to be converted into methane, a theoretical value of biogas and methane can be calculated, based in the 0.35Nm³ per kg COD removed.(van Lier et al. 2008) After that the losses of methane can be estimated, and a more accurate value of the biogas produced in the plant. Assuming the losses in the reactors as is mentioned in Table 4-6, and the data from the samplings campaigns, the fractions calculated are summarized in Table 4-7. In bold are the values taken from the Table 4-7 above.

Table 4-7: COD mass balance fractions calculated, data in bold are from (Lobato et al. 2012)

COD fractions (kgCOD/d)	Feb-Jun 2016	22 Nov 2016	15 Nov 2017	Feb 21 2017	Nov 2017	Referenc e values
COD soluble in the effluent	19%	15%	17%	19%		14-24
COD sludge in the effluent	15%	22%	10%	20%		10-20
COD converted in biomass	14%	14%	16%	13%		8-10
COD used by SRB	1.8%	1.1%	0.3%	4.2%		4.5-5
COD losses as CH ₄ in waste gas and atmosphere	7.5%	7.3%	8.6%	6.6%		
COD converted into CH ₄ dissolved in effluent	11%	10%	18%	20%		16-18
COD converted into CH ₄ and recovered	31%	31%	30%	17%		24-30

The concentration of sulphate in the influent and the low sulphate removal increases the amount of COD available for methane production. From the mass balance 50% of the COD is converted into methane, a high value considering the low activity of the sludge of the plant and values reported for full scale plants (Chernicharo et al. 2015). BMP analyses should be conducted to have accurate values. Moreover, the accumulation of COD in the sludge bed had been reported (Koster and Lettinga 1985; van Lier et al. 2008), as non-digested COD, but increasing the stoichiometric value of 1.42 kgCOD_{removed}/kgVSS. Hence, the fraction of COD retained in the sludge will be higher, decreasing the fraction converted into methane. Besides of these, the accumulation of solids in the sludge, could be the responsible of the low SMA of the sludge.(Chernicharo 2007)

Based on the estimations, the methane yield is between 0.10 to 0.17 Nm³CH₄/kgCOD_{removed}, in the range of the values reported by (Lobato et al. 2012), due to this, the biogas production average is 350 Nm³CH₄/d, assuming 70% of methane means 500Nm³/d of biogas. Regarding a calorific energy for methane of 35.9 MJ/Nm³, the potential energy is 12,565 MJ/d. In addition, regarding the conversions showed in (van Lier et al. 2015) considering a efficiency for the electric conversion in 40%, the electric power can be estimated as 124 kwh, that value represents the 15% of the daily consumption of the plant.

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4.2.4. Chemicals dosing: effect of the Iron chloride and Alkalizing

To avoid odour problem in the pump stations, related to the formation of H₂S, iron chloride is dosed in the pump station of Pando city. Under aerobic conditions H₂S can lead to H₂SO₄, much more corrosive, particular for the concrete structures, product of the biofilm where SRB grows.

The sulphide produced by biofilm is estimated by empirical equations, depending on the substrate available (COD, BOD), temperature, flow velocity, and the residence time in the pipeline. According to (Hvitved-Jacobsen et al. 2013), the formation of the biofilm, where the SRB grows, in the surface of pipelines in force mains, can be estimated by the next equation:

Equation 4-2: Biofilm Surface Rate

$$r_a = a(\text{COD}_{\text{sol}} - 50)^{0.5} 1.03^{T-20}$$

Where:

- **a**: empirical rate constant in gSgCOD^{-0.5}m^{-0.5}h⁻¹ : 0.001-0.002 domestic wastewater, 0.003-0.006: mixed domestic and industrial sources, 0.007-0.010 wastewater high content of biodegradable substrate (foodstuff industries)
- r_a: Biofilm surface rate in gSm⁻²h⁻¹
- T: temperature of the water in °C

From the sampling campaign of November 2016, assuming the COD soluble measured from Pando Pump Station, is 587 mgCOD/L, assuming an empirical rate constant of 0.002 gSgCOD^{-0.5}m^{-0.5}h⁻¹ by using Equation 4-2, the surface rate is 0.05 gSm⁻²h⁻¹. The impulsion pipeline from the city of Pando is made of GFRP (Glass-Fibre Reinforced Plastic) with an internal diameter of 483 mm (500 mm nominal). The residence time in the pipeline calculated is in average 19 hours, considering the full section, the hydraulic radius is 4/D, and 10 km of length as well. Then, the production of sulphide can be calculated as the product of these values by the rate, so the production per hour is 7.9mgSO₄-S/L.

According to (Flores-Alsina et al. 2016) in anaerobic digesters, where the relation of Fe:S is 1, most of the sulphate is bound with Fe, also in (Nielsen et al. 2005; Hvitved-Jacobsen et al. 2013) depending the pH, ratio of Fe⁺²/Fe⁺³, this ratio Fe:S is between 1.8 to 4.4 gFe:gS, in addition (Firer et al. 2008) suggest a minimum dose of 1.5molFe:molS. For instance, if 100%Fe⁺³ at pH 7.0 the ratio is 4.4 gFe per g of S (molar ratio 2.5molFe:molS). So if molar ratio of Fe:S is 1, is required 13.8 mgFe/L to reduce the sulphide produced (7.9 mgS/L) and 35mgFe/L, in case of 4.4gFe:gS. Regarding the average flow from pump station of 105 m³/h, the mass per day applied in each case is 35 kgFe/d and 87kgFe/d. Based in the concentration of sulphate in the septic tanks (without FeCl₃) founded in sampling campaigns (10 mgS/L), the average requirement of Fe dosage is between 36 kgFe/d to 223 kgFe/d, and these results are summarized in Table 4-8.

Table 4-8: Estimation of total iron required

Source	Flow	HRT	Sulphide	(1molFe:1molS)	(2.5molFe:1molS)
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Unit	m ³ /h	h	g/m ³	Iron required g/m ³	Mass of Iron required kg/d	Mass of Iron required g/m ³	Mass of Iron required kg/d
Biofilm production	105	18.7	11	18	46	46	116
Total Sulphate (biofilm and wastewater)	105	18.7	21	36	90	90	226

The iron salt dosed in Pando pump station is 50 L/d FeCl₃ (40% w/w, density of 1.4 kg/m³), hence, 28 kg/h FeCl₃ is applied in Pando city effluent, dividing by the flow means 266 gFeCl₃ per m³ of wastewater or 93 gFe/m³ is applied. Moreover, regarding the average of inflow to the plant, the daily mass rate of iron applied is 9.8 kgFe/h, that means 234 kgFe/d per day. Thus, the relation of the dosage and the sulphide generated is 0.84 molFe:molS, near the ranges recommended. (Nielsen et al. 2005; Zhang et al. 2008)

This mass is higher than the average, but can be insufficient due the variations of flow, COD, and sulphide. To be in safety place, the maximum production of sulphide can be determined, and from there estimate the dose required, based in a Fe: S ratio, and the purity of the salt used. In case of the sampling campaign day, the variation of iron requirements, and the dose applied can be seen in Figure 4-11, for the maximum relation and the sum of sulphate generated by biofilm and wastewater content. Even in this case, the dose applied apparently was enough to avoid the formation of H₂S. But it was assumed a constant value of COD, with this hourly variation, the results will be different.

Assuming iron as trace element in wastewaters (less than 1mg/L), the iron measured in the influent can be assumed as excess of the reaction with sulphate. In a simple mass balance, the iron consumed in the pipelines is in average 80 mgFe/L, then in a molar relation of 1Fe:1S, the sulphate consumed is 137 mgSO₄/L, thus the fraction reaching the plant is 25% of the total sulphate produced. However, the amount of sulphate in the influent is still high, regarding the classification in (Henze 2008) . So production of sulphate was higher than the estimated, or the variations in daily COD are larger than the measured, increasing the sulphide production in sewer system. Also the sulphates in the influents have to be monitored, to discard illegal dumping of industries.

Other factor, is the pH in the wastewater, at pH 7 the ratio recommended is 4.4gFe/gS, but at pH=8 the ratio required is 1.8gFe/gS, and according to Due to this, the pH in pumping station can be lower than 7, requiring more iron to reduce the sulphide.

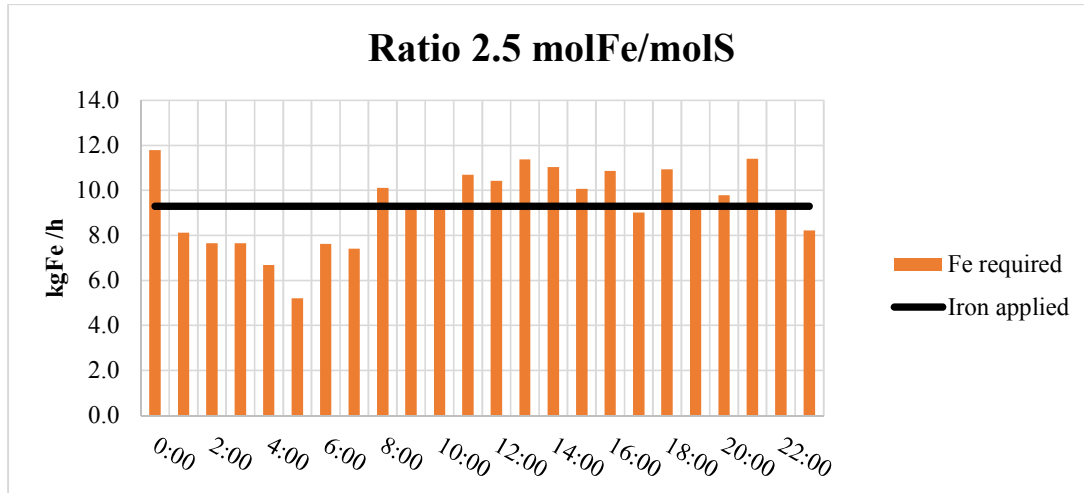


Figure 4-11: Iron required based in the hourly variation of the influent from Pando city pump station regarding 2.5 molFe/molS

Due to this, iron chloride reduces the formation of H_2S in the reactors, but due the daily variations of COD and flowrate, could be insufficient to remove all the sulphate. Hence, formation of H_2S can be expected in the WWTP. In addition, the sludge from the plant cannot be delivered to the municipal landfill, due to the high concentration of iron in the reactors and in the sludge, such as 8.6 gFe/kg sludge.

According to (Zhang et al. 2008) the methods to control the H_2S in the sewer, can be for eliminate the H_2S formation, such as use chemical oxidants, iron salts, or alternatives electron acceptors as oxygen, nitrite or nitrate, or inhibiting the biological activity of SRB, by increasing the pH, or adding biocides. For instance, the theoretical nitrate demand for sulphide oxidation is estimated in 0.18 to 0.44 mgNO₃-N per mgS,(Zhang et al. 2008) that means a requirement of 13 kgNO₃/d with an effectiveness between 65 to 100%.

4.2.5. Balance of the sulphur in the process

As was described above, depending on the pH, the hydrogen sulphide can be present as undissociated forms ($H_2S/HS/S^{-2}$) in gas and liquid phase, and due to high constant of dissociation for of S^{-2}/HS^{-} , the concentration of S^{-2} can be neglected, under normal conditions of pH (6.5-7.5). Depending on the method used in the determination of sulphide, losses can be expected in the H_2S , mainly from undissociated fractions, during sampling handling.(Poinapen et al. 2009). For these reason, measurements of H_2S can be underestimated.

