



Universidade de Aveiro
2021

**Nuno André
Araújo Silva**

**Valorização energética e material de efluentes de
branqueamento de pasta kraft**

**Energy and material recovery of kraft paste
bleaching effluents**



Universidade de Aveiro
2021

**Nuno André
Araújo Silva**

**Valorização energética e material de efluentes de
branqueamento de pasta kraft**

**Energy and material recovery of kraft paste
bleaching effluents**

Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia do Ambiente, realizada sob a orientação científica da Professora Doutora Maria Isabel Aparício Paulo Fernandes Capela, Professora associada do departamento de Ambiente e Ordenamento da Universidade de Aveiro.

o júri / the jury

presidente / president

Professora Doutora Maria Isabel da Silva Nunes
Professora Auxiliar do Departamento de Ambiente e Ordenamento da Universidade de Aveiro

vogais / examiners comitee

Professora Doutora Maria Isabel Aparício Paulo Fernandes Capela
Professora Associada do Departamento de Ambiente e Ordenamento da Universidade de Aveiro

Doutora Leonor Miranda Monteiro do Amaral
Professora Associado da Universidade Nova de Lisboa

Agradecimentos / Acknowledgement

Agradeço à Professora Isabel Capela por todo o acompanhamento e disponibilidade ao longo desta dissertação.

Agradeço também à Doutora Tânia Gameiro por todo o apoio na parte laboratorial deste trabalho e toda a ajuda no esclarecimento de dúvidas.

À Filipa Ribeiro por toda a motivação que me deu, pela compreensão e pelo companheirismo ao longo destes 6 anos.

A todos os amigos que fiz neste percurso académico pelo ao seu apoio incondicional.

Por fim agradecer aos meus pais por todos os sacrifícios que fizeram para que eu pudesse seguir os meus sonhos.

Palavras-chave

digestão anaeróbia, efluentes de branqueamento de pasta Kraft, compostos orgânicos halogenados adsorvíveis (AOX)

Resumo

A digestão anaeróbia é um processo de tratamento aplicado a resíduos sólidos e efluentes líquidos orgânicos realizado por microrganismos sob condições anaeróbias (sem oxigênio). Para além do tratamento de uma água residual, este processo tem como principal produto o biogás, uma mistura de metano e dióxido de carbono. Neste pressuposto, é fácil de entender como este processo biológico pode ser uma mais-valia no combate às alterações climáticas, por produzir não só energia renovável, como também contribuir para a diminuição dos impactos negativos decorrentes da descarga de resíduos orgânicos no meio ambiente.

O principal objetivo deste trabalho foi estudar os processos anaeróbios acidogénico e metanogénico aplicados a um efluente industrial de baixa biodegradabilidade e com compostos potencialmente inibidores para a produção de materiais, como os AGVs, e energia (metano), respetivamente. O efluente em estudo foi o efluente do 1º estágio do branqueamento do processo de produção da pasta Kraft, denominado D₀, que contém, entre outros materiais recalcitrantes, compostos AOX. A influência dos parâmetros operacionais na maximização destes produtos e no aumento da biodegradabilidade aeróbia do efluente tratado também foi analisada.

Para estudar o processo de digestão anaeróbia do efluente D₀, foram montados dois reatores, agitados magnética e mecanicamente, e volumes de 1,75 l e 7 l, respetivamente, operando na faixa de temperatura mesofílica. Foram realizadas quatro operações, com diferentes valores de pH na alimentação: pH 3, 4, 6 e 7. Os melhores resultados na eficiência de remoção de sCOD e AOX foram obtidos a pH 4, no qual foram removidos 58% do primeiro e 63% do último, usando um TRH de 1,461 dias (o menor usado em todas as operações) e 6 cargas diferentes (entre 0,419 g_{cod} l⁻¹ day⁻¹ e 1,282 g_{cod} l⁻¹ day⁻¹). A produção de metano também foi a melhor neste pH de alimentação. A biodegradabilidade aeróbia do efluente foi melhorada em todas as operações realizadas, tendo o maior aumento sido também alcançado no ensaio com pH 4 na alimentação (aumento de 4, 5 vezes). Assim, esta faixa de pH na alimentação é a mais adequada para o tratamento deste tipo de efluente.

Keywords

anaerobic digestion, bleaching effluents from Kraft pulp, adsorbable organically bound halogens (AOX)

Abstract

Anaerobic digestion is a treatment process applied to organic solid waste and wastewater carried out by microorganisms under anaerobic conditions (without oxygen). In addition to treating wastewater, this process's main product is biogas, a mixture of methane and carbon dioxide. On this assumption, it is easy to understand how this biological process can be an asset in the fight against climate change, as it not only produces renewable energy, but also contributes to reducing the negative impacts resulting from the discharge of organic waste into the environment.

The main objective of this work was to study the acidogenic and methanogenic anaerobic processes applied to an industrial effluent with low biodegradability and with potentially inhibitory compounds for the production of materials, such as VFAs, and energy (methane), respectively. The effluent under study was the bleaching effluent from the Kraft pulp production process, denominated D_0 , which contains, among other recalcitrant materials, AOX compounds. The influence of operational parameters in maximization of these products and increasing the aerobic biodegradability of the treated effluent were also analyzed.

To study the process of anaerobic digestion of the D_0 effluent, two reactors with magnetic and mechanical agitation, and volumes of 1.75 l and 7 l, respectively, operating in the mesophilic temperature range were set up. Four runs were carried out, with different feed pH values: pH 3, 4, 6 and 7. The best results in sCOD and AOX removal efficiencies were obtained at influent pH 4, which removed 58% of the first and 63% of the second, using an HRT of 1.461 days (the lowest used in all operations) and 6 different loads (between $0.419 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$ and $1.282 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$). The production of methane was also better at this feed pH. The aerobic biodegradability of the effluent was improved in all four operations carried out, with the greatest increase also being achieved in the test with pH 4 in the feed (4.5 times increase). Therefore, this pH range in the feed is the most suitable for the treatment of this type of effluent.

Contents

Contents	i
List of Figures	iii
List of Tables	v
Abbreviations	vii
1 Introduction	1
2 State of Art	3
2.1 Anaerobic Digestion	3
2.1.1 Parameters affecting Anaerobic Digestion	5
2.2 Reactors Used for Anaerobic Digestion	8
2.3 Continuous Stirred Tank Reactor	10
2.4 Paper Mill Industry	11
2.4.1 Anaerobic digestion of low biodegradable effluents	12
3 Methodology	15
3.1 Reactor assembly and sampling points	15
3.2 Analysis methods	18
3.2.1 pH	18
3.2.2 Chemical Oxygen Demand	18
3.2.3 Adsorbable Organically Bound Halogens	19
3.2.4 Volatile Fatty Acids	20
3.2.5 Biogas	21
3.2.6 Suspended Solids	21
3.2.7 Biochemical Oxygen Demand	22
3.3 Hydraulic Retention Time and Solids Retention Time	22
3.4 Calculations (anaerobic process performance)	23

4	Results and discussion	25
4.1	Influent pH 3	26
4.1.1	Operating Conditions	26
4.1.2	pH	26
4.1.3	Chemical Oxygen Demand	27
4.1.4	Adsorbable Organically Bound Halogens	29
4.1.5	Efficiencies	30
4.1.6	Biogas and Volatile Fatty Acids production	31
4.2	Influent pH 4	32
4.2.1	Operating Conditions	32
4.2.2	pH	33
4.2.3	Chemical Oxygen Demand	34
4.2.4	Adsorbable Organically Bound Halogens	35
4.2.5	Efficiencies	36
4.2.6	Biogas and Volatile Fatty Acids production	37
4.3	Influent pH 6	38
4.3.1	Operating Conditions	38
4.3.2	pH	39
4.3.3	Chemical Oxygen Demand	40
4.3.4	Adsorbable Organically Bound Halogens	41
4.3.5	Efficiencies	42
4.3.6	Biogas and Volatile Fatty Acids production	43
4.4	Influent pH 7	44
4.4.1	Operating Conditions	44
4.4.2	pH	45
4.4.3	Chemical Oxygen Demand	46
4.4.4	Adsorbable Organically Bound Halogens	47
4.4.5	Efficiencies	48
4.4.6	Biogas and Volatile Fatty Acids production	49
4.5	Comparisons between runs	50
5	Conclusions and Recommendations	55
	References	57
	Appendices	a

List of Figures

2.1	Anaerobic digestion process	4
2.2	Kraft Process	11
3.1	Reactor set-up	16
3.2	Reactor Scheme	16
3.3	Sampling process and analysis	18
4.1	Operating conditions at pH 3	26
4.2	pH evolution at pH 3	27
4.3	Soluble Chemical Oxygen Demand (sCOD) evolution at pH 3	28
4.4	sCOD balance per load at pH 3	28
4.5	Adsorbable Organically Bound Halogens (AOX) evolution at pH 3	29
4.6	AOX balance per load at pH 3	30
4.7	AOX and sCOD removal efficiencies at pH3	31
4.8	Methane and Volatile Fatty Acids (VFAs) produced at pH 3	32
4.9	Operating conditions at pH 4	33
4.10	pH evolution at pH 4	33
4.11	sCOD evolution at pH 4	34
4.12	sCOD balance per load at pH 4	35
4.13	AOX evolution at pH 4	36
4.14	AOX balance per load at pH 4	36
4.15	AOX and sCOD removal efficiencies at pH 4	37
4.16	Methane and VFAs produced at pH 4	38
4.17	Operating conditions at pH 6	39
4.18	pH evolution at pH 6	39
4.19	sCOD evolution at pH 6	40
4.20	sCOD balance per load at pH 6	41
4.21	AOX evolution at pH 6	41
4.22	AOX balance per load at pH 6	42
4.23	AOX and sCOD removal efficiencies at pH 6	43

4.24	VFAs produced at pH 6	44
4.25	Operating conditions at pH 7	45
4.26	pH evolution at pH 7	45
4.27	sCOD evolution at pH 7	46
4.28	sCOD balance per load at pH 7	47
4.29	AOX evolution at pH 7	47
4.30	AOX balance per load at pH 7	48
4.31	AOX and sCOD removal efficiencies at pH 7	49
4.32	VFAs produced at pH 7	49
4.33	sCOD removal in the different loads used	50
4.34	AOX removal in the different loads used	51
4.35	sBOD evolution of all operations	52

List of Tables

2.1	Advantages and disadvantages of the Anaerobic Digestion (AD) process. Adapted from de Lemos Chernicharo (2007)	4
2.2	Application of different anaerobic treatment process for different wastewaters from kraft mill industries. Adapted from Vidal et al. (2001)	13
3.1	D ₀ and sludge analysis	17
3.2	Sample collection, parameters and periodicity	18
3.3	BOD scale and correspondent sample volumes	23
4.1	Overall performance of the four operations	52
4.2	Biodegradability gained in the different runs	53

Abbreviations

AD	Anaerobic Digestion	sBOD	Soluble Biochemical Oxygen Demand
AOX	Adsorbable Organically Bound Halogens	sCOD	Soluble Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand	SRT	Solids Retention Time
COD	Chemical Oxygen Demand	tCOD	total Chemical Oxygen Demand
CSTR	Continuously Stirred Tank Reactor	thOD	Theoretical Oxygen Demand
HRT	Hydraulic Retention Time	TSS	Total Suspended Solids
OLR	Organic Loading Rate	VFA	Volatile Fatty Acid
PP	Pulp and Paper	VSS	Volatile Suspended Solids

Introduction

Fossil fuels were began to be used in the mid 18th century. This development in the energy department lead to the industrial revolution (Abbasi and Abbasi, 2011). In an increasingly globalized world, the need for energy is inevitably increasing (Owusu and Asumadu-Sarkodie, 2016) and today, society's energy demand is answered with a dominance of fossil fuels, which brings many problems, such as the production of greenhouse gases and fly ash, atmospheric and water pollution from coal, and depletion of fossil fuels (Asumadu-Sarkodie and Owusu, 2016). Renewable sources of energy appear to be the best solution to these problems (Balat, 2005). Examples of these sources are solar, wind, hydroelectric, geothermal, and biofuels such as biogas, bioethanol, biomethanol and biodiesel (Demirbas and Balat, 2009).

Anaerobic digestion AD is a process that involves the degradation and stabilisation of organic materials under anaerobic conditions by microbial organisms (Kelleher et al., 2002) and its main products are methane and carbon dioxide (biogas) (Aquino and Stuckey, 2008; Chen et al., 2008; Wilkinson, 2011). This process can be applied to a wide variety of types of wastewater, solid waste and biomass. The wide application of this technology can help to achieve sustainable development and renewable energy production (De Mes et al., 2003).

AD can be applied to complex wastewater such as that from the paper industry (Ekstrand et al., 2020), although this wastewater has a relatively low biodegradability and the presence of adsorbable halogenated organic compounds AOX (Rintala and Puhakka, 1994) which may be inhibitory to methanogens (Vidal et al., 1997) and have negative impacts on biogas production (Yu and Welander, 1996).

This work has as main objectives to characterize the bleaching effluent from the Kraft pulp production process, and to study the acidogenic and methanogenic process applied to effluents with low biodegradability and with potentially inhibitory compounds (AOX) for the production of VFAs and methane, respectively. The influence of several operational parameters in the maximization of these products and in the increase of the biodegradability of this effluent for further treatment will also be analyzed.