Sulphate can be used for growth of biomass, or released in the medium as sulphide in case of being used as electron acceptor. The sulphide can be precipitated by metal ions, as Fe^{+2} , or escaping in gas phase. Due to this, the stoichiometric relation in the reduction of sulphate into sulphide (H_2S) can be lower than of 0.33 mgS per mg of SO_4^{-2} in aqueous phase. (Subtil et al. 2012)

Therefore, the mass balances in the reactors are difficult to achieve, mainly due to the losses of H_2S during the measurements. However, the maximum H_2S produced, can be estimated

from the sulphate removed in the process, and taking into account the concentration of iron. The concentration of iron is relevant, because according to (Flores-Alsina et al. 2016) for ratios of Fe:S of 1 or higher, sulphate is mainly present as FeS precipitated, decreasing the production of H₂S. As example, the mass balance using the data available was done and is shown in Table 4-9

Table 4-9: Mass balance of the reactors during the monitoring

Day	Total Sulfur Influent (mgS/L)	Total Sulfur Effluent (mgS/L)	Sulfur precipitated as metal (mg/L)	Sulfur losses (mg/L)
22-Nov-16	16.6	7.6	4.5	4.5
15-Feb-17	14.3	12.5	-	1.8
21-Feb-17	13.5	3.2	-	10.3

From COD balance, and the inflow to the plant, assuming total conversion of sulphate in the reactors, production of H₂S can be estimated in 24 m³/d. Regarding the high solubility of H₂S, most of the H₂S produced, will be dissolved in the water. The release of H₂S gas to atmosphere is related to the turbulence in the collecting structures, as the channel of the effluent. (Souza et al. 2012) Nevertheless, due to the high amount of Fe in the reactors, most of the sulphate will be precipitated, so this volume of H₂S will be difficult to achieve.

However, the toxicity of the sulphide is related to the non-dissociated fraction of H₂S, and regarding the pH in the influent, is only 20% of the total sulphide, so inhibition problems can be discarded. But inside the reactors the pH is quite lower, so can be assumed that sulphide in form of H₂S is 53% of the total sulphide, so the average concentration in the bottom of the reactors is less than 140 mgH₂S/L, and with this value are not expected inhibitions problems. (Chernicharo 2007; Chen et al. 2014)

4.3. Model approach using PetWin™

The computational software for the design of a complete treatment plant is based in Activated sludge systems, including anaerobic digesters to treat the sludge produced. Due to this, in case of PetWin™, is required coupled the anaerobic digester, with a clarifier, to work as GLSS, and to create a link between these two units, to simulate the mixing in the reactor. Also, a grit chamber is included to reduce the TSS to the UASB, the addition of FeCl₃ and alkalizing as well. The final model structure is shown in Figure 4-12 and the data used for each unit is in Table 4-10 and Table 4-11.

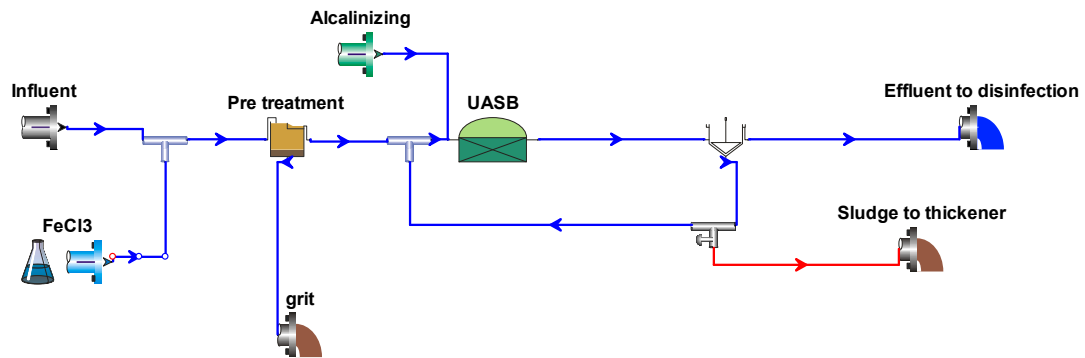


Figure 4-12: Model structure of Ciudad de la Costa WWTP

Table 4-10: Description of the units in the model.

Unit	Volume(m ³)	Depth (m ²)	Head space volume (m ³)	Head space pressure (kPa)
Grit tank	71	1.22		
UASB	2363	5	2.53	103

Table 4-11: Data from the inflows to the plant and recirculation UASB-UASB clarifier

Unit	Flow (m ³ /d)	%FeCl ₃ weight (g/g)	Alkalinity (mmol/L)	pH
Dosage FeCl₃	0.120	40	-	2
Dosage Alkaline	10	-	400	9
Internal recirculation UASB (splitter)	8*Q _{inf}	-	-	-

The information used for the model, was from the first sampling campaign, where almost all the parameters needed were analysed. PetWin™ simulator uses integrated Activate Sludge Digestion Model (ASDM); hence the influent fractionation required for the simulator, is based in STOWA protocol. But this protocol is based in activated sludge models, due to that, some relevant parameters, such as biodegradable substrate, are related to the process treatment.

According to (Lübken et al. 2015) for anaerobic digestion, the identification of COD fractions were developed in analogy of activated sludge models, through respirometry analysis. But the determination of biodegradability in anaerobic digestion, is based in the biochemical methane potential (BMP) from filtered samples, measuring the methane production per mass of COD of substrate added. Biodegradability (D) is determined, dividing

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the BMP by theoretical relation of 350NmLCH₄ per gCOD. Inert fraction is (1-D) of filtered COD. BMP was not performed for this work, then the biodegradability of the influent of the plant used, is based in the values reported, where biodegradability of the raw wastewater as fraction of COD_{TOTAL}, was determined between 70% to 79% at 30°C, and 65% at 20°C, (Seghezzo 2004)

So as a starter point, a first influent fractionation was done using STOWA protocol, then the fraction adjustment was done by trial and error. Nevertheless, for calibration of the model, kinetic and stoichiometric parameters have to be adjusted; particularly the growth rates of methanogenics, acetogenics and hydrolysis rate, also hydrogenotrophic SRB rates have to be checked.

After the calibration of the model, validation it is required using another set of values. In this work will be used the results from sampling campaign in February 2017. If the model calibrated fits in the measured data with acceptable deviations, dynamic simulations can be done.

4.3.1. Influent fractionation

Wastewater fractionation was based on STOWA protocol, whose synthesis in Appendix, based in the results from first sampling campaign. For modelling purpose, VFA was adjusted due to the high difference between the values obtained by Gas Chromatography (5mg/L) and titration (200mg/L). Also, the TKN was adjusted according to the COD fractionation, due to the low value reported in the sampling campaign, and the values of FSA higher than TKN. Another value adjusted in the influent was the PO₄ (0.8mg/L), this is because the low value compared with the two sources of the influent, 5.79 mg/L from Pando town and 4.64 mg/L from septic tanks. The parameters adjusted are shown in Table 4-12 and the data used for characterization of the influent is in Table 4-13.

Table 4-12: Parameters adjusted for Steady Model

Parameter	Unit	Value measured	Value adjusted
TKN	mgN/L	26.5	100
VFA	mgHAc/L	200	9
PO ₄	mgN/L	0.8	5.1

Table 4-13: Data used in the influent characterization

Influent	Concentration		
Flow	Q		
Total influent COD	COD _T	969	gCOD/m ³
Influent COD micro filtered	COD _{MF}	259	gCOD/m ³
COD from VFAs	COD _{VFA,eff}	4.3	gCOD/m ³
Total influent BOD5	BOD ₅	411	gBOD/m ³

Total Kjeldahl Nitrogen	TKN	100	gN/m ³
Total Nitrogen	TN	100.08	gN/m ³
Ammonium	NH ₄	66	gN/m ³
Nitrate & Nitrite	NO _x	0.08	gN/m ³
Total Phosphorus	TP	34.6	gP/m ³
Ortho Phosphate	PO ₄	5.1	gP/m ³
Total Sulphur	TS	16.6	gS/m ³
Sulphide	H ₂ S	5.5	gS/m ³
Total Suspended Solid	TSS	708	g/m ³
Volatile Suspended Solids	VSS	528	g/m ³
Effluent		Concentration	
Flow	Q		
Effluent COD micro filtered	COD _f	142	gCOD/m ³
Effluent BOD ₅	BOD ₅	107	gBOD/m ³
Total Sulphur	TS	5.8	gS/m ³
Sulphide	H ₂ S	1.8	gS/m ³
Total Suspended Solid	TSS	192	g/m ³
Volatile Suspended Solids	VSS	24	g/m ³
Reactor		Concentration	
Total Suspended Solid	TSS	9880	
Volatile Suspended Solids	VSS	3520	
pH		7.01	
Alkalinity	Alk	1550	
Sludge wasted	Q _{was}	3	

The fractions corresponding to soluble and biodegradable COD were adjusted, based on the BOD test, as is explained in STOWA protocol. Thus to this, biodegradable COD (COD_{BD}) is calculated in 49% of COD_{TOTAL}. Regarding the soluble COD measured, Readily Biodegradable COD (RBCOD) represents 14%, and Slowly Biodegradable COD (SBCOD) is 35% of total COD. These values are according to the high suspended solids in domestic wastewater (Gernaey et al. 2004; Henze 2008). That means that the time required to degrade the substrate will be considerable, due to the relation SBCOD/RBCOD. Also, the fractions of TKN and TP are determined based on the COD fractionation, according on the STOWA protocol (Meijer and Brdjanovic 2012). The results obtained after applying the STOWA protocol, are in Table 4-14.

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Table 4-14: Influent characterisation by STOWA protocol

Soluble compounds	Notation	Value	Units
Readily biodegradable COD	S_{BS}	131	mgCOD/L
Unbiodegradable soluble COD	S_{US}	128	mgCOD/L
Volatile Fatty Acids	S_A	9.9	mgCOD/L
Unbiodegradable Soluble TKN	S_{NUS}	1.28	mgCOD/L
Ammonia	S_{NA}	66	mgCOD/L
Phosphate	S_{PO4}	5.1	mgCOD/L
Reduced Sulphur	S_{H2S}	5.5	mgS/L
Particulate compounds			
Unbiodegradable particulate COD (Inert)	X_I	370	mgCOD/L
Slowly biodegradable COD	X_{BS}	340	mgCOD/L
Biodegradable particulate organic Nitrogen	X_{NOX}	11	mgCOD/L
Active Biomass	Z	0	mgCOD/L

4.3.2. Steady state calibration

The colloidal fraction is considered biodegradable compound included as particulate COD in the model, but in the determination of soluble COD, the colloidal particles passes through the membrane of 0.45 μ m. According to (Dursun et al. 2011), in ASDM models as used in PetWin™, the biogas production and the volatile solids reduction, are sensitive of the COD fractions, particularly the unbiodegradable fraction (F_{UP}) and the colloidal fraction (F_{XSP}) of SBCOD. Therefore, calibration process started with the adjustment of F_{US} , F_{UP} , F_{XSP} , and F_{BS} , fractions to fit with biodegradable COD, TSS and VSS of the simulations with the measured values, and SRT was fixed at 60 days as well.

The objective function to be minimized was the sum of the differences in percentage between TSS, VSS, BOD of the influent measured and simulated, thus two sets of parameters were selected. Of these, the dataset is chosen with the least difference in TSS, VSS and COD of the effluent. The detailed variation of the parameters is in Table 4-15; also the difference in the Table 4-16, is shown the difference between two scenarios with best approach

Table 4-15: Analysis of the parameters, in bold the scenarios selected

Influent	Values Measured	Simulation
Results and Discussion		

			1	15	16	17	18	22	24	26
VSS	mg/ L	528	488	458	485	482	497	485	485	503
TSS	mg/ L	708	673	644	670	667	682	669	670	710
BO D	mg/ L	411	285	328	321	332	332	335	336	335
Influent		$\sum \frac{ Vm - Vs }{Vm}$	43 %	42 %	35 %	34%	29 %	32 %	32 %	23 %
Effluent		$\sum \frac{ Vm - Vs }{Vm}$					68 %			53 %

The inert fraction affects the ratio $COD_{PARTICULATE}/VSS$, and this value is adjusted based in the measurements done in sampling campaign. In

Table 4-17 is the fractionation of the influent used. According to (Dursun et al. 2011; Meijer and Brdjanovic 2012) the inert fractions had larger influence in the biodegradability fraction of COD.

Table 4-16: Simulations selected

Parameter	Values tested	Simulation 18	Simulation 25
Fxsp	0.5-0.9	0.17	0.19
Fus=SI	0.08-0.15	0.85	0.85
Fup=Xi	0.25-0.38	0.08	0.08
Fbs	0.12-0.19	0.35	0.31
XI/VSS	0.7-1.6	1.6	1.35
Xs/VSS	0.7-1.6	1.6	1.35

Table 4-17: Model input of influent fractions

Name	Default	Value	Equation
Fbs - Readily biodegradable (including Acetate) (gCOD/g of total COD)	0.160	0.19	$Fbs = \frac{S_{BS}}{CODt}$

F_{AC} - Acetate (gCOD/g of RBCOD)	0.150	0.09	$F_{AC} = \frac{S_{VFA}}{S_{bs}}$
F_{xsp} - Non-colloidal slowly biodegradable (gCOD/g of SBCOD)	0.750	0.85	$F_{xsp} = \frac{S_{xsp}}{S_{US}}$
F_{US} - Unbiodegradable soluble (gCOD/g of total COD)	0.050	0.08	$F_{US} = \frac{S_{US}}{COD_T}$
F_{UP} - Unbiodegradable particulate (gCOD/g of total COD)	0.130	0.35	$F_{UP} = \frac{S_{UP}}{COD_T}$
F_{NA} - Ammonia (gNH ₃ -N/gTKN)	0.660	0.66	$F_{NA} = \frac{S_{NA}}{TKN}$
F_{NOX} - Particulate organic nitrogen (gN/g Organic N)	0.500	0.85	$F_{NOX} = \frac{X_{NOX}}{TKN_{ORGANIC}}$
F_{NUS} - Soluble unbiodegradable TKN (gN/gTKN)	0.020	0.013	$F_{NUS} = \frac{S_{NUS}}{TKN_T}$
$F_{UP,N}$ - N:COD ratio for unbiodegradable part. COD (gN/gCOD)	0.035	0.055	$F_{UP,N} = \frac{X_{IN}}{F_{UP}COD_T}$
F_{PO4} - Phosphate (gPO ₄ -P/gTP)	0.500	0.150	$F_{PO4} = \frac{PO_4}{TP}$
$F_{UP,P}$ - P:COD ratio for unbiodegradable part. COD (gP/gCOD)	0.011	0.009	$F_{UP,P} = \frac{X_{IP}}{F_{UP}COD_T}$
F_{SR} - Reduced sulfur (H ₂ S) (gS/gS)	0.250	0.330	$F_{SR} = \frac{H_2S}{TS}$

Kinetic and Stoichiometric parameters

Most of the reports of calibration parameters using PetWin™ or BioWin are related to anaerobic digestion of sludge. but according to (Dursun et al. 2011) hydrolysis rate and half saturation coefficient have to be calibrated. According with (Batstone 2006) this value is from 0.2 to 0.5 d⁻¹ for primary sludge as well, and it is similar for wastewaters with high content of COD particulate. The parameters of methanogens and SRB were slightly changed from default, due to the low variation in the model. In addition, these parameters are directly related to the production of methane and H₂S, then without measurements (off-line or on-line) is quite difficult to calibrate this parameters properly (Donoso-Bravo et al. 2011). However, regarding (Flores-Alsina et al. 2016) in anaerobic digesters with high ratio COD/SO₄ the SRB can be modelled as H₂ consumers, and the parameters in PetWin™ are according these hypotheses, the values used are the default ones.

Table 4-18: Parameters adjusted in calibration

METHANOGENICS	Default	Adjusted
Results and Discussion		

Acetoclastics maximum specific growth rate (μ_{\max})	d^{-1}	0.30	0.35
Acetoclastics decay rate (Kd)	d^{-1}	0.13	0.11
Acetoclastics yield	-	0.1	0.2
OHO			
Fermentation yield	-	0.1	0.1
Fermentation rate	d^{-1}	1.6	1.6
Hydrolysis rate	d^{-1}	2.1	2.1
Hydrolysis half saturation (K_s)		0.06	0.06
SRB			
Propionate max specific growth rate	d^{-1}	0.583	0.583
Acetotrophic max specific growth rate	d^{-1}	0.047	0.047
Hydrogenotrophic max specific growth rate	d^{-1}	2.8	2.8

As can be seen in

Table 4-19, the relevant results of the model are presented, and the model represents in an acceptable way the process, regarding the lack of information of biogas. However, one relevant difference is the removal of sulphates from the wastewater, reduced to produce H_2S , which is dissolved in the effluent. This is due to the fact that anaerobic models, don't includes the formation and precipitation of FeS , then for the model, all the sulphate is available to converted by SRB.

Table 4-19: Results

Parameter	Unit	Measured	Default parameters	Adjusted parameters
EFFLUENT				
COD	mgCOD/L	354	429	397
TSS	mgTSS/L	194	161	145
VSS	mgVSS/L	168	116.4	100
TS	mgS/L	8	13	13
SO₄	mgS/L	17.4	1	1
REACTOR				
TSS	mgTSS/L	9880	9334	10185
VSS	mgVSS/L	6360	6465	6843

Results and Discussion

Alkalinity	mgCaCO ₃ /L	1550	1701
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4.3.3. Validation of the model

Validation of the model has to be done with another set of measurements, in case of steady states is recommendable to use average data to avoid the noises of the data. (Meijer and Brdjanovic 2012) In this work, the data available is from the sampling campaign done in February, but Nitrogen and Phosphorus was not measured. In addition, during the sampling week, sludge was extracted from one of the reactors. Due to this, the values on TSS, VSS in reactors are higher than the values measured in November. Also, due to the high temperatures during this month (summer 35°C) the water consumption, hence the inflow to the plant increases. For this reason, the up flow velocity increases, expanding the height of the sludge bed, then the TSS in the effluent was quite high. Regarding all this considerations, the data set from the sampling campaign in February was proven in the model. In optimal conditions, this is part of the validation of the model, proving the model in other circumstances and verifying if it is capable to predict the process.

Firstly, the SRT was changed to 90 days due to the time of the sludge in the reactors, and to achieve the biomass minimum in the reactors. Also, the recirculation has to be decreased to 3 times the influent, because the high values, produced the wash out of the biomass. With these considerations, most of the parameters of the influent are quite close, that means the characterization of the influent is acceptable, but the solids in the effluent have differences of 50% between the measured and the simulated. Due to this, the parameters selected are not representative of the process, or the data selected to validate, represents a particular situation, which is not the average of the plant such as, the high content of TSS in the effluent. In Table 4-20 can be seen the values and the differences mentioned.

Table 4-20: Results of the simulations with data from sampling campaign in February

Parameter Unit	15-Feb			21-Feb			
	Measured	Simulated	Difference	Measured	Simulated	Difference	
INFLUENT							
COD	mgCOD/L	546	546	-	488	488	-
TSS	mgTSS/L	517	512	1%	246	289	14%
VSS	mgVSS/L	377	366	3%	216	244	12%
EFFLUENT							
COD	mgCOD/L	351	325	7%	191	364	46%
TSS	mgTSS/L	403	168	58%	303	158	49%
VSS	mgVSS/L	267	126	53%	203	106	42%
TS	mgS/L	12.5	13.1	5%	3.3	13.3	73%
REACTOR							

TSS	mgTSS/L	15802 ⁽¹⁾	14956	5%	7764 ⁽²⁾	10167	24%
VSS	mgVSS/L	9230	11187	17%	4335	6823	36%

(1) TSS of reactor 202, due sludge withdraw was executed during the sampling

(2) Average between two reactors, while one was near 1.4 gTSS/L the other was in 18gTSS/L

Model adjustment for February 2017 and biogas analysis

When the difference between the model and the measured biomass in the reactors, is less than 10%, the model is used, to estimate the biogas production and the percentage of H₂S in biogas, assuming that in three cases all the sulphate is reduced to H₂S even with low kinetics rates of the SRB, but the amount of H₂S gas is less than 1% of total biogas, and the content of methane is between 60 to 75%. In both cases, the hydrogenotrophic SRB is the predominant SRB, according to (Batstone 2006), because of the higher growth rate compared with the propionate and acetotrophic bacteria.

Table 4-21: Efficiencies in the different days modelled.

Parameter	Removal efficiencies					
	22-Nov		15-Feb		21-Feb	
	Model	Measured	Model	Measured	Model	Measured
COD	62%	45%	22%	36%	29%	59%
TSS	78%	87%	49%	22%	48%	-
SO₄	80%	48%	99%	6%	96%	76%

The data from simulations of biogas production are shown in

Table 4-22, in average 130 m³/d per reactor of biogas is produced, with a methane content of 68%, and less than 1% of H₂S. Compared with the calculations from COD mass balance, the production of methane is 382 m³CH₄/d, when the average production estimated by the model is 370 m³/d, slightly high but with acceptable coherence between the two approaches. The methane production per kgCOD removed is higher due to the low efficiency showed in the model. In addition, the model predicts the dissolved methane that escapes with the effluent, in the three cases evaluated, is near 20 mg/L, so represents in average 12% of the total COD. This is in the order of the values estimated in the COD balance.

Table 4-22: Biogas production and composition for one reactor

	Units	22-Nov	15-Feb	21-Feb
Biogas production yield	Nm ³ /d	171.7	112.3	78.5
CH₄	%	75	66	62
H₂S in biogas	%	0.26	0.21	0.19
Methane yield	Nm ³ CH ₄ /kgCOD _{removed}	0.27	0.23	0.24

Model validation with data from February to June 2016

Due to the variation of the data of February, the model was proved using average data of the plant, mostly from February to June, where the COD, BOD were done. Also, is available data of the effluent and TSS, VSS, alkalinity and VFA in the reactors. The dosage of alkaline is lower during these periods. Average data used as input was flow of 1890 m³/d, 899 mgCOD/L, pH 7.4, temperature of 20°C, COD/BOD ratio is 0.40, similar to the data in November. Also, was consider an excess of sludge of 19m³/d, regarding the production calculated before. As can be seen at Table 4-23, the model is quite close to the average data, and SRT was calculated in 104 days. Due to this, can be a good approximation for performance of 2016.