State of Art

2.1 Anaerobic Digestion

The anaerobic digestion is a biological process that takes place in the absence of oxygen (Akunna, 2018) in which organic compounds are converted into various products, mainly methane and carbon dioxide (Chelliapan et al., 2012). This process can be used in the treatment of a wide range of wastes, from dairy manure, food processing waste and plant waste, to other organic wastes, such as municipal wastewaters, food waste, fats, oils and greases (Chen and Neibling, 2014). Thus, the application of this process can help reduce pollution from agricultural and industrial activities and also offset the fossil fuels used in these activities (Chen et al., 2008). Other advantages and disadvantages of the AD process are shown in **Table 2.1**.

The AD occurs typically in four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis as it can be seen in **Figure 2.1**. The AD process can be strongly impacted by the organic matter composition and can show a relationship between the organic matter used and the biogas produced (Lesteur et al., 2010). Therefore, it is understandable that the rate-limiting step of the AD process also depends on the kind of substrate used (Li and Noike, 1992), although some authors refer the hydrolysis to be the rate limiting step (Zhang et al., 2014).

Once microorganisms can not assimilate particulate organic matter, this matter needs to be hydrolyzed into simpler dissolved materials. This hydrolysis process is carried out by exoenzymes produced by fermentative bacteria (de Lemos Chernicharo, 2007).

This dissolved matter is then converted by acidogens (Li and Noike, 1992) into a mixture of VFAs (acetic, propionic and butyric acids) and other products such as hydrogen (H_2), carbon dioxide (CO_2) and acetic acid (Chen and Neibling, 2014). VFAs produced in acidogenesis are the most important intermediates in the AD process (Appels et al., 2008). This step is the fastest in the AD process (Chen and Neibling, 2014), which can result in the VFAs accumulation, which can inhibit methanogenesis (Appels et al., 2008).

Table 2.1: Advantages and disadvantages of the AD process. Adapted from de Lemos Chernicharo (2007)

Advantages	Disadvantages
Low production of solids, about 3 to 5 times lower than that in aerobic processes	Anaerobic microorganisms are susceptible to inhibition by a large number of compounds
Low energy consumption, usually associated with an influent pumping station, leading to a very low operational costs	Process start-up can be slow in the absence of adapted seed sludge
Low land requirements	Some form of post-treatment is usually necessary
Low construction costs	The biochemistry and microbiology of AD are complex and require further studies
Production of methane, a highly calorific fuel gas	Possible generation of bad odors, although they are controllable
Possibility of preservation of the biomass, with no reactor feeding, for several months	Possible generation of effluents with unpleasant aspects
Tolerance to high organic loads	Unsatisfactory removal of nitrogen, phosphorus and pathogens
Application in small and large scale	
Low nutrient consumption	

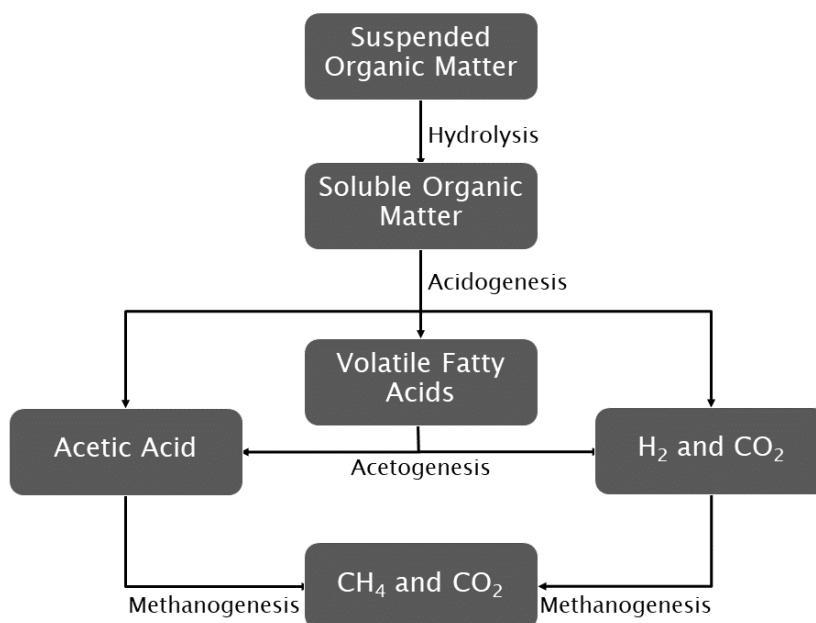


Figure 2.1: Anaerobic digestion process

Adapted from Appels et al. (2008)

The produced VFAs are then oxidized by acetogenic organisms into acetate, hydrogen and

carbon dioxide (Pavlostathis and Giraldo-Gomez, 1991). In the acetogenesis step, acetate is also produced during the catabolism of bicarbonate and hydrogen by homoacetogenic bacteria (Akunna, 2018). Acetogenic bacteria are very sensitive to the hydrogen concentration, once they can only survive in very low hydrogen concentrations. Therefore high concentrations of hydrogen can inhibit this step (Braguglia et al., 2017).

The last step of the AD process, methanogenesis, is carried out by two groups of methanogenic archaea (de Lemos Chernicharo, 2007). These microorganisms use acetate, methanol, carbon dioxide and hydrogen to produce methane (Akunna, 2018). Depending on which substrate is used and the extent of methane (CH_4) produced these methanogens are divided into two main groups, the first that uses acetate or methanol to form methane (acetoclastic methanogens) and the second that uses hydrogen and carbon dioxide to form also methane (hydrogenotrophic methanogens). Acetoclastic methanogens are crucial in the formation of methane, as 70% of methane is produced from acetic acid (Mata-Alvarez, 2003; de Lemos Chernicharo, 2007).

2.1.1 Parameters affecting Anaerobic Digestion

The AD process can be affected by a wide variety of parameters (Appels et al., 2008). In this section it will be discussed how these parameters can affect the AD process.

Temperature

AD, like all biological processes, can be strongly affected by temperature (Appels et al., 2008).

There are 3 main temperature ranges in which the anaerobic process can occur, the psychrophilic ($< 20^\circ\text{C}$), mesophilic (25°C - 40°C) and thermophilic (45°C - 60°C), although the first one is not commonly used, given its low biodegradation rate (Akunna, 2018).

Thermophilic is the optimal temperature range for Chemical Oxygen Demand (COD) removal and biogas production (Bolzonella et al., 2012). It can also cause other benefits, such as, enhanced biological and chemical reaction rates and increased death of pathogens. This range of temperature has some counter parts, such as decreasing the stability of the AD process, increasing toxicity and the fraction of free ammonia, which can inhibit the roles of microorganisms, in addition to weak methanogenesis (Appels et al., 2008). Moreover, the thermophilic range is more susceptible to environmental changes than the mesophilic one. (Mao et al., 2015).

Although mesophilic temperatures can improve the process stability, AD in this range of temperatures produces lower yields of methane and can have problems with nutrient imbalances and poor biodegradability (Bowen et al., 2014). Mao et al. (2015) consider that the best way to carry out the AD process is to do it in two phases, where the hydrolysis and acidogenesis processes are done at a thermophilic temperature and the methanogenic process is done at a mesophilic temperature. However, given the greater amount of net economic gain, usually the mesophilic range is the one used when performing the AD process (Akunna, 2018; Kamali et al., 2016).

pH

The AD process is highly affected by pH (Akunna, 2018). The different types of microorganisms used in AD have their own optimal pH range, with methanogenic being the most impacted by this parameter (Hwang et al., 2004). Their optimum pH range has been reported between 6.5 and 7.2 (Turovskiy and Mathai, 2006), although other authors consider it to be between 7 and 8 (Akunna, 2018) and between 6.5 and 8.2 (Lee et al., 2009). Fermentative microorganisms are less sensitive to this parameter (Akunna, 2018) and can function in a range between 4 and 8.5 (Hwang et al., 2004). Kim et al. (2003) reported a optimum restrictive range of 5.5 to 6.5 for this type of organisms.

The difference between the optimum pH range explains how a two-stage system that separates hydrolysis and acidification from acetogenesis and methanogenesis can be advantageous (Mao et al., 2015). When AD is done within a single reactor the optimum pH range is generally between 6.8 and 7.4 (Mao et al., 2015; Akunna, 2018).

Hydraulic Retention Time

The Hydraulic Retention Time (HRT) is the theoretical amount of time that the wastewater being treated remains inside the reactor (Akunna, 2018) and is one of the most significant influencing factors in the AD process (Kamali et al., 2016). HRT is defined by the following equation: $HRT = \frac{V}{Q}$, where V is the volume of the biological reactor and Q is the influent flow rate. When HRT is decreased, the extent of reactions also decreases (Appels et al., 2008) and generally leads to VFA accumulation (Mao et al., 2015). On the other hand, when the HRT is increased, it can enhance the COD removal, since the contact time will also increase (Kamali et al., 2016).

The COD removal variations by HRT changes are also dependent on the temperature range. For instance, changes in HRT may impact COD removal in a thermophilic rather than mesophilic ranges (Ahn and Forster, 2002).

Nutrients concentration

Nutrient concentration can influence the AD process. The optimum carbon to nitrogen ratio is important for the good efficiency of the AD process (Kamali et al., 2016). The optimum values of the C:N ratios have been shown to be between 20 and 30 (Zhang et al., 2013).

A low C:N ratio can cause an accumulation of total ammonia nitrogen or VFAs which can inhibit the AD performance (Kamali et al., 2016; Mao et al., 2015; Akunna, 2018).

Although high C:N ratios can cause a decrease in bacterial growth due to nitrogen deficiency (Akunna, 2018), it can also cause a low total ammonia nitrogen (Mao et al., 2015) and through rapid consumption of nitrogen by methanogens it can inhibit methane production (Kamali et al., 2016).

Micronutrients, such as iron, cobalt, nickel and zinc are also needed. These nutrients, when present in small amounts, can promote methanogenic activities. Their optimum concentration depends on the type of wastewater to be treated (Akunna, 2018).

Organic Loading Rate

Organic Loading Rate (OLR) represents volatile solids or COD fed into a digester per day (Akunna, 2018). Adding a larger volumes of new wastewater can result in imbalances in the environment of the digester which can temporarily inhibit bacterial activity during the early stages of fermentations (Mao et al., 2015).

Chelliapan et al. (2012) found that an OLR of $1.560 \text{ kg COD m}^{-3}\text{d}^{-1}$ with an HRT of 1.6 days was capable of removing 98% of the COD when treating paper mill wastewater. The authors caution, however, that higher OLRs need further study.

Ammonia

Ammonia is produced through the biological degradation of nitrogenous matter and urea (Akunna, 2018). The most predominant forms of ammonia are ammonium ion (NH_4^+) and free ammonia (NH_3), the latter being the most toxic of both (Yenigün and Demirel, 2013) and methanogens being the organisms most affected by this parameter (Kayhanian, 1994).

The free ammonia concentration depends on three parameters: temperature, pH and total ammonia concentration and its concentration increases with higher temperatures and pH values (Akunna, 2018). Therefore, thermophilic digestion is more susceptible to inhibition than mesophilic one (Hansen et al., 1998). Akunna (2018) reported that the toxicity threshold for free ammonia is 100 mg NH_3 , although, when acclimatization occurs, higher tolerance levels can be obtained.

Volatile Fatty Acids

Volatile Fatty Acids VFAs are very important intermediate compounds in the AD process (Mechichi and Sayadi, 2005) and therefore, need to be considered when assessing AD performance (Wang et al., 1999). The VFAs production can, however, be toxic to microorganisms, specially methanogens (Hill and Bolte, 1989). Higher VFAs concentrations result from accumulation due to process imbalances (Wang et al., 1999) and when this accumulation occurs, methanogens cannot remove hydrogen and VFAs fast enough (Appels et al., 2008), resulting in an accumulation of even more acids, which will decrease the pH in such a way that hydrolysis can also be inhibited (Palmisano and Barlaz, 1996). This problem can be solved by using a two-stage digester that can facilitate the buildup of VFA in the hydrolysis and acidogenesis phase (Wang and Banks, 2000).

Adsorbable Organically Bound Halogens

The term adsorbable organically bound halogens (AOX) first appeared in 1976 at the Heidelberg Conference and was considered the organohalogenic compounds present in water (chloride, bromide and iodide) that could be adsorbed by activated carbon. Meanwhile this parameter has been extended to include the thousands of natural, biotic and abiotic organohalogens and exclude the insoluble adsorbed organohalogens (Müller, 2003). Therefore, it is clear that the AOX parameter considers a sum of compounds and not a specific chemical (El-Hadj et al., 2007).

The Pulp and Paper (PP) industry is highly dependent on water, once it has a high freshwater withdrawal (Kallas and Munter, 1994; Kamali et al., 2016; Thompson et al., 2001). Of all waste streams (solid, gaseous and liquid) produced by PP industries, bleach plant effluents are the most toxic, due to the various chlorinated organic compounds generated in this process (Savant et al., 2006). Therefore, PP industries are the main source of AOX generation, specially in the bleaching process (Salkinoja-Salonen et al., 1995; Savant et al., 2006).

The toxic effects of AOX range from carcinogenicity, mutagenicity to very acute and chronic toxicity. Faced with these effects, several countries have developed a discharge limit of AOX for wastewater from PP mills wastewater (Savant et al., 2006). AOX removal has been studied mainly in PP wastewater (El-Hadj et al., 2007).

The use of anaerobic treatment in PP wastewater began in the 70's and is considered the most reliable and economically viable method of AOX removal (Savant et al., 2006). Hakulinen et al. (1982) were the first authors to report this type of treatment for the removal of AOX. Hakulinen et al. (1982) reported a removal efficiency of 64 – 94% of chlorophenol toxicity, mutagenicity and chloroform in the bleaching effluent. The removal of AOX using this type of treatment shows that methanogens, when acclimated, can, not only withstand the inhibitory effects, but also thrive in such environments. However, the removal mechanism is not totally understood and there should be more studies on this topic (El-Hadj et al., 2007).

2.2 Reactors Used for Anaerobic Digestion

The first parameter to keep in mind when considering the choice of anaerobic digesters is made considering their HRT. Digesters like the "semi-batch" used in some developing countries need a high HRT (40 – 50 *days*) to digest their effluents (Abbasi et al., 2012). Due to their high HRT, these systems are called low-rate systems (Tauseef et al., 2013). Due to this slow process, in the 1950's, an intense mechanical mixing was introduced in anaerobic reactors which led to the emergence of the hydraulics of the Continuously Stirred Tank Reactor (CSTR). This type of hydraulic system leads to better performance, which is 2 – 3 times more efficient than non-stirred or intermittent stirred low-rate digesters. Although the system could work with lower HRTs, it would require a lot more time to biodegrade matter to the same degree as the aerobic activated sludge process and its variants (Tauseef et al., 2013). These high HRTs happen because microorganisms were washed out of the reactors with the treated effluent. One solution to this problem was to separate the microorganisms from the effluent and reintroduce them into the reactors (Abbasi and Abbasi, 2012). HRTs of AD were not low enough, being a setback for the widespread use of this type of treatment (Abbasi et al., 2012).

This need to accelerate the AD process led to the development of other technologies such as the anaerobic filter, which was followed by other types of reactors, whose variety, enabled the application of the AD process to a wide variety of effluents (Appels et al., 2008).

Mao et al. (2015) classify reactors into conventional anaerobic reactors, sludge retention reactors and anaerobic membrane reactors. Anaerobic sequencing batch, anaerobic plug-flow reactors and CSTR are considered conventional reactors.

The anaerobic sequencing batch reactor is a single tank where each step of the AD process occurs. It is considered a good option for low flow effluents and allows applications for a wide variety of wastewater strengths (Mao et al., 2015). This type of reactor is operated intermittently which results in a high initial substrate and high biogas production. The operation of these technologies consists of four steps: feeding, reaction, settling and liquid withdrawal (Zaiat et al., 2001).

Its main advantages are operational simplicity, efficient effluent quality control, flexibility to use low input process and mechanical requirements (Mao et al., 2015).

The anaerobic plug-flow reactor, used for the treatment of animal waste, is a cylindrical tank in which gas and other by-products are pushed out by new waste that is fed at the other end. It consists of a long, narrow, insulated and heated tank, built partially or completely below ground with a rigid or flexible cover. These reactors are not stirred and are usually loaded with thick residues (Mao et al., 2015).

The CSTR will be considered in more detail the next subchapter.

The sludge retention reactors considered by Mao et al. (2015) are the anaerobic contact reactor, the up-flow anaerobic sludge bed reactor, the up-flow anaerobic solid-state reactor, the anaerobic baffled reactor and the internal circulation reactor.

The first type of reactor is mostly used for the treatment of effluents with high concentrations of suspended solids (Mao et al., 2015). This type of reactor consists of an agitated reactor and a solids settling tank for the recycling of microorganisms (Şentürk et al., 2013). This reactor reaches steady-state quickly due to its mixing, and has short HRTs and relatively high effluent quality (Şentürk et al., 2010).

The up-flow anaerobic sludge bed reactor has as its main structure a dense sludge bed located at the bottom that allows good contact between the wastewater and the sludge. As main advantages, these reactors require less volume, allow higher flow velocity and biogas production. When compared to flocculent sludge reactors, it also accommodates significantly higher OLRs (Mao et al., 2015).

Of all the up-flow anaerobic solid-state reactor considered by Mao et al. (2015), they all consist of an up-flow anaerobic solid-state reactor and an anaerobic filter to prevent VFAs accumulation. These reactors exhibit higher processing efficiency and higher volume loading rate while permitting a lower investment cost and simpler operation and management.

The anaerobic baffle reactor consists of a series of compartments in a single reactor (Mao et al., 2015), which use a series of baffles to force wastewater to flow under, over or through the baffles as it passes from the inlet to the outlet (Barber and Stuckey, 1999). Changing the order of these compartments allows treating different wastewaters and the use of granules and or internal media helps to improve the system's stability. Thus, the Solids Retention Time (SRT) can be separated from the HRT, helping to achieve a good COD and solids removal, while producing a low amount of sludge (Mao et al., 2015).

The internal circulation reactor is basically two up-flow anaerobic sludge blanket reactors working one on top of the other, one high loaded and one low loaded (Habets et al., 1997). This type of reactor has two sets of three phase separation modules, which can separate gas, liquid and solids simultaneously. This improves biomass retention, which improves the quality of the effluent, as well as permitting for high COD removal (Mao et al., 2015).

Mao et al. (2015) recognizes a last type of reactors, the anaerobic membrane reactors, which include the anaerobic filter reactor, the fluidized bed reactor and the expanded granular sludge blanket.

The anaerobic filter uses a porous medium packed in the reactor to support biomass and the wastewater has an upward movement (Tauseef et al., 2013), which helps to enhance the treatment efficiency. On the other hand, this type of digester is very susceptible to clogging problems, which can reduced the wastewater flow and cause an incomplete treatment of the effluent (Bodkhe, 2008). These reactors can be applied to very high-strength wastewaters and demonstrates an outstanding adaptability of biomass to a new carbon source and organic load changes, also in addition to be able to use dilute feeds (Mao et al., 2015).

In the anaerobic fluidized bed reactor, biomass is grown on inert particles (such as sand or alumina) that are kept in suspension by the upward velocity of the effluent (Tauseef et al., 2013). These types of reactors are suitable for easily biodegradable effluents (Switzenbaum, 1983), which allow higher OLRs and have greater resistance to inhibitors (Mao et al., 2015). Zhang et al. (2007) also report short HRTs and good mixing characteristics of these reactors types.

The expanded granular sludge blanket is a modification of the traditional up-flow anaerobic sludge bed reactor, using granular sludge as the latter, but operating at higher superficial velocities (Jeison and Chamy, 1999). These technologies have better mixing than their predecessor (Mao et al., 2015) and can be applied in the treatment of very low strength wastewaters and can even be used in psychrophilic temperature ranges (Lettinga et al., 1997).

2.3 Continuous Stirred Tank Reactor

As stated earlier, CSTRs are considered the earliest high rate anaerobic reactor. It is one of the most common technologies used in process industries (Zhao et al., 2015) and a suitable technology when treating a wide range of effluents (Tauseef et al., 2013), especially wastewater containing high concentrations of suspended solids. In a CSTR, microorganisms are suspended through intermittent or complete mixing that stimulates contact between the sludge and effluent, promoting better performance, but at the same time consuming more energy (Mao et al., 2015).

Although the usage of a series of CSTRs is more efficient than using a single reactor, it is also more sensitive to easily degradable organic loads (Boe and Angelidaki, 2009). Boe and Angelidaki (2009) also report that a series of CSTRs present a complicated control and that it is necessary to adjust the conditions of the effluent of the acidogenic reactor before feeding it to the methanogenic reactors, when using a two-phase system.

The microorganisms in a single CSTR are prone to be washed out with the effluent. Due to this fact, the CSTR can be operated together with a sedimentation tank or as a membrane reactor in order to mitigate this problem and improve its efficiency (Mao et al., 2015).

2.4 Paper Mill Industry

The kraft pulping process is a process for conversion of wood into wood pulp, which consists of almost pure cellulose fibers, the main component of paper, being the dominant method for producing paper. The objective of any chemical pulping process is to remove lignin to separate cellulosic fibers from one another, producing a pulp suitable for the manufacture of paper and other products (Chakar and Ragauskas, 2004).

As shown in **Figure 2.2**, in the first step, the white liquor, an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) reacts with the wood chips in a large pressure vessel (digester). White liquor and wood chips are heated to 170°C and cooked for about two hours (Smook et al., 1982). In this step the hydroxide and hydrosulfide anions react with the lignin, causing it to break down into smaller soluble fragments (Chakar and Ragauskas, 2004).

The cooked pulp is then washed before being submitted to a bleaching process where the remaining lignin (4 – 5% by weight) is removed (Smook et al., 1982). After bleaching, the pulp is drained, pressed and thermally dried (Mateos-Espejel et al., 2010).

Figure 2.2 shows yet another output from the digestion process, black liquor. This output is separated from the pulp and is concentrated before being burned in a recovery boiler to produce steam. The inorganics produced in the boiler (sodium carbonate and sodium sulfide)

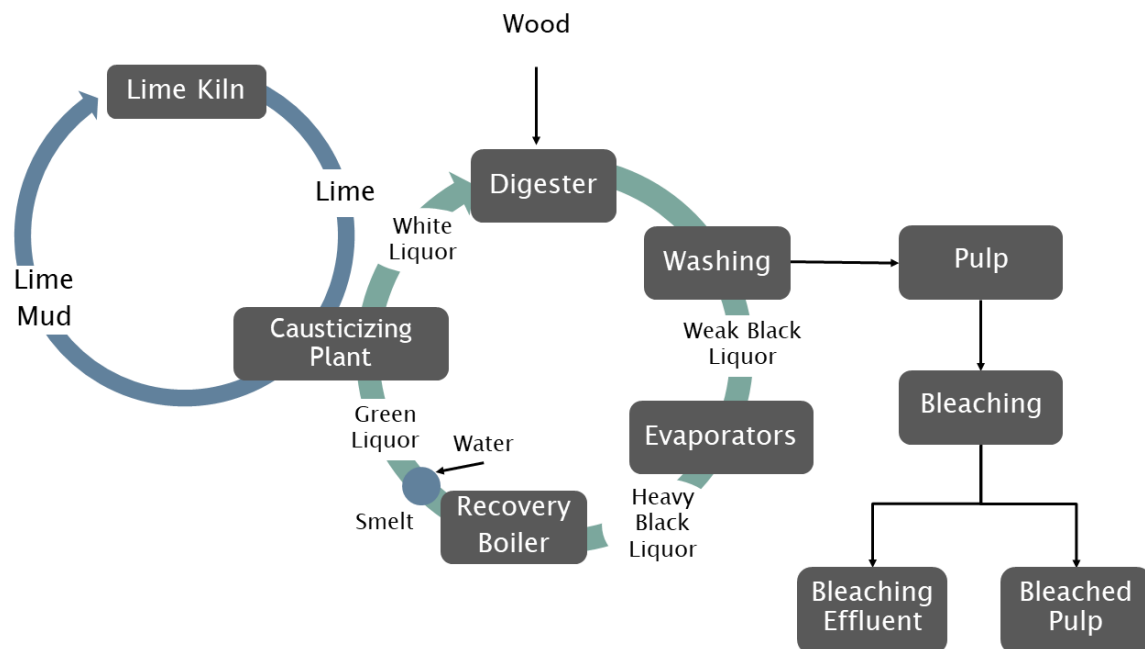


Figure 2.2: Kraft Process

Adapted from Tran and Vakkilainen (2008)

are collected and dissolved to form green liquor which is then causticized with quick lime to regenerate white liquor (Mateos-Espejel et al., 2010).

As mentioned previously, pulp and paper (PP) production industry is a water intensive industry and generates roughly 175 m^3 of wastewater per ton of paper produced. Even though wastewaters are produced at various steps of the process, those produced during bleaching are considered the most polluting, producing $2 - 4\text{ kg}$ of organochlorines for each ton of pulp produced (Nagarathnamma et al., 1999). As already mentioned, the discharge of these compounds can have really severe negative impacts on ecosystems, therefore, it is crucial to treat this effluent.

2.4.1 Anaerobic digestion of low biodegradable effluents

The effluents produced in the bleaching process were first treated with aerobic processes. Due to the high operation costs and large quantities of waste sludge produced, these effluents started to be treated with AD processes (Vidal et al., 1997) with fairly good results, as it can be seen in **Table 2.2**. The first anaerobic digester used to treat PP effluents was constructed with a CSTR configuration, with low loading rates, which resulted in large reactor volumes (Habets and Driessen, 2007). Later, upflow anaerobic sludge bed reactors and internal circulation reactors were used, although today more than half of AD treatment is done in an upflow anaerobic sludge bed reactor (Larsson et al., 2015).

The use of anaerobic digesters can achieve higher removals of AOX than the aerobic ones (Ferguson, 1994) which is very important when treating bleaching effluents. This type of effluents have a relatively low biodegradability (Rintala and Puhakka, 1994) and may also be inhibitory to methanogens (Vidal et al., 1997) due to the quality of the substrates present and the large effluent flow rates to be treated (Larsson et al., 2015). This can limit methane production, although organic matter can still be removed. Yu and Welander (1996) report that the of these effluents is the main factor limiting the efficiency of their AD treatment, especially of bleaching wastewater.

Biodegradability and toxicity vary, as expected, depending on the characteristics of the wastewater, which, in the case of PP wastewaters, can change for several reasons, such as the technology of the production process, the type of raw material used and the specific management of the process water (Vidal et al., 2001).