Table 4-23: Results of model using data from February to June 2016

Effluent	Unit	Data	Model
COD	mgCOD/L	330	276
BOD₅	mgCOD/L	85.6	49
pH		7.3	6.72
TSS	mgTSS/L	142	131
Reactor			
TSS	mgTSS/L	14773	12222
VSS	mgTSS/L	7728	8682
Alkalinity	mgCaCO ₃ /L	1500	2220

Table 4-24: Biogas production and methane content from model simulation

Parameter	Unit	Value
Biogas production per reactor	m ³ /d	96
Methane content	%	70
Dissolved methane in the effluent	mg/L	20
SRT	d	101

4.3.4. Dynamic simulation

Dynamic simulation is performed to evaluate the impact of the discharges of the vacuum trucks done between 8:00 to 17:00, during a week. Due to, the lack of dynamic data, will be used the calibrated model of 2016, considering constant flowrate with the characteristics measured of the septic tanks, and out this time, the characteristic used will be the same as the steady state. The data used for septic tanks is based in the measurements done in November, from a grab sample.

Table 4-25: Data from sampling campaign used in the model

Description	Unit	Septic tanks
Flow	m ³ /d	1787
TSS	mg/L	824
VSS	mg/L	668
pH		7.35
Dissolved Oxygen	mg/L	0.21
Alkalinity	mg/L	875
Total Phosphorus	mg/L	44.2
Total COD	mg/L	1320
BOD	mg/L	686
Free saline ammonia	mg/L	108
Sulphate	mgS/L	4.8

As can be seen in Figure 4-13, the biomass inside the reactor decreases with the time, that can be changed, decreasing the volume of sludge extracted from the reactor, by increasing the SRT.

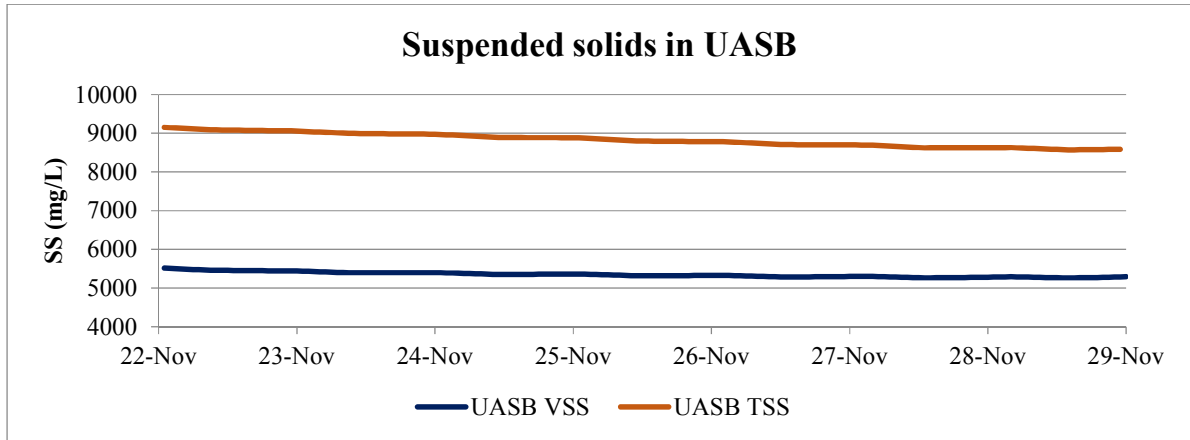


Figure 4-13: Suspended solids in the reactor during simulation

The alkalinity is between 1500 to 2000 mg/L, and VFA are from 300 to 450 mg/L, as can be seen in Figure 4-14. Due to this the Buffer Index (VFA/Alk) factor increases from 0.15 to 0.30, and that means the bicarbonate is being consumed by the acids produced. Then, the dosage has to be adjusted, to prevent the acidification. (Chernicharo 2007). Also, sulphates and sulphides in the reactor remained low as in the steady state.

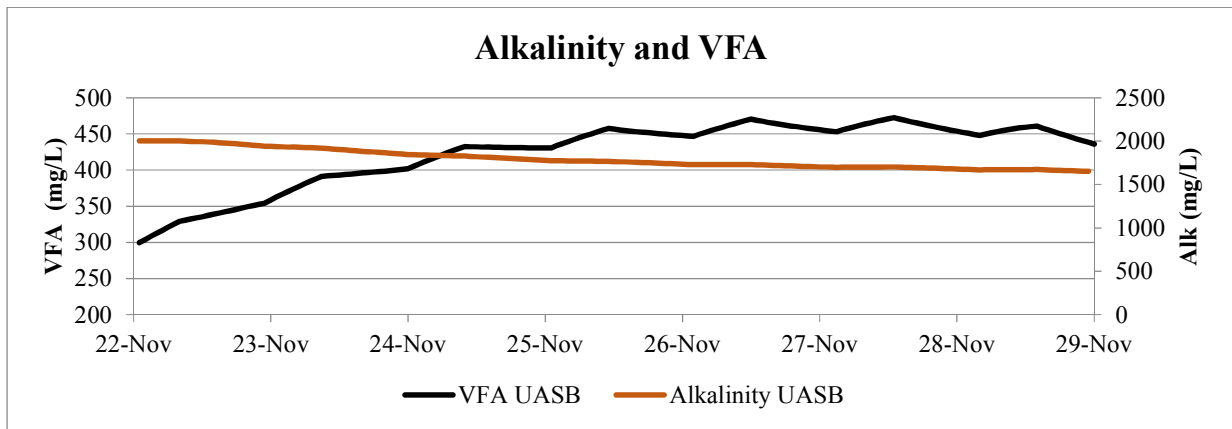


Figure 4-14: Evolution of alkalinity and VFA during the simulation

The suspended solids in the effluent have low variation compared with the influent, which is probably related to the unit used as clarifier, with a fixed removal efficiency of TSS at 99.8%. Then, the TSS in the effluent is 151 ± 2 mg/L, as can be seen in Figure 4-15. COD in the effluent present values of 354 ± 4 mgCOD/L, due to that the impact of the septic tanks seems to be more related to the acidification in the reactors, but with these loadings, the reactor is slightly over the standards of TSS, because BOD in the model is under 100 mg/L.

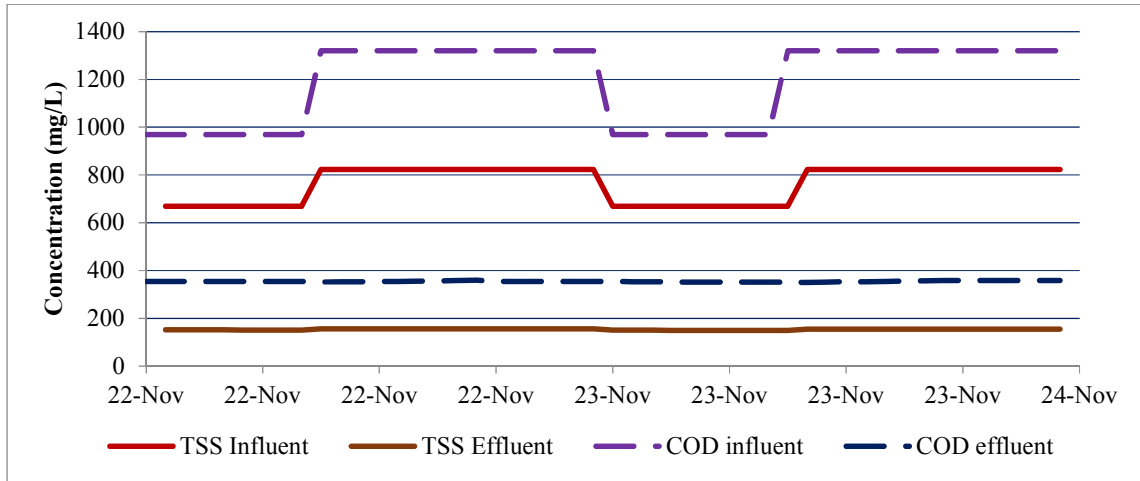


Figure 4-15: Concentration of TSS and COD in the effluent and influent during the simulation

4.3.5. Further analysis

From biogas production, the hydrolysis rate can be adjusted, also, the fractionation of the COD. With this information, the model can be used to analyse the situation under 20°C. Also, include the scums and the rejected water into the plant that in this case was neglected. For dynamic simulations, hourly sampling is required to adjust to these variations.

CHAPTER 5

Recommendations and Conclusions

From February to June of 2016, two reactors were in operation, with an good efficiency according the ranges reported (Chernicharo 2007), in terms of BOD of 75%, with an HRT of 19 hours. This effectiveness is relevant due the high COD/BOD ratio founded in the first months. The standards for the plant are accomplished in terms of BOD, less than 130 mg/L, as well as the TSS are less than 150 mg/L, in 80% of the samplings. But, this result is highly dependent of the sludge withdrawal procedure from the UASB reactors, and HRT in the reactors, as well. Since the velocities in the reactors are low, is no advisable to use a third reactor, then, an optimal procedure of discharge the sludge generated is required, to achieve the 150mgTSS/L in the effluent. Moreover, this parameter is relevant to the next step of disinfection with chloride, because the efficiency depends on the low concentrations of solids in the wastewater.

Considering this, the optimal sludge wasting should be near of 8.6 m^3 , to maintain an average of 18 gTSS/L in the reactors, and a concentration of TSS under 50 mg/L, with an SRT of 100 days. For achieve this flow, a routine of wasting each five days, can be performed. This value can be lower in the coldest months, due the production of biomass in the reactor will be lower as well.

Based in the evolution of the alkalinity indexes of the UASB reactors, the buffer capacity and the relation of the VFA/Alk, the values are according to a stable situation in the reactors, the pH is stable from 6.5 to 7.2 as well. But the dosage of alkalinizing is required to maintain this equilibrium. According the average values of pH of the influent and pH of the reactors, a minimum dosage of $200 \text{ mgCaCO}_3/\text{L}$ is required to maintain the pH from 7 to 7.2.

The SMA is according to the literature, but seems to be affected by the accumulation of the inerts solids in the reactor. However, the minimum mass required in the reactors, according to the SMA is too high. Also, the sludge digester capacity from SMA is $0.15 \text{ kgCOD}/\text{m}^3\text{d}$, when during this time was between 0.5 to $1.0 \text{ kgCOD}/\text{m}^3\text{d}$. But considering the stable behaviour of the reactors against an organic load greater than that established from the SMA, it is possible that this value is not representative of the current sludge. Due to this, should be relevant to analyse again the SMA, to confirm the state of the sludge.

Another measurement relevant to monitor and control the plant is the biogas production and the composition as well. Due to the lack of calibration of the gas meters, these values were estimated from the COD balance. The methane yield estimated is between $0.10 - 0.17 \text{ Nm}^3\text{CH}_4/\text{kgCOD}_{\text{removed}}$, due to this, the biogas production average is $350 \text{ Nm}^3\text{CH}_4/\text{d}$, assuming 70% of methane means $500 \text{ Nm}^3/\text{d}$ of biogas. These calculations were done assuming the worst scenario in terms of methane losses. The potential energy can be calculated as $2.3 \text{ MJ}/\text{m}^3$ per day, with a daily production of $13000 \text{ MJ}/\text{d}$, for the actual inflow.