Bleaching methods, in particular, use consecutive bleaching sequences and can be done using different reagents such as, chlorine dioxide, extraction with sodium hydroxide, alkaline hydrogen peroxide, oxygen, sodium dithionite and ozone which will affect the anaerobic biodegradability of effluents (Meyer and Edwards, 2014). Bleaching effluents are not suitable for anaerobic digestion (Vidal et al., 1997) due to their high content in organo-chlorine compounds (Meyer and Edwards, 2014), although dilution with other wastewater streams can

Table 2.2: Application of different anaerobic treatment process for different wastewaters from kraft mill industries. Adapted from Vidal et al. (2001)

Reactor	Wastewater characteristics			T (°C)	HRT (days)	OLR (g/l d)	Removal (%)			References
	BOD ₅	COD	AOX UV				COD	BOD ₅	AOX UV	
AFB KBC	0.4-0.8		0.5-2.2	36	0.8-0.1	1.5-2.5	50-90	50-95		Hakulinen and Salkinoja-Salonen (1982)
AFB KBE	0.4-0.5	0.8-1.1	0.6-2.2	36	0.33	1.4-2.1	60	40	70-90	Hakulinen and Salkinoja-Salonen (1982)
AF BE	0.58	3.5		35-38			61	78	68	Hagblom and Salkinoja-Salonen (1991)
UASB KBC	0.3-0.7	0.9-2.1	47-190	55	1.1-1.5	0.6-1.9				Rintala et al. (1992)
UASB KBE	0.5-0.9	1.1-1.6	6-13	55	1.1-1.2	0.6-1.9				Rintala et al. (1992)
UASB HSWBL	5.8	19.3	113 ^b	36		3.7-3.8	62-78	98	28-58b	Kortekaas et al. (1998)
UASB EFBM		52	287 ^c	36	9.9-20.6	0.5-1.6	82-91		38-75c	Soto et al. (1991)

Unit. OLR: $g\ COD\ l^{-1}\ d^{-1}$, HRT: $days$, COD: g/l , Biochemical Oxygen Demand (BOD)₅: g/l , AOX: $mg\ Cl\ /l$.

Reactors. UASB: Upflow Anaerobic Sludge Blanket. AFB: Anaerobic Fluidized Bed. AF: Anaerobic Filter. Wastewater.

KBC: Kraft Bleaching Chlorine. KBE: Kraft Bleaching Extraction. BE: Bleaching Extraction. HSWBL: Hemp Stem Wood Black Liquor. EFBM: Eucalyptus Fiber Board Manufacturing

^b UV280: absorption unit 1, 1 cm.

^c UV215: absorption unit 1, 1 cm

be used to improve anaerobic degradability and/or microbial adaptation (Meyer and Edwards, 2014).

Methodology

To study the anaerobic processes of methanogenesis and acidogenesis, four runs were performed in two different reactors. One was carried out in a 7 l reactor of which was mechanically stirred and the other three were carried out in another 1.75 l reactor of which was magnetically stirred. The main difference from these runs was the pH of the influent. The larger reactor operated with an influent with pH 3, while the smaller reactor operated with an influent with a pH of 4, 6 and 7. The influent under study (D_0) came from a pulp and paper factory using the Kraft process, more precisely from the first step of pulp bleaching.

3.1 Reactor assembly and sampling points

In addition to the differences mentioned above, the reactors operated in a similar way. In **Figure 3.1** is presented one of the reactor set-ups (the smaller one). **Figure 3.2** shows the schematic representation of both reactors set-ups. Their assembly consisted of three main parts, the sedimentation tank, the reactor and the gas apparatus. Reactors were operated anaerobically in a bath at a mesophilic temperature ($35^\circ C$) in all four runs.

As can be seen in **Figure 3.2**, the influent entered the bottom of the reactors and exited at the top part to a sedimentation tank. In this tank, the treated effluent is separated from the sludge. This sludge was then recirculated back to the top of the reactors. The reactors were heated by a heating jacket and the volume of biogas produced was quantified using a water displacement system.

As can also be seen in **Figure 3.2**, the reactors had six sampling points for collecting gas and liquid samples:

- In the influent (position 1)
- In the treated effluent (position 5)
- In the sludge re-circulation (position 7)
- In the reactor (liquid) (position 3)
- In the reactor (gas) (position 8)

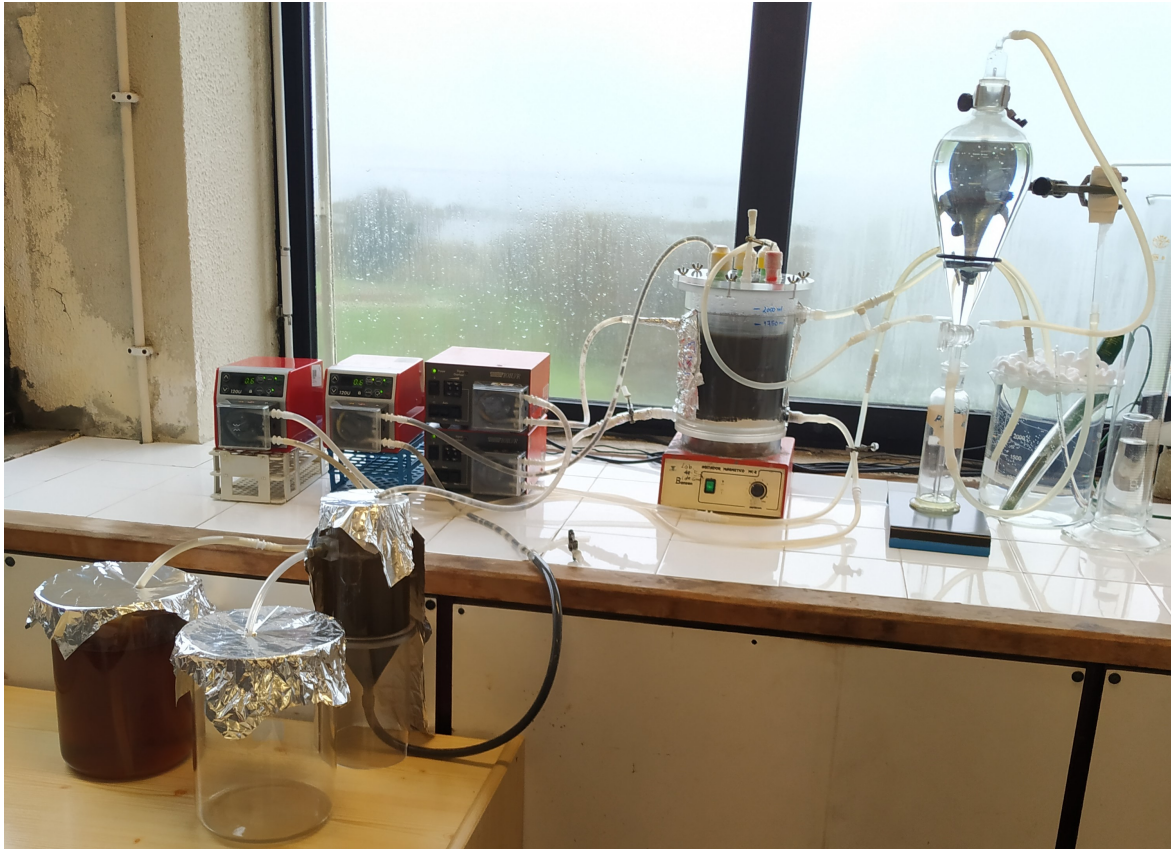


Figure 3.1: Reactor set-up

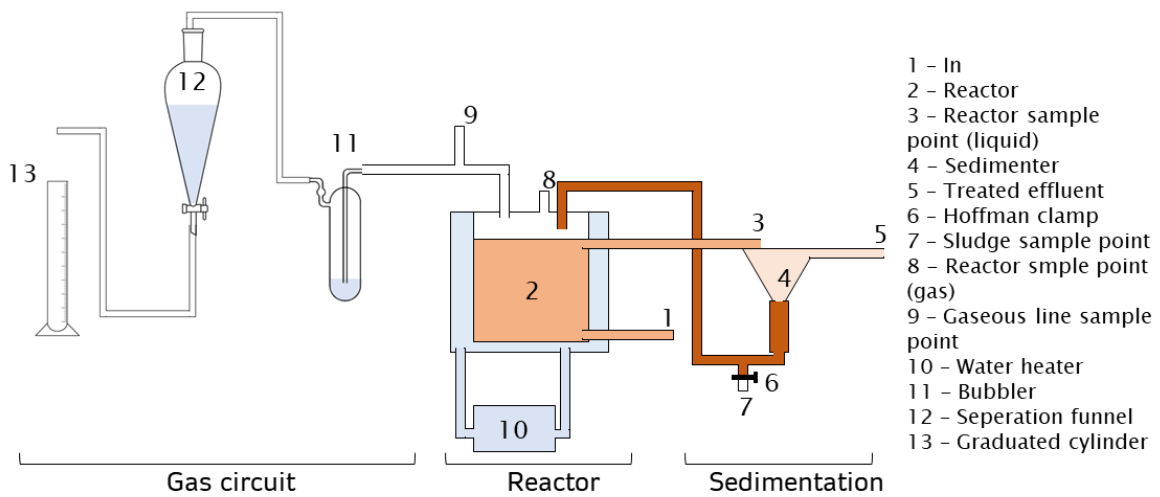


Figure 3.2: Reactor Scheme

- In the gas circuit (position 9)

The run at pH 4 was started with an anaerobic sludge concentration of 4 g VSS/l, whereas all the other runs had an initial anaerobic sludge concentration of 3 g VSS/l. Tap water was used in a thermostated bath to acclimate the sludge in all runs. The anaerobic sludge and

the D_0 effluent used in each operation were previously analyzed and the results are shown in **Table 3.1**.

As can be seen in **Table 3.1**, the concentration of the sCOD and the total Chemical Oxygen Demand (tCOD) of the bleaching effluent (D_0), which was used to prepare the reactors feed, have values close to each other due to the low value of suspended solids present. Anaerobic sludge has, as expected, high suspended solids values and low sCOD concentration. The pH value is also very different between sludge and D_0 , being neutral in the former and very acidic in the latter.

Given the high COD concentration in D_0 , this effluent was diluted, and its pH was then adjusted to the desired value by adding a concentrated solution of NaOH. Nutrients were also added (1 milliliter of each nutrient solution per liter of influent) to it. The compositions of these nutrient solutions are presented in the appendix.

The monitoring of the evolution of the anaerobic processes performed was carried out through the determination of various physicochemical parameters. **Table 3.2** shows the parameters analyzed at each sampling point of the reactor set up, as well as their periodicity. As can be seen in **Table 3.2**, pH and suspended solids were analyzed at all liquid sampling points. COD was analyzed on the Inlet, Outlet and Reactor sampling points and AOX was analyzed at the Inlet, Outlet and Sludge sampling points. The VFAs and BOD were sampled only at Outlet sampling point. The biogas composition was sampled the reactor and the gas line sampling points.

Collection were made twice a week, except for the sludge sampling point, which was done twice a month, and for the outlet BOD sampling point, which was done only once per operation.

Figure 3.3 shows how the sampling process for liquid samples took place.

Looking at **Figure 3.3** it is possible to understand how a single sample can be used to analyse all the different parameters. It is also visible that, after sampling, the pH and tCOD were analyzed before the sample was filtered. The filtrate was then used to analyze the concentrations of sCOD, VFAs and AOX (in the soluble state) and the filter cake was subjected to the analysis of suspended solids and AOX (present in the sludge) concentrations.

Table 3.1: D_0 and sludge analysis

Runs		Parameters					
		pH	SST (g/l)	SSV (g/l)	sCOD (g O_2 /l)	tCOD (g O_2 /l)	AOX (mg/l)
pH 3, pH 6 and pH 7	Sludge	7.32	26	18	0.243	N.A.	N.A.
	D_0	2.57	0.054	0.052	2.57	2.59	49.22
pH 4	Sludge	7.10	22	15	0.307	N.A.	N.A.
	D_0	2.78	0.14	0.10	2.64	2.72	43.90

N.A. - Not analyzed

Table 3.2: Sample collection, parameters and periodicity

Parameter	Samples					
	In	Out	Reactor (liquid)	Sludge	Reactor (gas)	Gas circuit
pH	✓	✓	✓	✓		
COD	✓	✓	✓			
VFA		✓				
AOX	✓	✓		✓		
Suspended Solids	✓	✓	✓	✓		
Biogas Composition					✓	✓
BOD		✓*				
Frequency	2x a week			2x a month	2x a week	

*BOD analysis were done once in each operation

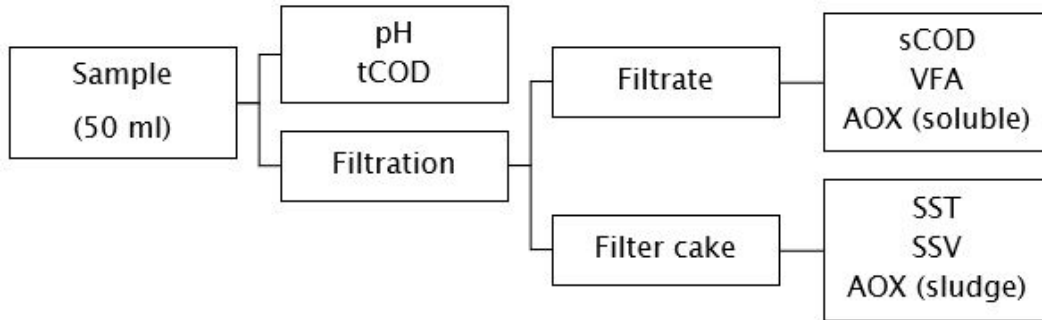


Figure 3.3: Sampling process and analysis

3.2 Analysis methods

In this section it will be explained how the different analysis were carried out.

3.2.1 pH

The pH measurement was performed on magnetically stirred samples with a volume of about 50 ml, using a pH-meter (Consort P602) equipped with a xerolite electrode. The calibration of the pH-meter was performed periodically with commercial solutions at pH=4.01 and pH=7.00 (at 25°C). The electrode was stored in a 3 M solution of KCl.

3.2.2 Chemical Oxygen Demand

The procedure to quantify the Chemical Oxygen Demand (COD) was based on the Closed Reflux Colorimetric Method (method 5220 D) (Federation et al., 2005). To measure the total COD, 2.5 ml of the sample was added to a digestion vessel previously filled with 1.5 ml of the digestion solution (K₂CrO₇ and H₂SO₄) and 3.5 ml of the sulfuric acid solution (H₂SO₄) with Ag₂SO₄. Samples were mixed and digested at 150°C for 2 hours. COD determination

was performed in triplicate. For the blank determination, the same procedure was followed, using 2.5 *ml* of distilled water instead of the sample.

After cooling to room temperature, the COD amount in the samples was determined using an adapted spectrophotometer (Aqualytic PC compact COD vario) which measures its absorption at 600 *nm*. For better accuracy of the results, the absorption of each sample was analyzed three times. The COD value considered was the lowest of the three determinations. Occasionally, it was necessary to dilute the samples to adjust the measurements to the equipment range (between 100 and 900 *mg O₂/l*).

sCOD was measured in the filtered samples using a glass microfiber filter.

3.2.3 Adsorbable Organically Bound Halogens

The measurement of adsorbable organically bound halogens (AOX) in liquid samples was based on ISO 9562. This method is suitable for measuring samples with an inorganic chloride ion concentration less than 1 *g/l*. Given the typical high concentration of samples, most of them had to be diluted prior to analysis.

Samples for AOX analysis were previously filtered in a glass microfiber filter and acidified with HNO₃ (1 *M*), preserved in the refrigerator at 4 °C until analysis. For the analysis, 100 *ml* of filtered and previously diluted samples were transferred to 250 *ml* capped Erlenmeyer flask and 5 *ml* of stock nitrate solution (0.2 *M*) and 50 *mg* of activated carbon were added. Samples were stirred at 200 rpm for 2 hours and then filtered using track-etched polycarbonate membranes. The membrane was then combusted at 1000 °C using an equipment for AOX determination (AOX/TOC analyzer ECS 1220 by Thermo Fisher Scientific TM) to determine the AOX concentration.

Blanks were determined by adding 100 *ml* of distilled water instead of sample to a capped Erlenmeyer flask and proceeding in the same way as for samples.

To determine the AOX concentration in the samples it was followed **Equation 3.1**.

$$AOX(mg/l) = \frac{(A_1 - A_0) * M_{Cl} * D}{(V * F)} \quad (3.1)$$

Where:

A_1 - Sample area (μC);

A_0 - Blank average area (μC);

M_{Cl} - Molar mass of chloride ($34.45 * 10^3$ *mg/mol*);

V - Volume of sample (*ml*);

F - Faraday constant ($9.648533289 * 10^{10}$ $\mu C/mol$);

D - Dilution factor.

When it was necessary to quantify the AOX concentration in the sludge, the sample was filtered using a glass microfiber filter and the filter cake was then dried (after the quantification of Volatile Suspended Solids (VSS) at 60°C for 24 hours. The again dried filter cake was then homogenized with a mortar. About 10 *mg* of the homogenized sludge with 10 *ml* of NaNO₃ (0.2 *M*) and 50 *mg* of activated carbon was added to a capped Erlenmeyer flask. The Erlenmeyer was stirred at 200 *rpm* for 3 hours. The samples were then filtered using

track-etched polycarbonate membranes, and the membrane was combusted at 950°C in the same equipment used for liquid samples. For the blanks, the same procedure was used for the samples, without sludge. The quantification of the AOX present in the sludge was done using **Equation 3.2**.

$$AOX(mg/g) = \frac{A_1 - A_0 * M_{Cl}}{m_T * F} \quad (3.2)$$

Where:

A_1 - Sample area (μC);

A_0 - Blank average area (μC);

M_{Cl} - Molar mass of chloride ($35.45 * 10^3 mg/g$);

m_T - mass of dried sludge (g);

F - Faraday constant ($9.648533289 * 10^{10} \mu C/mol$).

For both AOX analysis two replicates of each sample and at least two replicates of blanks were performed.

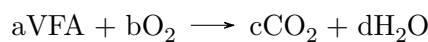
3.2.4 Volatile Fatty Acids

To determine the VFAs content, the samples were first filtered with a glass microfiber filter. The filtered sample was acidified with formic acid (99 – 100 % w/w) and stored in the refrigerator at 4°C until analysis.

The samples were analyzed in a Gas Chromatograph (PerkinElmer Clarus 480). Samples were injected manually using 0.5 μl of filtered sample containing 10 % (v/v) of formic acid (Panreac™) on gas chromatograph with injector set at 300°C, flame ionization detector set at 240°C, and a 25 mm * 0.25 mm Chrompack™CPSIL-5CB column. Helium and Nitrogen were used as carriers and make-upgases, respectively. The temperature program was used as follows: 1 min at 70°C, rise of 20°C min^{-1} to 100°C and then held for 2 min; rise of 10°C min^{-1} to 140°C and maintained for 3 min (11.70 min of total running time).

Standard solutions were used to obtain a calibration curve which was then used to determine the VFA concentration (expressed in g/L). Calibration curves and the standard solutions are presented in appendix.

To standardize the results, VFAs concentrations were expressed as COD equivalent. Therefore, oxidation stoichiometry was used to convert concentrations in g/l into COD equivalents, using theoretical oxygen demand (Theoretical Oxygen Demand (thOD)). The thOD was determined using the following chemical reaction:



This reaction resulted in the **Equation 3.3**.

$$thOD(gO_2/gVFA) = \frac{b * M_{O_2}}{a * M_{VFA}} \quad (3.3)$$

Where:

M_{O_2} - Molar mass of O_2 (32 g/mol);

M_{VFA} - Molar mass of the considering VFA.

The thOD constants calculated are presented in appendix.

3.2.5 Biogas

The procedure to quantify the biogas produced was based on method number 2720 C. Gas Chromatographic Method (Federation et al., 2005). Samples were taken in a 2 ml syringe and inserted in a gas chromatograph (SRI 8610C) with thermal conductivity detector (TCD) set at 75°C using an 80/10 * 2.5 m CRS HayesepTM column set at 61°C and helium as a carrier gas.

The concentrations of CH_4 and CO_2 in the samples were calculated using **Equations 3.4 and 3.5**

$$CH_4(\%) = 0.9896 * \frac{A_{CH_4}}{A_t} * 100 \quad (3.4)$$

$$CO_2(\%) = 0.9924 * \frac{A_{CO_2}}{A_t} * 100 \quad (3.5)$$

Where:

A_{CH_4} - Area of CH_4 ;

A_{CO_2} - Area of CO_2 ;

A_t - Area of CH_4 + Area of CO_2 .

3.2.6 Suspended Solids

The procedure to quantify Total Suspended Solids (Total Suspended Solids (TSS)) was based on method 2540 D. Total Suspended Solids Dried at 103 – 105°C (Federation et al., 2005). The sample was filtered using a glass microfiber filter, previously dried at 550°C for 1 hour (M_0). After filtration, the filter was dried at 105°C for 24 hours (M_e) (WTCTM Binder E28) and, after cooling to room temperature, the weight was determined using an analytical scale (Precisa XB 120A).

The procedure to quantify Volatile Suspended Solids (VSS) was based on method 2540 E. Fixed and Volatile Solids Ignited at 550°C (Federation et al., 2005). After TSS quantification, the crucible and filter were ignited at 550°C for 2 hours (M_f) in a furnace (ThermolabTM Fuji PXR-9). After cooling to room temperature, the mass was measured again. The TSS and VSS values were obtained using **Equations 3.6 and 3.7**, respectively.

$$TSS(g/l) = \frac{M_e - M_0}{V} \quad (3.6)$$

$$VSS(g/l) = \frac{M_e - M_f}{V} \quad (3.7)$$

Where:

M_e - Mass of the dried filter and crucible (g);

M_0 - Mass of the filter and crucible before filtering (g);

M_f - Mass of the ignited filter and crucible (g);
 V - Volume filtered (l);

3.2.7 Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) is related to the amount of biodegradable organic matter in a water sample.

The procedure to quantify BOD was based on method 5210 B. Respirometric Method (PROPOSED) (Federation et al., 2005). The sample was filtered and the pH was adjusted to value of 6.5 - 7.5. The volume of sample to be introduced in the bottle will vary with the range to be considered. The range and the sample volume are described in **Table 3.3**.

After adding the sample, a small volume of sodium sulfite (0.025 N) was added to neutralize the disinfecting agents present in it. A small amount of seed culture was also added. Given the low nutrient content of the sample, 1 ml of each nutrient solution per liter of sample was added to the bottle. The nutrient solutions were as follows:

- Solution A – 0.25 g of ferric chloride hexahydrate ($FeCl_3 \cdot 7H_2O$) to 1 liter of distilled water;
- Solution B – 27.5 g of calcium chloride anhydrous ($CaCl_2$) to 1 liter of distilled water;
- Solution C – 22.5 g of magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) to 1 liter of distilled water;
- Solution D (buffer) – 8.5 g of potassium monobasic phosphate (KH_2PO_4), 33.4 g of disodium phosphate heptahydrate ($Na_2HPO_4 \cdot 7H_2O$), 21.7 g of dipotassium phosphate (K_2HPO_4), 1.7 g of ammonium chloride (NH_4Cl) to 1 liter of distilled water.

For the blank it was added 400 ml of distilled water instead of sample to the bottle. After it was followed the same process as for samples. The bottles were then incubated at 20°C and the BOD content was registered each day until the end of the incubation. The BOD content was calculated following **Equation 3.8**

$$BOD_{adjusted}(mg/l) = BOD_{sample} - BOD_{blank} \quad (3.8)$$

3.3 Hydraulic Retention Time and Solids Retention Time

The HRT is the average time the liquid sludge spend inside the reactor and the SRT is the average time the solids sludge stays in the reactor. The HRT and SRT was calculated using **Equations 3.9 and 3.10** , respectively.

$$HRT(days) = \frac{V}{Q_{in}} \quad (3.9)$$

Where:

V - Reactor volume (l);

Q_{in} - Flow entering the reactor (l/day).

Table 3.3: BOD scale and correspondent sample volumes

Scale	Volume of sample (ml)
A - 0 : 1000 mg O ₂ /l	100
B - 0 : 600 mg O ₂ /l	150
C - 0 : 250 mg O ₂ /l	250
D - 0 : 90 mg O ₂ /l	400

$$SRT(days) = \frac{V * TSS_{reactor}}{Q_{withdrawn} * TSS_{withdrawn} + Q_{out} * TSS_{out}} \quad (3.10)$$

Where:

V - Reactor volume (l)

$TSS_{reactor}$ - TSS concentration in the reactor (g/l)

$Q_{withdrawn}$ - Flow withdrawn from the sludge (l/day)

$TSS_{withdrawn}$ - TSS concentration in the withdrawn sludge (g/l)

Q_{out} - Flow of the treated effluent (l/day)

TSS_{out} - TSS concentration in the treated effluent (g/l)

3.4 Calculations (anaerobic process performance)

To evaluate the performance of the reactors, it was necessary to calculate the COD and AOX removals. The removals of COD and AOX were calculated using **Equations 3.11 and 3.12**, respectively.

$$\%COD_{removed} = \frac{COD_{in} - COD_{out}}{COD_{in}} * 100 \quad (3.11)$$

Where:

COD_{in} - COD concentration at the entry of the the reactor (mg O₂/l);

COD_{out} - COD concentration at the exit of the reactor (mg O₂/l).

$$\%AOX_{removed} = \frac{AOX_{in} - AOX_{out}}{AOX_{in}} * 100 \quad (3.12)$$

Where:

AOX_{in} - AOX concentration at the entry the reactor (mg/l);

AOX_{out} - AOX concentration at the exit of the reactor (mg/l).

Results and discussion

The main objective of this research work is to study the AD process applied to a complex effluent containing potentially toxic materials (AOX) for the biological process (D_0 stream from the 1st stage of the kraft pulp bleaching process). In this context, the main objective of using the anaerobic process is the removal of organic matter (COD) and AOX, in addition to obtaining biogas and/or VFAs. In addition to removing organic matter and potentially inhibiting compounds, it is also intended to obtain a treated effluent with greater aerobic biodegradability, in order to increase the efficiency of a treatment plant for this type of effluent, and at the same time obtain an effluent treated with a better quality.