Recommendations and Conclusions

That represents 15% of the daily energy used in the plant, based in an efficiency of 40% of electric conversion. Hence, could be analysed the real production, and if is feasibility to use the energy in the plant.

The concentration of sulphate in the influent, is between 30- 40 mgSO₄/L, a bit lower compared with values reported in Brazil and Colombia (Cheremisinoff 2002) But, these values might be reduced, by the addition of FeCl₃ in the pump station. Regarding the average COD in the influent, the sulphate produced in the pipeline is 7.9mgSO₄-S/L per hour. The dose of FeCl₃ estimated for reduce this amount of sulphate produced, is 116 kgFe/d, or 250 kgFe/d, including the sulphate contribution from the householders. The dosage of FeCl₃ in the pump station is 234 kgFe/d, quite close to the required for the average of the time. Then, the reduction estimated is 75% on the sulphate in the influent from Pando city. In addition, the sulphate that reaches the plant will be reduced in to H₂S.

From sampling campaigns, the efficiency in the removal of sulphate is 43% that leads in to a 24 m³/d of H₂S regarding all the sulphate will be reduced. However, from the mass balance of the sulphates, a fraction will be in the sludge, reducing the H₂S produced. Regarding the pH and the solubility will be dissolved into the water phase. But, the due to the low concentration is not expected inhibition of the methanogenesis. The release of the gas is produced in the discharges structures, such as the weir for the effluent, where the turbulence increases. Also, regarding the iron in the wastewater, part will be binding to FeS, and accumulated in the sludge, the value obtained is 8.6 g/kg of dry sludge. The use of other electron acceptor as nitrite, can be reduce this accumulation, due the nitrate required per gram of sulphide is lower than the iron. (Zhang et al. 2008)

Most of the problems founded in the plant, are related to the protocols of operation, and the learning of the personal to handle it. Due to lack of staff, tasks such as collecting information systematically, and reporting, have been left out. As far as the information that is generated, it is difficult to use it to take actions in time. Also laboratory procedures are adjusting, so some results are not reliable.

Finally, the model obtained from November, requires accurate data to calibrate it. The hydrolysis rate, can be adjusted if the biogas production is known. The parameters most sensitive were the methanogens yields, while the yields of the SRB don't affect the model. In these case, all the sulphate was used to produce H₂S, and the results shows values less than 1% of the biogas composition However, the model doesn't fit in to the data form February. Adjustments, into the recirculation, the SRT and the solids retained in the clarifier, have to be done, as well. These differences can be related, to the change of the reactors used from November to February. Also, operative procedures, as wasting of the sludge from the reactors, due the high TSS in the effluent, were implemented during this week. However, for the average data of 2016, the model is applied, and represents quite well the situation, regarding the lack of the parameters for this time. Also, the analysis of the changes of the load was analysed, but the adjustment required is the dose of alkalinizing, that was commented before. Due to this, is required more measurements, for instance the biogas production, and composition, if an accurate model is required.

References

- Batstone DJ (2006) Mathematical Modelling of Anaerobic Reactors Treating Domestic Wastewater: Rational Criteria for Model Use. *Rev Environ Sci Bio/Technology* 5:57–71. doi: 10.1007/s11157-005-7191-z
- Batstone DJ, Keller J, Angelidaki I, et al (2002) The IWA Anaerobic Digestion Model No 1 (ADM1). *Water Sci Technol* 45:65–73. doi: 10.2166/wst.2008.678
- Batstone DJ, Puyol D, Flores-Alsina X, Rodríguez J (2015) Mathematical modelling of anaerobic digestion processes: applications and future needs. *Rev Environ Sci Bio/Technology* 14:595–613. doi: 10.1007/s11157-015-9376-4
- Chen JL, Ortiz R, Steele TWJ, Stuckey DC (2014) Toxicants inhibiting anaerobic digestion: A review. *Biotechnol Adv* 32:1523–1534. doi: 10.1016/j.biotechadv.2014.10.005
- Chen Y, He J, Mu Y, et al (2015) Mathematical modeling of upflow anaerobic sludge blanket (UASB) reactors: Simultaneous accounting for hydrodynamics and bio-dynamics. *Chem Eng Sci* 137:677–684. doi: 10.1016/j.ces.2015.07.016
- Cheremisinoff NP (2002) *Handbook of Water and Wastewater Treatment Technologies*.
- Chernicharo CA de L (2007) *Biological Wastewater Treatment Vol 4-Anaerobic Reactors*. IWA Publishing, London, UK
- Chernicharo CAL, van Lier JB, Noyola A, Bressani Ribeiro T (2015) Anaerobic sewage treatment: state of the art, constraints and challenges. *Rev Environ Sci Biotechnol* 14:649–679. doi: 10.1007/s11157-015-9377-3
- Dhaked RK, Singh P, Singh L (2010) Biomethanation under psychrophilic conditions. *Waste Manag* 30:2490–2496. doi: 10.1016/j.wasman.2010.07.015
- Donoso-Bravo A, Mailier J, Martin C, et al (2011) Model selection, identification and validation in anaerobic digestion: a review. *Water Res* 45:5347–64. doi: 10.1016/j.watres.2011.08.059
- Dursun D, Jimenez J, Bratby J (2011) Whole Plant Modeling to Optimize the Biogas Production in Anaerobic Digesters. *Proc Water Environ Fed* 2011:655–665. doi: 10.2175/193864711802836607
- Elmitwalli T (2013) Mathematical modeling of upflow anaerobic sludge blanket (UASB) reactor treating domestic wastewater. *Water Sci Technol* 67:24–32. doi: 10.2166/wst.2012.512
- EnviroSim Associates Ltd PetWin Help Manual.
- Fedorovich V, Lens P, Kalyuzhnyi S (2003) Extension of Anaerobic Digestion Model No. 1 with Processes of Sulfate Reduction. *Appl Biochem Biotechnol* 109:33–46. doi: 10.1385/ABAB:109:1-3:33
- Firer D, Friedler E, Lahav O (2008) Control of sulfide in sewer systems by dosage of iron salts: Comparison between theoretical and experimental results, and practical implications. *Sci Total Environ* 392:145–156. doi: 10.1016/j.scitotenv.2007.11.008
- Flores-Alsina X, Solon K, Kazadi Mbamba C, et al (2016) Modelling phosphorus (P), sulfur (S) and iron (Fe) interactions for dynamic simulations of anaerobic digestion processes. *Water Res* 95:370–382. doi: 10.1016/j.watres.2016.03.012
- Gernaey K V, van Loosdrecht MC., Henze M, et al (2004) Activated sludge wastewater treatment plant modelling and simulation: state of the art. *Environ Model Softw* 19:763–783. doi: 10.1016/j.envsoft.2003.03.005
- Grau P, Copp J, Vanrolleghem PA, et al (2009) A comparative analysis of different approaches for
- References
-

- integrated WWTP modelling. *Water Sci Technol* 59:141–147. doi: 10.2166/wst.2009.589
- Hao T, Xiang P, Mackey HR, et al (2014) A review of biological sulfate conversions in wastewater treatment. *Water Res* 65:1–21. doi: 10.1016/j.watres.2014.06.043
- Henze M (2008) *Biological wastewater treatment : principles, modelling and design*. IWA Publishing
- Hvitved-Jacobsen T, Vollertsen J, Nielsen AH (2013) *Sewer processes : microbial and chemical process engineering of sewer networks*. CRC Press
- Jones R, Takacs I (2004) Modelling the impact of anaerobic digestion on the overall performance of biological nutrient removal wastewater. In: *Proceedings of the Water Environment Federation, WEFTEC 2004*. Water Environment Federation, pp 244–257
- Kalyuzhnyi SV V, Fedorovich VV V (1998) Mathematical modelling of competition between sulphate reduction and methanogenesis in anaerobic reactors. *Bioresour Technol* 65:227–242. doi: 10.1016/S0960-8524(98)00019-4
- Koster W, Lettinga G (1985) Application of the Upflow Anaerobic Sludge Bed (UASB) Process for Treatment of Complex Wastewaters at Low Temperatures.
- Li L, He Q, Wei Y, et al (2014) Early warning indicators for monitoring the process failure of anaerobic digestion system of food waste. *Bioresour Technol* 171:491–494. doi: 10.1016/j.biortech.2014.08.089
- Liu Y, Zhang Y, Ni BJ (2015) Evaluating enhanced sulfate reduction and optimized volatile fatty acids (VFA) composition in anaerobic reactor by Fe (III) addition. *Environ Sci Technol* 49:2123–2131. doi: 10.1021/es504200j
- Lobato LCS, Chernicharo CAL, Souza CL (2012) Estimates of methane loss and energy recovery potential in anaerobic reactors treating domestic wastewater. *Water Sci Technol* 66:2745. doi: 10.2166/wst.2012.514
- Lübken M, Kosse P, Koch K, et al (2015) Influent Fractionation for Modeling Continuous Anaerobic Digestion Processes.
- Meijer SCF, Brdjanovic D (2012) *A practical guide to activated sludge modeling*. UNESCO-IHE Institute for Water Education
- Nielsen A, Lens P, Vollrsten J, Hvitved-Jacobsen T (2005) Sulfide–iron interactions in domestic wastewater from a gravity sewer. *Water Res* 39:2747–2755. doi: 10.1016/j.watres.2005.04.048
- O'Reilly J, Chinalia FA, Mahony T, et al (2009) Cultivation of low-temperature (15°C) anaerobic wastewater treatment granules. *Lett Appl Microbiol* 49:421–426. doi: 10.1111/j.1472-765X.2009.02682.x
- Pérez A, Torres P (2008) Indices de alcalinidad para el control del tratamiento anaerobio de aguas residuales fácilmente acidificables. (Spanish). *Ing y Compet* 10:41–52.
- Poinapen J, Ekama G, Wentzel M (2009) Biological sulphate reduction with primary sewage sludge in an upflow anaerobic sludge bed (UASB) reactor – Part 2: Modification of simple wet chemistry analytical procedures to achieve COD and S mass balances.
- Ripley LE, Boyle WC, Converse JC (1986) Improved Alkalimetric Monitoring for Anaerobic Digestion of High-Strength Wastes. *J Water Pollut Control Fed*. doi: 10.1016/S0262-1762(99)80122-9
- Rosa AP, Lobato LCS, Chernicharo CAL, et al (2012) Improving performance and operational control of UASB reactors via proper sludge and scum discharge routines. *Water Pract Technol*. doi: 10.2166/wpt.2012.046
- Seghezzo L (2004) *Anaerobic treatment of domestic wastewater*. Wageningen University,
- References
-

Wageningen, the Netherlands

Souza CL, Chernicharo CAL, Melo GCB (2012) Methane and hydrogen sulfide emissions in UASB reactors treating domestic wastewater. *Water Sci Technol* 65:1229–1237. doi: 10.2166/wst.2012.854

Subtil EL, Cassini STA, Gonçalves RF (2012) Sulfate and dissolved sulfide variation under low COD/Sulfate ratio in Up-flow Anaerobic Sludge Blanket (UASB) treating domestic wastewater. *Ambient e Agua - An Interdiscip J Appl Sci* 7:130–139. doi: 10.4136/ambi-agua.849

Sun H, Wu S, Dong R (2016) Monitoring Volatile Fatty Acids and Carbonate Alkalinity in Anaerobic Digestion: Titration Methodologies. *Chem Eng Technol* 39:599–610. doi: 10.1002/ceat.201500293