One of the parameters with the greatest influence on the anaerobic biological process applied to the D_0 effluent is the feed pH of the reactor. Thus, the methodology for presenting the results in this chapter is based on the discussion of the operation of each reactor fed at a different pH (pH 3, 4, 6 and 7). All studies started with a feed made with diluted D_0 (lower organic load) which was later concentrated in order to evaluate the impacts of different organic loads on the process performance for the same HRT. After reaching an undiluted feed of D_0 effluent, the load increase was made with the increase in flow and consequent decrease in HRT. The discussion of each operating condition, equivalent to a specific feed pH, is divided into four parts: the reactor operating conditions (applied organic load, flow rate and hydraulic retention time); the evolution of the process operating parameters (pH, sCOD and AOX); the evaluation of organic matter (COD) and AOX removal efficiencies; evaluation of the production of biogas and VFAs. At the end of the chapter, a comparison is made of the behaviour of the reactors as a function of the feed pH and an evaluation of the aerobic biodegradability of the effluent after application of the anaerobic process in relation to the effluent under study (D_0).

4.1 Influent pH 3

4.1.1 Operating Conditions

As previously mentioned in **Section 3.1**, the operation of the reactor was started with a concentration of anaerobic sludge of $3\text{ g}_{VSS}/\text{l}$, and the sludge was acclimated to 35°C with tap water. The effluent D_0 was diluted to prepare the feed solution and its pH remained unchanged after the addition of nutrients solution. The reactor was operated for 43 days (ending due to the low pH in the treated effluent) with increasing organic loads (total of 5 OLRs) and two flow rates which corresponded to 2 HRTs.

As shown in **Figure 4.1**, the reactor was started with an OLR of $0.153\text{ g}_{COD}\text{ l}^{-1}\text{ day}^{-1}$ and an HRT of 6.076 days . OLR was increased, by increasing COD, twice in the first 25 days to 0.216 and to $0.298\text{ g}_{COD}\text{ l}^{-1}\text{ day}^{-1}$ on days 8 and 13, respectively. On day 26, the OLR was increased to $0.470\text{ g}_{COD}\text{ l}^{-1}\text{ day}^{-1}$ due to the increase of the flow rate, achieving an HRT of the reactor of 3.739 days . On day 36 the OLR was again increased to a final load of $0.581\text{ g}_{COD}\text{ l}^{-1}\text{ day}^{-1}$.

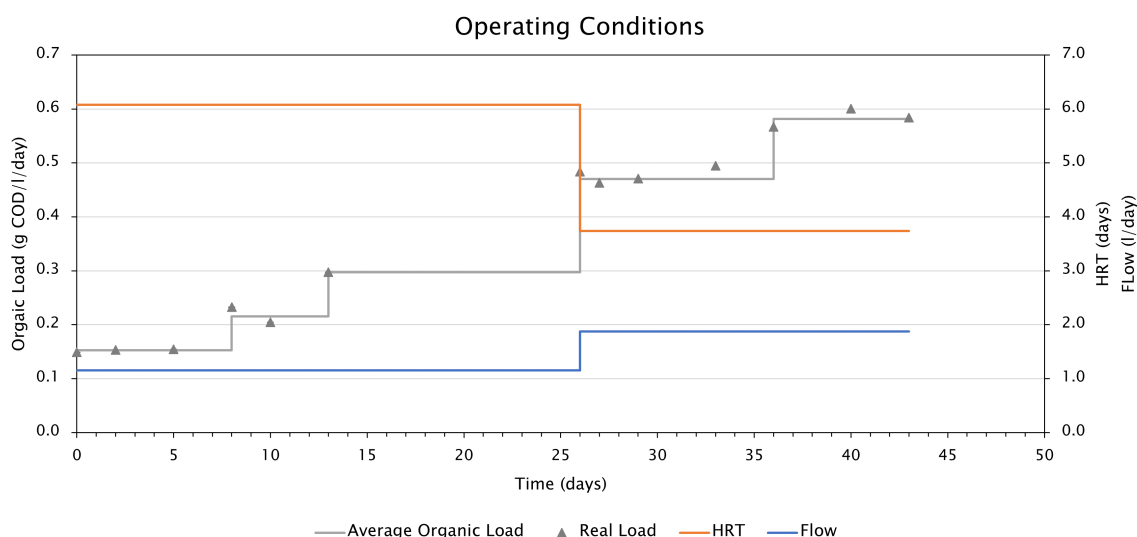


Figure 4.1: Operating conditions at pH 3

4.1.2 pH

Since the influent's pH was not controlled before feeding, its acidity depended only on the dilution made to D_0 . Therefore, the inlet pH decreased throughout the run, as shown in **Figure 4.2**, due to the increase reactor load.

The influent pH was 3 at the beginning of the operation and decreased to 2.56 at the end of it. **Figure 4.2** also shows that the pH of the treated effluent started around 8 and slowly decreased for the first 26 days (6.93 at that time of operation). Afterwards, after decreasing the HRT, the pH of the treated effluent began to decrease at a higher rate and, at the end of the operation, it had a value of 2.83 (almost as acidic as the influent). The pH of the sludge,

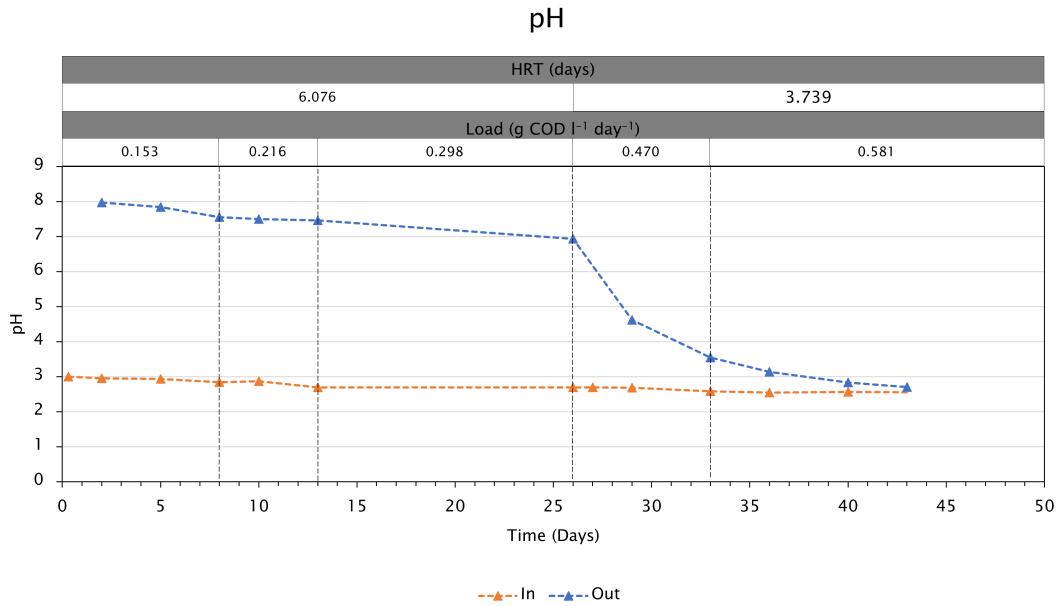


Figure 4.2: pH evolution at pH 3

measured on days 13 and 26 before the decrease in HRT, was close to neutral (at 6.5 and 6.7 respectively). On the other hand, the pH of the reactor, measured on the 26th day, after decreasing the HRT, was already below 5 (4.8).

From the analysis of **Figure 4.2**, it can be seen that the decrease in HRT from 6,076 to 3,739 was detrimental to the reactor operation and a very sharp drop in pH was observed.

4.1.3 Chemical Oxygen Demand

Figure 4.3 shows the sCOD evolution throughout the reactor operation. The graph shows that in the first 5 days of operation, the influent sCOD was around 0.9 g_{COD}/l , and on day 8 the sCOD concentration was raised to around 1.4 g_{COD}/l . On day 13, the sCOD concentration was again raised to around 1.8 g_{COD}/l , to simulate a further increase in the reactor load. After this change, the sCOD concentration in the influent remained constant, with the next increase in reactor load being carried out by an increase in flow rate (decrease in HRT). In the last phase of the operation, the load was increased again on day 36 by increasing the sCOD to around 2.2 g_{COD}/l until the end of the operation.

Figure 4.3 also shows that the sCOD of the treated effluent remained somewhat constant for the first 26 days of operation, varying from 0.370 g_{COD}/l on the 1st day to 0.530 g_{COD}/l on day 26. On day 29, the sCOD concentration nearly doubled (to about 1.0 g_{COD}/l) after the change decrease in HRT, which also coincided with the decrease in pH mentioned in **Subsection 4.1.2**. The sCOD concentration in the treated effluent increased to 1.5 g_{COD}/l after the last load increase.

Figure 4.4 shows the sCOD balance for the different applied organic loads. The figure shows the fractionation of the input sCOD in the removed and not removed components, complementing what was previously observed in **Figure 4.3**. The reactor had a removal

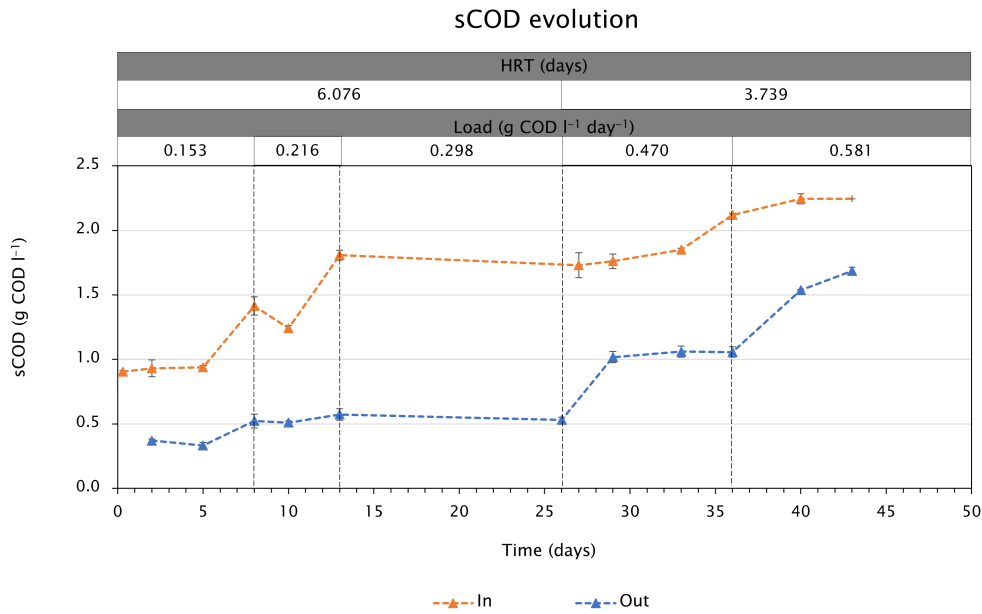


Figure 4.3: sCOD evolution at pH 3

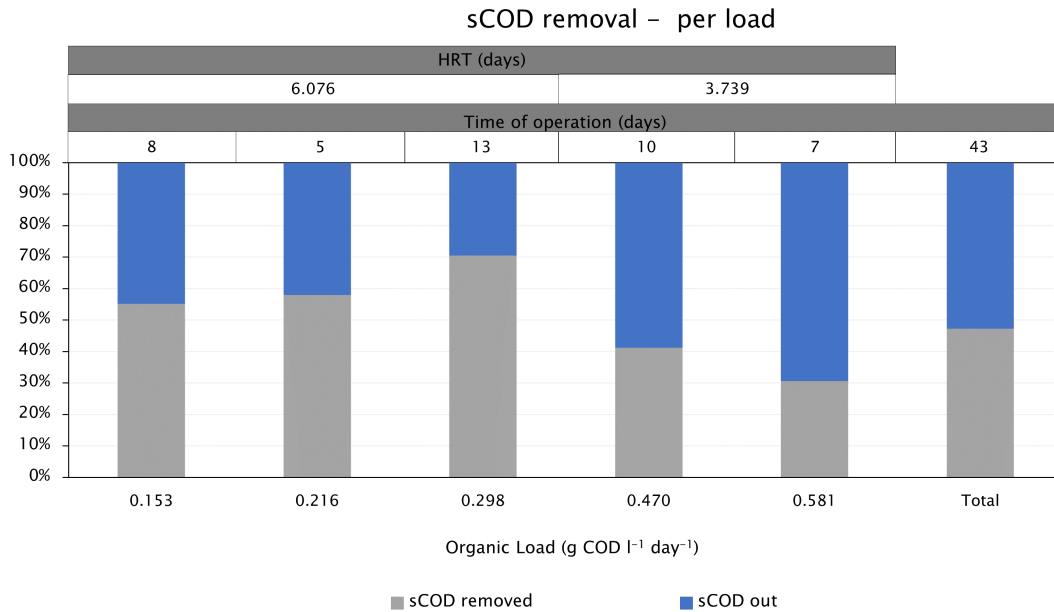


Figure 4.4: sCOD balance per load at pH 3

efficiency of sCOD of 55% at the first OLR used ($0.153 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$), and it increased to 58% once the load was increased to $0.216 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$. At a load of $0.298 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$ the reactor presented the best removal efficiency of the entire operation (71%), but as soon as the HRT was decreased from 6.076 to 3.789 days, the removal efficiency was greatly affected. In the first OLR after this change ($0.470 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$), the removal efficiency dropped to 41% and with the increase in load to $0.581 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, the decrease was even greater, removing only 31% of the sCOD present in the influent. This drop in the organic

matter removal efficiency was caused by the sharp decrease in HRT, which led to a decrease in the pH in the treated effluent (which may indicate a low pH inside the reactor) which led to the have inhibition of the AD process. Overall, and in average terms, the reactor was able to remove about 47% of all sCOD from the influent fed in the 43 days of operation of the reactor, which corresponds to 49 g of sCOD of the 103 g of sCOD fed to it in that period.

4.1.4 Adsorbable Organically Bound Halogens

Figure 4.5 shows the daily evolution of AOX during operation. In the first 5 days of operation, the concentration entering the reactor was around 20 mgCl/l before being increased to 26 mgCl/l in the 8th day of operation with the increase of the OLR, where it remained until day 13. On the 13th day, the concentration fed to the reactor was increased to 39 mgCl/l with a new increase of the OLR. This concentration remained around the same value until day 33, when it was increased to around 44 mgCl/l, according with the last increase in the OLR. The influent's concentration remained around this value until the end of the run.

Figure 4.5 shows that the treated effluent was constantly increasing in concentration in the first 26 days of operation, from less than 1 mgCl/l (0.82 mgCl/l) on the 2nd day to 9 mgCl/l on the 26th, reflecting the increase in the influent concentration. Once the HRT was decreased, the rate of increase was greater, and on day 40, the effluent's AOX concentration was around 29 mgCl/l. At the end of the run (day 43), the concentration of AOX on the treated effluent was 40 mgCl/l, close to the feed concentration.

Figure 4.6 shows the AOX balance for the different applied OLRs and for the total operation of the reactor. The figure shows the fractionation of the input AOX in the removed and not removed components, complementing **Figure 4.5**. The graph shows that, in the

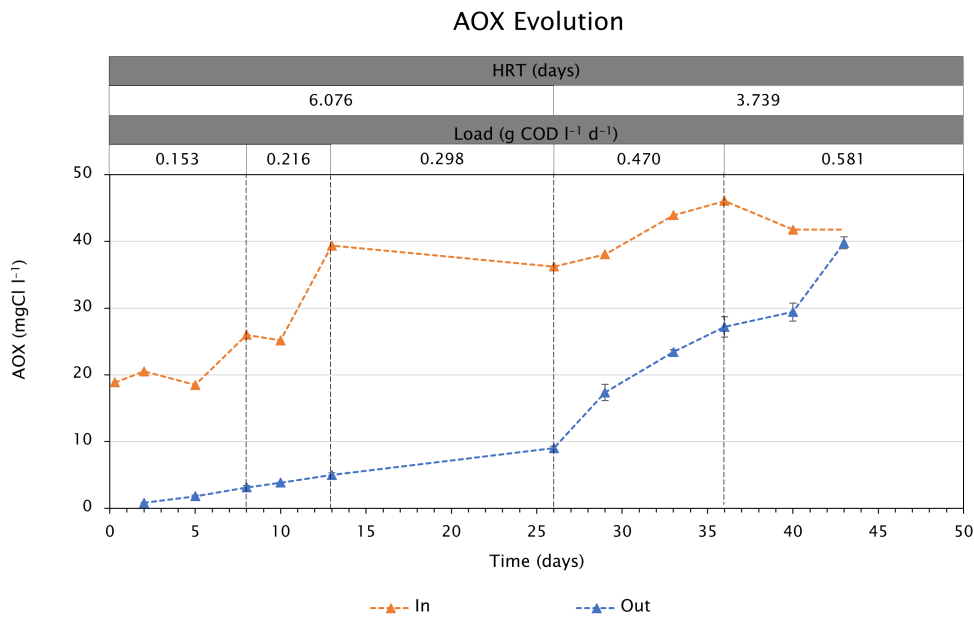


Figure 4.5: AOX evolution at pH 3

first load applied ($0.153 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$), the reactor had an AOX removal efficiency of 89%. When the load was increased to $0.216 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, this efficiency dropped to 82% before decreasing, once again to 62% when the load was raised again to $0.298 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$. With the sharp decrease in HRT, these efficiencies were even more affected, reaching a removal efficiency of 33% for the load $0.470 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$. At the highest load of $0.581 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, the reactor had its worst performance, having an AOX removal efficiency of only 23%. Overall, and in average terms, the reactor was able to remove about 49% of the AOX present in the influent fed in the 43 days of its operation, which corresponds to $1.089 \text{ g}_{\text{Cl}}$ of the $2.223 \text{ g}_{\text{Cl}}$ fed to it in that period.

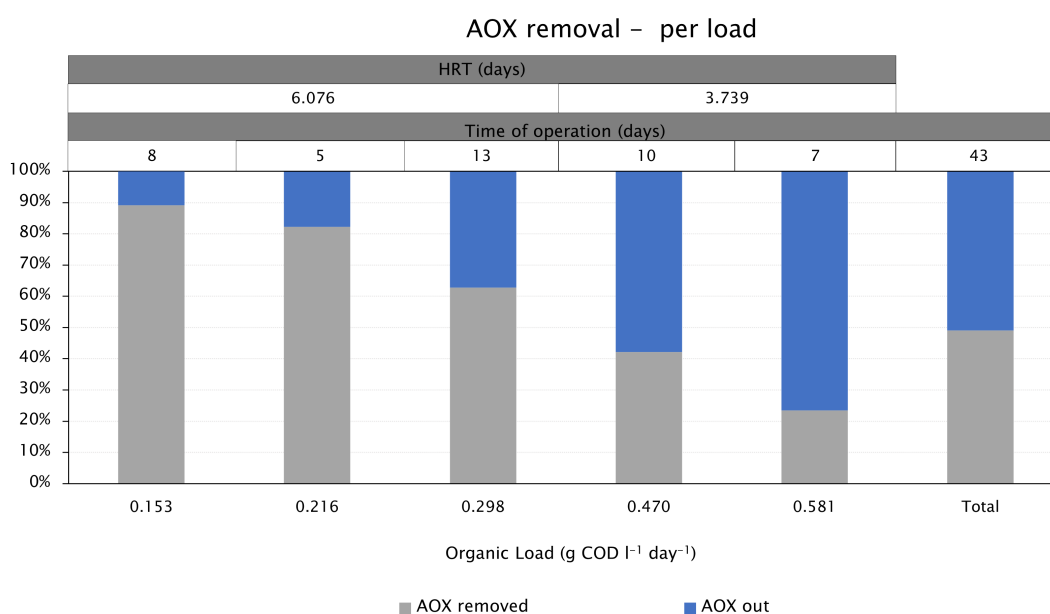


Figure 4.6: AOX balance per load at pH 3

4.1.5 Efficiencies

Figure 4.7 shows the daily efficiency removals of AOX and sCOD throughout the entire operation time.

The sCOD removal for the first load applied, ranged from 59% on day 2 to 44% on day 8. When the organic load was increased for the first time, on day 8, the reactor responded positively and the removal efficiency of sCOD increased to 64% (on day 10), subsequently decreasing until reaching 54% on the 13th day. On this day, the OLR was increased again, and, once again, the reactor responded positively by increasing the removal to 71% on day 26. On this day there was another increase in the load, but now through the increase in flow, which resulted in a decrease in the HRT, leading to the removal efficiency of sCOD falling to around 40% in the next 10 days. On day 40, after a new load increase on day 36, it led to a decrease in sCOD to 25%, where it remained until the end of the operation.

When considering the AOX removal efficiency, **Figure 4.7** shows that the removal of these compounds had a good start with 96% on the 2nd day of operation, although it decreased in

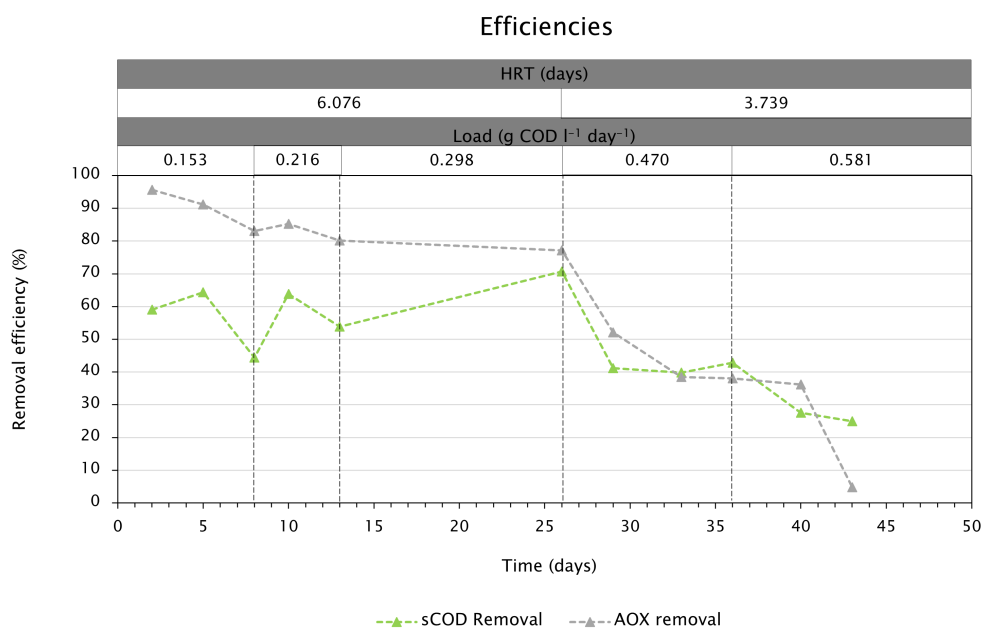


Figure 4.7: AOX and sCOD removal efficiencies at pH3

the following days. On day 26 the efficiency was 77%. After the decrease in the HRT, the performance of the reactor was severely affected (especially after day 40) and at the end of the run, it was at 5%.

In both cases, it is clear that, the decrease in HRT and consequent decrease in pH had a severe negative impact on the performance of the reactor.

4.1.6 Biogas and Volatile Fatty Acids production

Figure 4.8 shows the methane and VFA produced in this operation. As can be seen from the graph, the reactor produced methane in day 5 and 8 (31 and 7 ml, respectively).

The VFAs produced were quite irregular throughout the run, with the best production being obtained after the disappearance of methane, i.e., between day 8 (23 mg_{O_2}/l) and day 26 (26 mg_{O_2}/l), with a peak of 42 mg_{O_2}/l in the 10th day. On days 2, 33 and 40 the production of VFAs was around 17 mg_{O_2}/l , although on the remaining days the production of these compounds were very low (less than 25 mg_{O_2}/l).

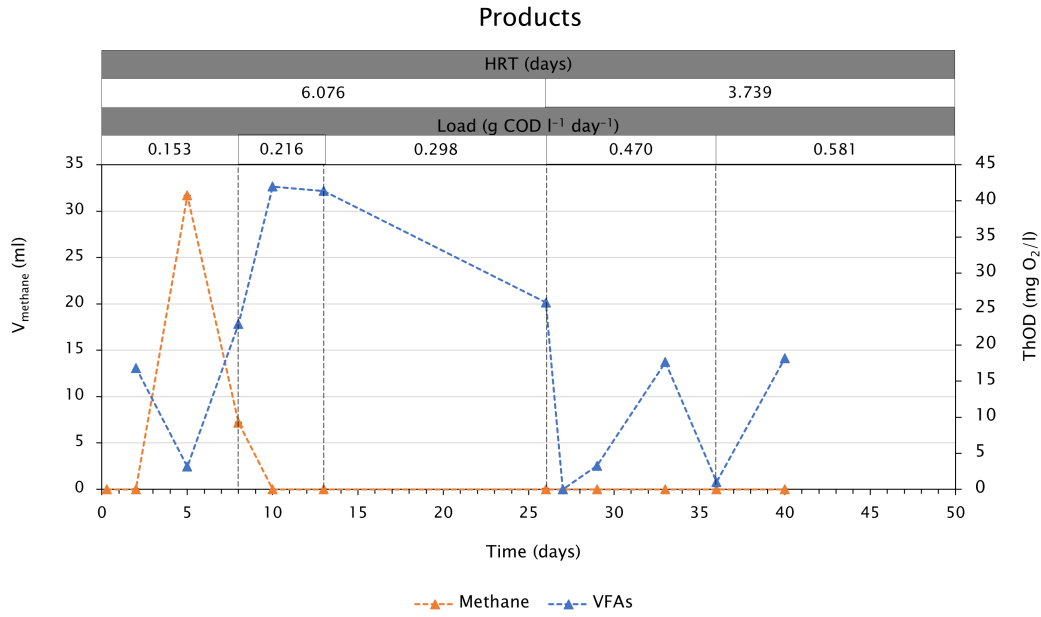


Figure 4.8: Methane and VFAs produced at pH 3

4.2 Influent pH 4

4.2.1 Operating Conditions

As mentioned previously in **Section 3.1**, this operation was started with an anaerobic sludge concentration of $4 \text{ g}_{VSS}/\text{l}$, and the sludge was acclimated with tap water. The influent was diluted and its pH adjusted to 4 when the nutrients solutions were added. The digester was operated during 60 days with 6 increasing OLRs and 1 HRT.

As shown in **Figure 4.9**, the reactor was started with an OLR of $0.419 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$ and a HRT of 1.461 days (with a flow rate of 1.20 l/day). The load was increased to $0.624 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$ on day 11 and on day 21 the OLR was raised once more to $0.745 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$. On days 32 and 42, the load was raised again to $0.835 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$ and $1.056 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$, respectively. The last load increase was done on the 53^{rd} day to $1.282 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$.