Turkdogan-Aydinol FI, Yetilmezsoy K, Comez S, Bayhan H (2010) Performance evaluation and kinetic modeling of the start-up of a UASB reactor treating municipal wastewater at low temperature. *Bioprocess Biosyst Eng* 34:153–162. doi: 10.1007/S00449-010-0456-0

Uemura S, Harada H (2000) Treatment of sewage by a UASB reactor under moderate to low temperature conditions. *Bioresour Technol* 72:275–282. doi: 10.1016/S0960-8524(99)00118-2

Van Haandel AC (1994) Influence of the digested COD concentration on the alkalinity requirement in anaerobic digesters. *Water Sci. Technol.* 30:23–34.

van Lier J, Mahmoud N, Zeeman G (2008) Anaerobic wastewater treatment. In: Henze M, van Loosdrecht MCM, Ekama GA, Brdjanovic D (eds) *Biological Wastewater Treatment: Principles, Modelling and Design*. IWA Publishing,

Van Lier JB, Rebac S, Lettinga G (1997) High-rate anaerobic wastewater treatment under psychrophilic and thermophilic conditions. *Water Sci Technol* 35:199–206. doi: 10.1016/S0273-1223(97)00202-3

van Lier JB, Zee FP, Frijters CTMJ, Ersahin ME (2015) Celebrating 40 years anaerobic sludge bed reactors for industrial wastewater treatment. *Rev Environ Sci Bio/Technology* 14:681–702. doi: 10.1007/s11157-015-9375-5

Zhang L, De Schryver P, De Gussem B, et al (2008) Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. *Water Res* 42:1–12. doi: 10.1016/j.watres.2007.07.013

Appendices

Appendix A Results of Samplings Campaigns

Table 5-1 Result sampling campaign 22 of November 2016

Date: 22-23 November 2016			Septic tanks	Pando PS	Influent	UASB reactors		Effluent	Sludge excess
Description	Code	Unit	grab	grab	24 com	grab	grab	grab	grab
Flow	Q	m ³ /d	1787	2497	4284	1428	1428	4284	
Total Solids	TS	g/L	1.26	1.33	1.21			-	22.6
Inorganic Solids	IS	g/L	0.504	0.472	0.532				3.87
Total Suspended Solids	TSS	mg/l	824	856	708	9.88	4.9	192	13.4
Inorganic suspended solid	ISS	mg/l	156	172	180	3.52	1.76	24	4.88
VSS	VSS		668	684	528	6.36	3.14	168	8.52
pH	pH		7.35	7.28	7.67	6.92	7.19	7.24	
Dissolved Oxygen	DO	mg/L	0.21	0.13	0.18			0.23	
Alkalinity	Alk	mg/L	875	500	650	2088	1025		
VFA	VFA	mg/L	302	274	173	826	672		
Total Phosphorus	TP	mg/L	44.2	42.6	34.6			36.2	
Phosphorus soluble	PO4	mg/L	5.79	4.54	0.8	0.36	4.16	4.67	5.58
Oil and Grease	O&G	g/L			42				2.22

Total COD	TCOD	g/L	1.32	1.59	0.969	12.8	9.74	0.354	
Filtered COD	COD MF	mg/L	406	587	259	333	440	142	
BOD5	BOD ₅	mg/L	686	773	411	1.92	1.37	184	
Filtered BOD	BOD ₅ MF	mg/L	243	389	166	0.27	0.38	107	
Total Kjeldahl Nitrogen	TKN	mg/L	67.2	133	26.5	393	1028	12	
Free saline ammonia	NH ₄	mg/L	108	93.6	84.4	122	110	89.6	603
Nitrates	NO ₃	mg/L	0.07	0.08	0.08	0.08	0.09	0.07	0.5
Nitrites	NO ₂	mg/L	ND	ND	ND	ND	ND	ND	ND ¹
Sulphide	S	mgS/l			5.5	159	49.7	1.8	254
Sulphate	SO ₄	mgSO ₄ /L	14.4	13.8	33.3	2.5	2.57	17.4	144
Magnesium	Mg	mg/L	16	14	14			14	18
Calcium	Ca	mg/L	56	49	51			52	70
Total iron	T Fe	mg/L			11			3.2	28

(1) Detection limit 0.018 mgN/L

Table 5-2: Data from sampling campaign 15 February 2017

Date: 15-16 February 2017			Septic tanks	Influent	UASB reactors		Effluent	Sludge excess
Description	Code	Unit	comp	24 com	comp	comp	comp	comp
Flow	Q	m ³ /d	4193	7039	3520	3520	5364	4193
Sulphide	S	mgS/L		2.2	43.2	33.8	1.1	43.2
Sulphate	SO ₄	mg SO ₄ /L		36.3	53.8	38.1	34.2	53.8
pH				7.8	7.3	7.7	7.3	
VFA (composition GC)	VFA gc	mgHAc/L			5.24	4.6		
VFA (titration)	VFA t	mg/L		235		298		
Bicarbonate Alkalinity	BA	mg/L		755		754		
Total Suspended Solids	TSS	mg/L		517		15802	403	
Volatile suspended solids	VSS	mg/L		377		9230	267	
Total COD	TCOD	mg/L		546			351	
Filtered COD	CODMF	mg/L		143			91	
BOD ₅	BOD ₅	mg/L	644	208			241	644
Filtered BOD	BOD ₅ MF	mg/L	320	102			115	320
Total Iron	TF	mg Fe/L		7.2				3.9

Table 5-3: Data from sampling campaign 21 February 2017

Date: 21-22 February 2017			Septic tanks	Influent	UASB reactors		Effluent	Sludge excess
Description	Code	Unit	comp	24 com	comp	comp	comp	comp
Flow	Q	m ³ /d	3765	6235	3117.5	3118	3118	6215
Sulphide	S	mgS/L						
Sulphate	SO ₄	mg SO ₄ /L		40.4	14.8	1.96	9.59	
pH	pH			7.68	7.48	7.44	7.16	
VFA (composition GC)	VFA gc	mgHAc/L			13.625	3.59	4.89	
VFA (titration)	VFA t	mgHAc/L			357	370		
Alkalinity	Alk	mg/L		632	761	919		
Total Suspended Solids	TSS	mg/L		246	1042	14486	303	
Volatile suspended solids	VSS	mg/L		216	508	8162	203	
Total COD	TCOD	mg/L		488	645	3690	191	
Filtered COD	CODMF	mg/L						
BOD ₅	BOD5	mg/L	358	211		774	155	358
Filtered BOD	BOD5 MF	mg/L	225	94	164	184	114	225
Total Iron	TF	mg Fe/L		1.8				79

Appendix B Sludge wasting and SRT calculations

Table 5-4: Data from the plant from February to June of 2016

Date	TSS 203 (mg/L)	VSS 203	TSS 204 (mg/L)	VSS 203	TSS eff (mg/L)	VSS eff (mg/L)	Sludge wasted reactor 203 (m3/d)	TSS in sludge 203 (g/L)	Sludge wasted reactor 204 (m3/d)	TSS in sludge 204 (g/L)
	mg/L									
22-Feb	8970	5200	7990	4530	61	45				
23-Feb	6900	5533	4770	3170				11.43		
25-Feb	8120	5250	5770	2200						14.62
26-Feb					89	87				14.62
03-Mar	10750	6430	9890	5630				17.62		23.99
04-Mar	12220	7020	11070	6250				17.62		23.99
08-Mar	13620	8000	12620	7020				26.9		
10-Mar					88	38		26.9		
16-Mar	12990	7660	13510	7940						31.1
19-Mar					98	58		31.45		
22-Mar	15110	8840	13820	8240				28.83		
24-Mar							31			
29-Mar	14130	8420	15190	8830	24	16				25.12
05-Apr	16500	6510	17900	7050				31.52		
06-Apr					46	34	28			
07-Apr									30	

08-Apr	16000	6190	17880	6920						25.12
13-Apr	17900	7220	14290	5690	78	68		43.57		
14-Apr							20			
19-Apr	18250	7130	20280	8420			29			
20-Apr									35	
21-Apr					53	44		43.57		42.16
25-Apr							10			
26-Apr	18140	7590	18020	7590						
05-May	19200	7832	19350	11289	151	144		24.5		
11-May	19500	7833	19750	11542						24.47
12-May					131	116				
17-May	18510	7253	18160	10785						
25-May	17050	6867	19100	11449				23.51		
26-May							70			
27-May					250	172			65	
31-May	14800	5600	15250	9350				21.16		
01-Jun					63	53	34			
02-Jun					69	62				25.71
03-Jun					114	83			20	
06-Jun					72	62		23.18		
07-Jun					144	116			23	28
08-Jun	12950	7600	18930	11220	100	93			22	
09-Jun					99	66	38			

13-Jun									32	
14-Jun					123	113				24.05
15-Jun							87	23.79		
17-Jun	17530	10810	16930	10480	141	118				
20-Jun									34	
22-Jun	13540	8780	16210	10190				21.46		
23-Jun					97	85				26.54
24-Jun					104	91				
26-Jun							29			
28-Jun	13100	8500	18230	9400	93	66			23	
29-Jun							27			

Table 5-5: Calculations of the SRT based in Equation 4-1 in terms of TSS

	Feb to June	May-Jun	Scenario 1	Scenario 2	Scenario 2
Excess sludge (m3/d)	1	4	8.50	8.5	19
TSS sludge (g/L)	26	24	26.00	25	26
MTSS, sludge (kg/d)	20	99	221.00	212.50	494.00
TSS reactor (g/L)	16.6	17.1	18	18	15
MTSS (kg/d)	31445	40445	42534	42534	35445
Flow	3780	2747	3780.00	3780	3780
TSS eff (g/L)	0.10	0.117	0.130	0.050	0.150
SRT (d)	79	96	60	106	33

Table 5-6: Calculations of the SRT based in Equation 4-1 in terms of VSS

	Feb to June	May-Jun	Scenario 1	Scenario 2	Scenario 2
Excess sludge (m ³ /d)	0.75	2.34	8.50	16.00	10.00
VSS sludge (g/L)	14	12	13.00	13.00	13.00
MVSS, sludge (kg/d)	10	22	110.50	208.00	130.00
VSS reactor (g/L)	9.87	9.27	9.00	9.00	9.00
MVSS (kg/d)	23313	21895	21267	21267	21267
Flow (m ³ /d)	3780	2747	3780	3780	3780
VSS eff (g/L)	0.031	0.096	0.050	0.050	0.050
SRT (d)	181	77	71.01	53.57	66.67

Table 5-7: Volume produced in function of the yield of production

Yield	COD applied	TSS sludge	TSS produced	Volume of sludge produced
kgTSS/CODapplied	kgCOD/d	%	kgTSS/d	m ³ TSS/d
0.09	950	30	277	0.90
0.12	950	30	369	1.19
0.13	950	30	400	1.29
0.14	950	30	430	1.39
0.15	950	30	461	1.49
0.16	950	30	492	1.59
0.17	950	30	523	1.69
0.18	950	30	553	1.79

Appendix C Iron chloride calculations

Table 5-8: Dosage of iron chloride per day of sampling

Parameter	Unit	Feb to June 2016	22-Nov-16	Average 2016	21-Nov-16
Q Pando	m ³ /d	2670	2497	2902	2480
	m ³ /h	111	104	121	103
Q _{total}	m ³ /d	3708	4284	4031	4044
	m ³ /h	155	179	168	169
Dose applied (g/h)	gFeCl ₃	28000	28000	28000	28000
Dose per m ³ (g/m ³)	gFeCl ₃ /m ³	252	269	232	271
Dose of Fe	gFe ⁺³ /m ³	88	94	81	94
Mass of iron applied	kgFe/d	325	401	325	381
Iron in the influent	mg/L	6.9	11	7.9	1.8
Mass of iron in the inf	kgFe/d	18.4	27.5	22.9	4.5
Iron consumed	kgFe/d	306	374	302	377
mgFe/L consumed	mgFe/L	115	150	104	152
mgSO ₄ /L reduced	mgSO ₄ /L	197	256	178	260
SO ₄ , inf	mgSO ₄ /L		33	36	40
%SO ₄ to the plant	%		22%	28%	25%

Table 5-9: Calculation of iron required to avoid sulphate formation in pipelines molar ratio Fe:S=1

Time	Flow	HRT	Sulfide	Sulfide	Fe:S	Fe	Fe	Fe
hours	m ³ /h	hours	g/m ³	mol/m ³	mol/mol	mol/m ³	g/m ³	kg/hour
0	131	19.0	10.7	0.3	1.0	0.3	18.6	2.4
1	90	19.3	10.8	0.3	1.0	0.3	18.8	1.7
2	85	19.1	10.7	0.3	1.0	0.3	18.6	1.6
3	83	19.7	11.1	0.3	1.0	0.3	19.3	1.6
4	75	18.5	10.4	0.3	1.0	0.3	18.1	1.4
5	59	18.2	10.2	0.3	1.0	0.3	17.8	1.1
6	88	17.8	10.0	0.3	1.0	0.3	17.4	1.5
7	86	17.5	9.8	0.3	1.0	0.3	17.1	1.5
8	118	17.2	9.7	0.3	1.0	0.3	16.9	2.0
9	108	17.6	9.9	0.3	1.0	0.3	17.2	1.9
10	107	17.9	10.0	0.3	1.0	0.3	17.5	1.9
11	121	18.3	10.3	0.3	1.0	0.3	17.9	2.2
12	113	19.9	11.2	0.3	1.0	0.3	19.5	2.2
13	126	19.2	10.8	0.3	1.0	0.3	18.8	2.4
14	122	19.3	10.8	0.3	1.0	0.3	18.9	2.3
15	111	19.4	10.9	0.3	1.0	0.3	19.0	2.1
16	119	19.4	10.9	0.3	1.0	0.3	19.0	2.3

17	99	19.4	10.9	0.3	1.0	0.3	19.0	1.9
18	121	19.2	10.8	0.3	1.0	0.3	18.8	2.3
19	104	19.2	10.8	0.3	1.0	0.3	18.8	2.0
20	112	18.1	10.2	0.3	1.0	0.3	17.7	2.0
21	126	19.1	10.7	0.3	1.0	0.3	18.7	2.4
22	107	17.2	9.6	0.3	1.0	0.3	16.8	1.8
23	99	16.2	9.1	0.3	1.0	0.3	15.8	1.6

Table 5-10: Iron calculations for avoid sulphate in pipelines and concentration of 10 mg/L from households. Molar ratio Fe:S=1

Time	Flow	HRT	Sulfide	Sulfide	Fe:S	Fe	Fe	Fe required
hours	m ³ /h	hours	g/m ³	mol/m ³	mol/mol	mol/m ³	g/m ³	kg/hour
0	131	19.0	20.7	0.6	1.0	0.6	36.0	4.7
1	90	19.3	20.8	0.6	1.0	0.6	36.3	3.2
2	85	19.1	20.7	0.6	1.0	0.6	36.1	3.1
3	83	19.7	21.1	0.7	1.0	0.7	36.7	3.1
4	75	18.5	20.4	0.6	1.0	0.6	35.5	2.7
5	59	18.2	20.2	0.6	1.0	0.6	35.2	2.1
6	88	17.8	20.0	0.6	1.0	0.6	34.8	3.0
7	86	17.5	19.8	0.6	1.0	0.6	34.5	3.0
8	118	17.2	19.7	0.6	1.0	0.6	34.3	4.0
9	108	17.6	19.9	0.6	1.0	0.6	34.6	3.7

10	107	17.9	20.0	0.6	1.0	0.6	34.9	3.7
11	121	18.3	20.3	0.6	1.0	0.6	35.4	4.3
12	113	19.9	21.2	0.7	1.0	0.7	36.9	4.2
13	126	19.2	20.8	0.6	1.0	0.6	36.2	4.6
14	122	19.3	20.8	0.6	1.0	0.6	36.3	4.4
15	111	19.4	20.9	0.7	1.0	0.7	36.4	4.0
16	119	19.4	20.9	0.7	1.0	0.7	36.4	4.3
17	99	19.4	20.9	0.7	1.0	0.7	36.4	3.6
18	121	19.2	20.8	0.6	1.0	0.6	36.2	4.4
19	104	19.2	20.8	0.6	1.0	0.6	36.2	3.8
20	112	18.1	20.2	0.6	1.0	0.6	35.1	3.9
21	126	19.1	20.7	0.6	1.0	0.6	36.1	4.6
22	107	17.2	19.6	0.6	1.0	0.6	34.2	3.7
23	99	16.2	19.1	0.6	1.0	0.6	33.3	3.3

Table 5-11: Iron calculations for avoid sulphate in pipelines. Molar ratio Fe:S=2.5

Time	Flow	HRT	Sulfide	Sulfide	Fe:S	Fe	Fe	Fe
hours	m3/h	hours	g/m3	mol/m3	mol/mol	mol/m3	g/m3	kg/hour
0	131	19.0	10.7	0.3	2.5	0.8	46.5	6.1
1	90	19.3	10.8	0.3	2.5	0.8	47.1	4.2
2	85	19.1	10.7	0.3	2.5	0.8	46.6	4.0

3	83	19.7	11.1	0.3	2.5	0.9	48.2	4.0
4	75	18.5	10.4	0.3	2.5	0.8	45.1	3.4
5	59	18.2	10.2	0.3	2.5	0.8	44.4	2.6
6	88	17.8	10.0	0.3	2.5	0.8	43.5	3.8
7	86	17.5	9.8	0.3	2.5	0.8	42.8	3.7
8	118	17.2	9.7	0.3	2.5	0.8	42.1	5.0
9	108	17.6	9.9	0.3	2.5	0.8	43.0	4.7
10	107	17.9	10.0	0.3	2.5	0.8	43.7	4.7
11	121	18.3	10.3	0.3	2.5	0.8	44.8	5.4
12	113	19.9	11.2	0.3	2.5	0.9	48.8	5.5
13	126	19.2	10.8	0.3	2.5	0.8	46.9	5.9
14	122	19.3	10.8	0.3	2.5	0.8	47.1	5.7
15	111	19.4	10.9	0.3	2.5	0.8	47.4	5.3
16	119	19.4	10.9	0.3	2.5	0.8	47.4	5.7
17	99	19.4	10.9	0.3	2.5	0.8	47.4	4.7
18	121	19.2	10.8	0.3	2.5	0.8	47.1	5.7
19	104	19.2	10.8	0.3	2.5	0.8	47.0	4.9
20	112	18.1	10.2	0.3	2.5	0.8	44.2	4.9
21	126	19.1	10.7	0.3	2.5	0.8	46.7	5.9
22	107	17.2	9.6	0.3	2.5	0.8	42.0	4.5
23	99	16.2	9.1	0.3	2.5	0.7	39.6	3.9

Table 5-12: Iron calculations for avoid sulphate in pipelines and concentration of 10 mg/L from households. Molar ratio Fe:S=2.5

Time	Flow	HRT	Sulfide	Sulfide	Fe:S	Fe	Fe	Fe required
hours	m3/h	hours	g/m3	mol/m3	mol/mol	mol/m3	g/m3	kg/hour
0	131	19.0	20.7	0.6	2.5	1.6	90.1	11.8
1	90	19.3	20.8	0.6	2.5	1.6	90.6	8.1
2	85	19.1	20.7	0.6	2.5	1.6	90.1	7.7
3	83	19.7	21.1	0.7	2.5	1.6	91.8	7.7
4	75	18.5	20.4	0.6	2.5	1.6	88.7	6.7
5	59	18.2	20.2	0.6	2.5	1.6	88.0	5.2
6	88	17.8	20.0	0.6	2.5	1.6	87.0	7.6
7	86	17.5	19.8	0.6	2.5	1.5	86.3	7.4
8	118	17.2	19.7	0.6	2.5	1.5	85.7	10.1
9	108	17.6	19.9	0.6	2.5	1.5	86.5	9.4
10	107	17.9	20.0	0.6	2.5	1.6	87.2	9.3
11	121	18.3	20.3	0.6	2.5	1.6	88.4	10.7
12	113	19.9	21.2	0.7	2.5	1.7	92.3	10.4
13	126	19.2	20.8	0.6	2.5	1.6	90.4	11.4
14	122	19.3	20.8	0.6	2.5	1.6	90.7	11.0
15	111	19.4	20.9	0.7	2.5	1.6	91.0	10.1
16	119	19.4	20.9	0.7	2.5	1.6	90.9	10.9
17	99	19.4	20.9	0.7	2.5	1.6	91.0	9.0

18	121	19.2	20.8	0.6	2.5	1.6	90.6	10.9
19	104	19.2	20.8	0.6	2.5	1.6	90.5	9.4
20	112	18.1	20.2	0.6	2.5	1.6	87.7	9.8
21	126	19.1	20.7	0.6	2.5	1.6	90.2	11.4
22	107	17.2	19.6	0.6	2.5	1.5	85.5	9.1
23	99	16.2	19.1	0.6	2.5	1.5	83.2	8.2

Appendix D Calculations of biogas production and H₂S estimation

Table 5-13: Equations used in the calculation in biogas production based in (Lobato et al. 2012)

$\text{COD}_{\text{CH}_4\text{-converted}} = \text{COD}_{\text{removed}} - \text{COD}_{\text{sludge}} - \text{COD}_{\text{SO}_4\text{-converted}}$
$\text{COD}_{\text{removed}} = Q_{\text{inf}} * \text{Eff}_{\text{COD}}$
$\text{COD}_{\text{sludge}} = \text{COD}_{\text{removed}} * Y_{\text{sludge COD}} = \text{COD}_{\text{removed}} * Y_{\text{sludge}} * 1.42$
$C_{\text{SO}_4\text{-converted}} = \text{SO}_{4,\text{INF}} * Q * \text{Eff}_{\text{rem SO}_4} * k_{\text{COD-SO}_4}$
$Q_{\text{CH}_4} = \text{COD}_{\text{CH}_4\text{-converted}} * \frac{R * (T + 273)}{1000 * P * K_{\text{COD}}}$
$Q_{\text{CH}_4\text{-recovered}} = Q_{\text{CH}_4}(1 - p_w - p_o) + Q * p_L * f_{\text{CH}_4} * \frac{R * (T + 273)}{1000 * P * K_{\text{COD}}}$

Table 5-14: Parameters used

Parameter	Unit	Worst Case	Best Case	Average	22-Nov-16	15-Feb-17	21-Feb-17
Sulfate concentration	S _{SO4} kgSO ₄ /m ³	0.08	0.04	40	33.3	36.3	40.4
Efficiency of sulfate reduction	E _{SO4} %	80	70	60	48	6	76
COD CH₄ lost as waste gas	p _w %	2.5	7.5	7.5	7.5	7.5	7.5
Other cod ch4 loses	p _o %	2.5	7.5	7.5	7.5	7.5	7.5
Dissolved COD_{CH4} lost with effluent	Q _L kg/m ³	0.015	0.025	0.025	0.025	0.025	0.025
Percentage of CH₄ in biogas	%	80	70	75	75	75	75
COD of one mole of CH₄	K _{CO_D} kg COD _{CH4} mol ⁻¹	-	-	0.064	0.064	0.064	0.064
Sludge yield as TVS	Y _{sludge} kgTVS/kgCOD removed			0.15	0.15	0.15	0.15

Conversion factor of methane to COD mass	f_{CH_4}	kgCOD/kgCH ₄	4	4	4	4
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Table 5-15: Summarize of the results from the equations in

Parameter	Unit	Feb-Jun 2016	22 Nov 2016	15-Feb-2017	21-Nov-2017
Flow	m ³ /d	3780	4284	7040	6237
COD INF	kgCOD/d	899	969	546	488
COD EFF	kgCOD/d	308	354	146	191
COD sol, inf	kgCOD/d	899	254	351	
Temperature	°C	23.5	20	22	24
Loading rate	kgCOD/m ³ .d	3398	4151	3844	3044
COD soluble in the effluent	kgCOD/d	646	608	641	578
COD in the effluent	kgCOD/d	1164	1517	1028	1191
COD removed	kgCOD/d	2234	2635	2816	1852
COD sludge	kgCOD/d	476	561	600	395
COD so4-converted	kgCOD/d	61	45	10	128
COD available for production CH ₄	kgCOD/d	1698	2028	2206	1330
CH ₄ losses in waste gas and atmosphere	kgCOD/d	255	304	331	199

COD as CH ₄ dissolved in effluent	kgCOD/d	378	428	704	624
COD as CH ₄ recovered in GLSS	kgCOD/d	1065	1295	1171	507
Q dissolved in the effluent	m ³ /d	144	161	266	238
Q CH ₄ produced	m ³ /d	645	762	835	506
	m ³ /d	405	487	443	193
Methane recovered as biogas	Nm ³ /d	373	453	410	177

Table 5-16: Biogas and methane yields

Unitary yield of methane production per m³ of influent	Nm ³ /m ³ flow	0.10	0.11	0.06	0.03
Unitary yield of methane per kg COD removed	Nm ³ /kgCOD removed	0.17	0.17	0.15	0.10

Table 5-17: H₂S production from mass balances

H₂S Production				
Parameter	Unit	22-Nov	15-Feb	21-Feb
Flow	m ³ /d	4284	7039	6235
Concentration SO ₄ removed	g/L	0.0159	0.0021	0.0317
SO ₄ *Q	kg/d	68.1156	14.7819	197.6495
Molar mass SO ₄	g/mol	96	96	96
Molar mass H ₂ S	g/mol	34	34	34
N mol SO ₄	mol	1.66E-04	2.19E-05	3.30E-04
mol H ₂ S produced	mol	1.66E-04	2.19E-05	3.30E-04
pH		7.67	7.79	7.68
pka		7.1	7.1	7.1

Temperature	C	23.50	23.60	23.10
Soluble molar fraction	mol/l	1.92E-03	1.92E-03	1.92E-03
Molar fraction H ₂ S solubilized	mol/l	1.66E-04	2.19E-05	3.30E-04
Molar fraction H ₂ S released	mol/L	0.00E+00	0.00E+00	0.00E+00
Volume of H ₂ S produced per liter of WW	L/Lww	4.03E-03	5.32E-04	8.02E-03
Total V of H ₂ S produced	m ³ /d	17	4	50
H ₂ S gas phase	ppm	1669	220	3328

From sulphate removed, based in the stoichiometric relation of 1molSO₄ oxidized per mol of H₂S produced, the production of H₂S is calculated. Regarding the solubility for H₂S in water, the molar fraction can be determined, the difference will be released. Due to the high solubility (0.192 mmol/L at 23 °C) H₂S will be dissolved in the water. Also, due to the pH and the pKa, the sulphide mainly is in form of HS⁻ (80%). If the undissociated H₂S produced is released in the atmosphere the concentration in the air will be near to 360 ppm.

Table 5-18: Correction for pH, regarding only the non-dissociated fraction of sulphide

Date	Unit	22-Nov	15-Feb	21-Feb
pH		7.67	7.79	7.68
Fraction sulphide in H₂S form	%	21%	17%	21%
Moles of H₂S* non dissociated	mol	3.51E-05	3.71E-06	6.88E-05
Temperature	C	23.50	23.60	23.10
Mol H₂S solubilized	mol/l	1.66E-04	2.19E-05	3.30E-04
Volume of H₂S produced per L of influent	L/Lww	8.55E-04	9.03E-05	1.67E-03
Volume of H₂S produced per day	m ³ /d	4	1	10

Table 5-19: Mass balance of Sulphur

Day	22-Nov-16	15-Feb-17	21-Feb-17
SO_{4IN} (mg/L)	33.3	36.3	40.4
SO₄ as S	11.1	12.1	13.5
Sdiss, in	5.5	2.2	
TS in	16.6	14.3	13.5
SO₄, eff	17.4	34.2	9.59
SO₄ as S	5.8	11.4	3.2

Sdiss, out	1.8	1.1	
TS out	7.6	12.5	3.20
Fein	11	7.2	1.8
Fe out	3.2	-	-
Sused	4.46	-	-
Fe Sludge	28	3.9	39

Appendix E Influent fractionation based in STOWA protocol

Table 5-20: Equation used in the determination of the initial fractions based in (Meijer and Brdjanovic 2012)

STOWA method
COD influent fractions
TCOD = COD _x + COD _{mf}
COD _{BD} = SA+SF+XS (from BOD test)
COD _{mf} =SA+SF+SI
COD _{BM} = XH+XPAO+XAUT = 0
COD _x =XI+XS
Soluble components
SA = COD _{VFA}
SI = 0.9 * COD _{f,eff}
SF = COD _f - (SA + SI)
SS = SA + SF
SNH ₄ = TKN - (i _N ·XI+i _N ·XS+i _N · A+i _N · F+i _N · I)
SPO ₄ = TP - (i _P ·XI+i _P ·XS+i _P · A+i _P · F+i _P · I)
Particulate Components (BOD model)
$X_S = (BOD_t / (1 - \text{EXP}(-t \cdot k))) / (1 - f_{BOD}) - S_S$
$X_I = COD_x - X_S$

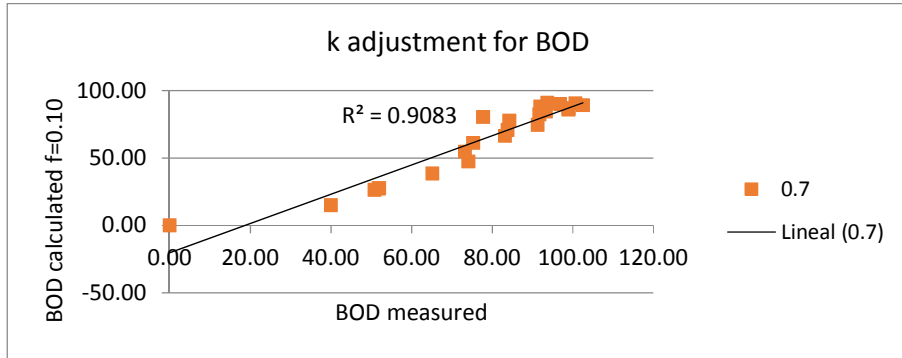


Table 5-21: Determination of biodegradable COD from BOD measurements

	Measured	Ranges
BOD 5	411	
K adjusted	0.7	0.5-0.8
BOD _t	424	
f	0.1	0.10-0.20
X _s +S _s	471	
COD _{eff,sol}	142	

Table 5-22: COD fractionation

COD	
S _s	S _{us} =S _i
F _{bs} =0.14	F _{us} =0.13
131	128
X _s	X _{us}
F _{xs} =0.35	F _{up} =0.38
340	370

Table 5-23: TKN and TP fractionation from STOWA protocol

TKN	100	TP	34.6
FSA	66	PO ₄	5.1
iNSa	0	iPSa	0
iNSf	0.04	iPSf	0.085
iNSi	0.01	iPSi	0.008
iNxi	0.055	iPXs	0.046
iNXs	0.022	iPXi	0.009
Sf	122.0	fup	0.02
FupN	0.06	TP	34.6
Fnox	0.85	PO ₄	5.1
Fnus	0.0128	iPSa	0

Fna	0.66	iPSf	0.085
		iPsi	0.008
		iPXs	0.046

Appendix F Sensitive analysis

Table 5-24: Variation of the influent fractions

	Model	1		2		3		4		5	
Fractions	Fbs	0.19		0.19		0.14		0.19		0.19	
	Fxsp	0.85		0.85		0.85		0.85		0.85	
	Fus=SI	0.08		0.08		0.13		0.08		0.08	
	Fup=Xi	0.35		0.35		0.38		0.35		0.35	
	SBCOD	0.38		0.38		0.38		0.38		0.38	
Effluent											
354	COD	424.8	17%	425.76	0%	405.82	5%	429	5%	394	8%
194	TSS	161	17%	234	31%	149.6	36%	161	7%	145.13	10%
168	VSS	116.4	31%	279	58%	110	61%	116.4	5%	100	14%
184	BOD	88.22	52%	85.76	3%	34.13	60%	88.22	61%	2	98%
Influent											
528	VSS	484.6	8%	966.57	50%	487.83	50%	484.6	1%	411	15%
708	TSS	669.45	5%	1151.42	42%	627.68	45%	669.45	6%	596	11%
411	BOD	335.05	18%	335	0%	284.52	15%	335	15%	335	0%

Table 5-25: Variation of kinetics parameters

METHANOGENICS										
Acetoclastic max	0.3	0.35	0.35	0.3	0.25	0.3	0.35	0.35	0.4	0.31
Acetoclastic decay	0.13	0.13	0.13	0.1	0.1	0.1	0.1	0.1	0.1	0.11
Yield ACETOCLASTICS	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
OHO										

Yield fermentation OHO	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Fermentation rate OHO	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Hydrolysis rate	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Hydrolysis half sat	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
SRB										
SRB ACETOTROPHIC MAX	0.612	0.612	0.612	0.612	0.612	2	0.3	0.03	0.612	0.612
SRB YIELD	0.047	0.047	0.047	0.047	0.047	0.06	0.3	0.03	0.047	0.047
EFFLUENT										
COD	429	399.43	407	407.6	407	407.4	384	384	373	397.15
TSS	161	144.6	151.7	151.7	152	151.5	145	145	145	145
VSS	116.4	100	111.7	111.57	111	111.4	100	100	100	100
BOD	88.22	67.75	71	71	71	70.8	55	55	46	65.9
TS	13	13	13	13.29	13.29	16	13.31	13.31	13.31	13.31
Sulfate	0.33	0.33	0.33	0.34	0.32	0.32	0.32	0.32	0.32	0.32
TSS reactor	9333.6	9367	8225	8225	8224	8241	9413	3415	9427	9395
VSS reactor	6464.5	6481	6049	6049	6041	6041	6509	6501	6517	6499