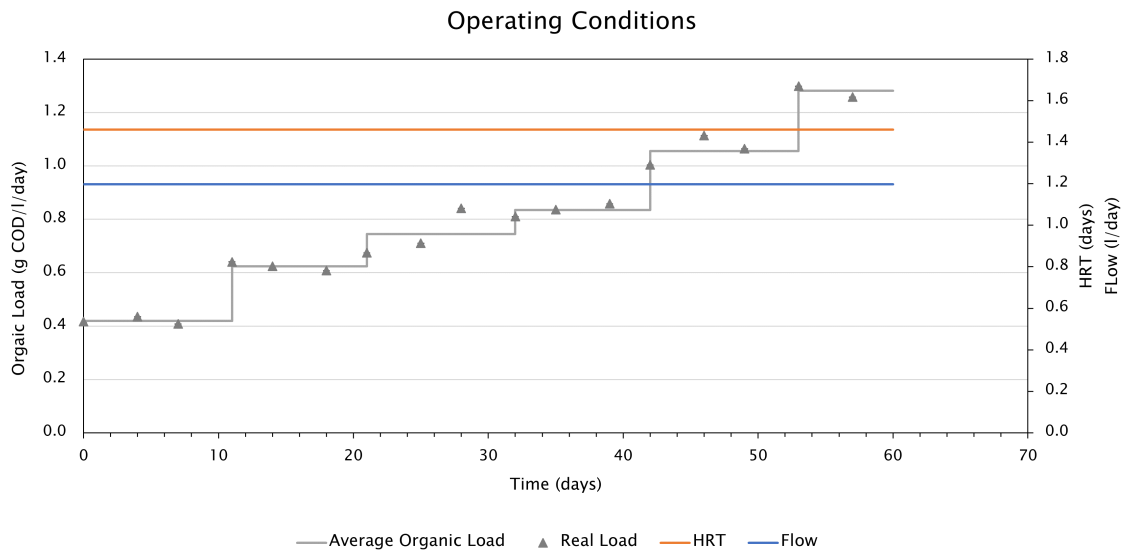


Figure 4.9: Operating conditions at pH 4

4.2.2 pH

In Figure 4.10 is presented the pH evolution throughout the run. As shown in the graph, the influent pH was around 4 throughout the operation.

The treated effluents pH was very low (2.09) on the first day analyzed (day 7), though in day 11 it was already 7.18. The treated effluent pH was around 7 until day 39. Thereafter, the pH of the effluent continued to increase and at the end of the run it was almost 8 (7.97).

Figure 4.10 also shows that the pH of the sludge was around 6.5 throughout the operation, although at the end of the operation it was slightly higher (6.80). When considering the

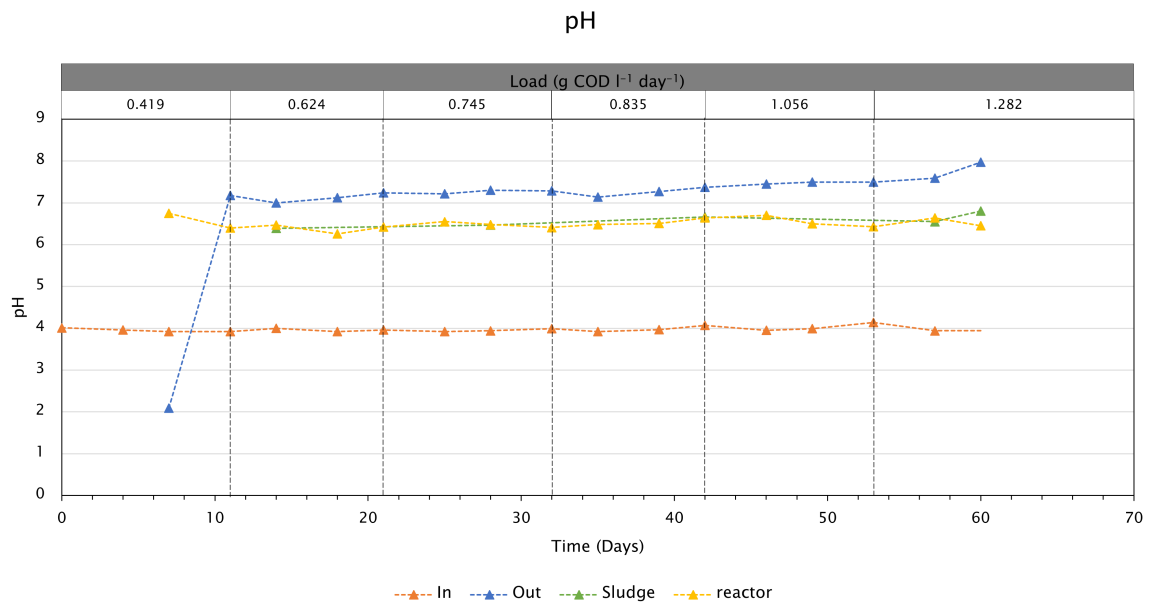


Figure 4.10: pH evolution at pH 4

reactor's pH, the graph shows that on day 7 it was at 6.75, but then stabilized at around 6.5 for the rest of the run.

4.2.3 Chemical Oxygen Demand

In **Figure 4.11** is presented the daily evolution of sCOD. As shown in the graph, the run started with an influent sCOD concentration of around $0.6 \text{ g}_{\text{COD}}/\text{l}$ and on day 11 was increased to around $0.9 \text{ g}_{\text{COD}}/\text{l}$. On day 21, the influent concentration was raised again to around $1.0 \text{ g}_{\text{COD}}/\text{l}$ and on the 32th day, the sCOD concentration in the influent was around $1.2 \text{ g}_{\text{COD}}/\text{l}$. On day 42, the sCOD concentration was already in the range of $1.5 \text{ g}_{\text{COD}}/\text{l}$, before being increased one last time on day 53 to $1.9 \text{ g}_{\text{COD}}/\text{l}$, where it remained until the end of the operation.

When considering the treated effluent sCOD concentration, **Figure 4.11** shows that on the first measured day (on day 7) it was at $0.300 \text{ g}_{\text{COD}}/\text{l}$, although there were some variations in the following days, on day 18 it stabilized around $0.350 \text{ g}_{\text{COD}}/\text{l}$. The treated effluent sCOD concentration on day 25 was already $0.400 \text{ g}_{\text{COD}}/\text{l}$ and remained there until day 35, when it started to increase again. The biggest change in sCOD concentration was observed after day 42, when it continued to increase and at the end of the operation it was almost at $0.850 \text{ g}_{\text{COD}}/\text{l}$.

Looking at the concentration of sCOD in the reactor, **Figure 4.11** shows a similar evolution to the treated effluent concentration. The reactor concentration was usually higher than that of the treated effluent, which may suggest that the removal of sCOD continued into the sedimentation phase.

In **Figure 4.12** is shown the sCOD evolution through the different OLRs used. The graph shows that the removal efficiency in the first load used ($0.419 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$) was the

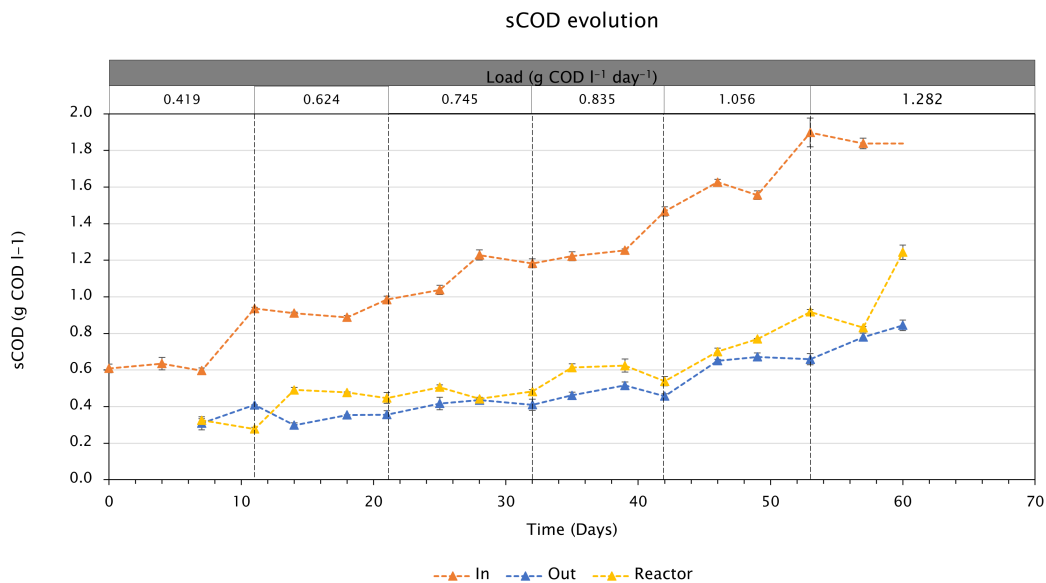


Figure 4.11: sCOD evolution at pH 4

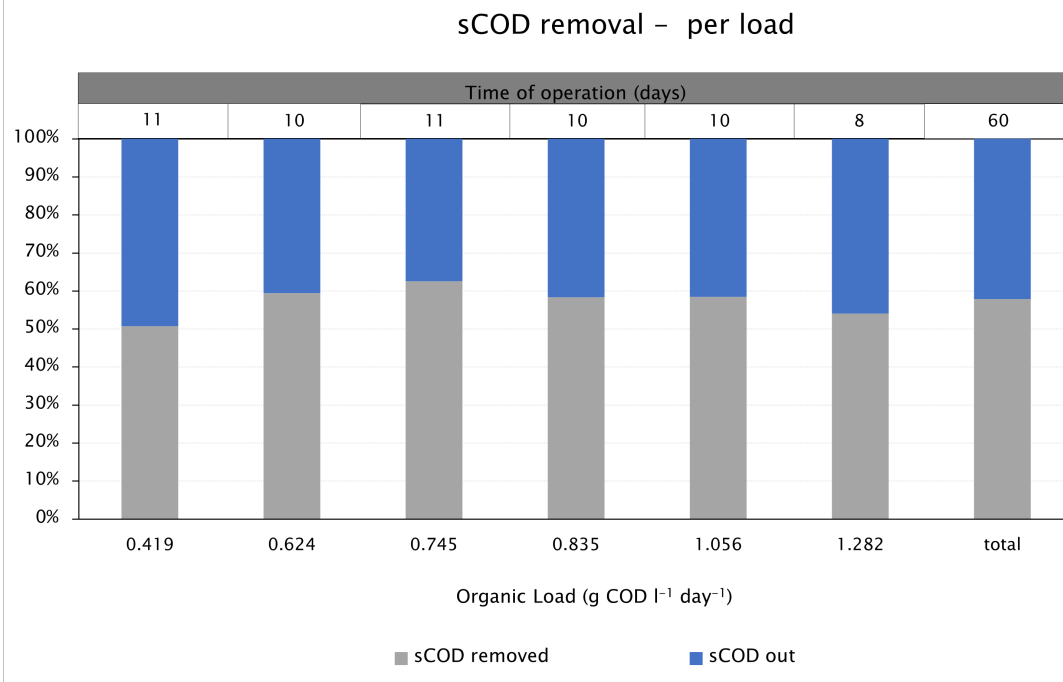


Figure 4.12: sCOD balance per load at pH 4

worst of the run, removing 51% of the influent sCOD. In the next four loads, $0.624 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, $0.745 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, $0.835 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$ and $1.056 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, the digester had a performance around 60%. At the last load used ($1.282 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$), the reactor performed slightly worse, removing only 54% of the fed sCOD. When considering the overall performance, the reactor removed 58% (48.60 g) of the total sCOD fed (83.98 g).

4.2.4 Adsorbable Organically Bound Halogens

In **Figure 4.13** the AOX evolution of this run is represented.

The graph shows that the reactor was started with an influent AOX concentration of around $10 \text{ mg}_{\text{Cl}}/\text{l}$. This concentration was increased twice on the following days (on day 11 to $15 \text{ mg}_{\text{Cl}}/\text{l}$ and on day 21 to around $18 \text{ mg}_{\text{Cl}}/\text{l}$). On day 32, the AOX concentration in the influent was raised to around $22 \text{ mg}_{\text{Cl}}/\text{l}$ and on day 42 it was $24 \text{ mg}_{\text{Cl}}/\text{l}$. Finally, on the 53th day, the influent AOX concentration was raised one last time to $31 \text{ mg}_{\text{Cl}}/\text{l}$.

When considering the AOX content of the treated effluent, **Figure 4.13** shows a steady increase throughout the entire run, starting at around $2.5 \text{ mg}_{\text{Cl}}/\text{l}$ and ending the run at $11.7 \text{ mg}_{\text{Cl}}/\text{l}$.

Figure 4.14 shows the digester performance removing the AOX present in the influent through the different OLRs used. As the graph shows, the reactor performance was quite similar in the different loads applied. The removal performance fluctuated only 10%, with its maximum being reached in the first OLR used (69%) and its minimum in the fifth load (59%). In overall performance, the reactor removed $856 \text{ mg}_{\text{Cl}}$ from the $1353 \text{ mg}_{\text{Cl}}$ fed, which corresponds to an efficiency of around 63%.

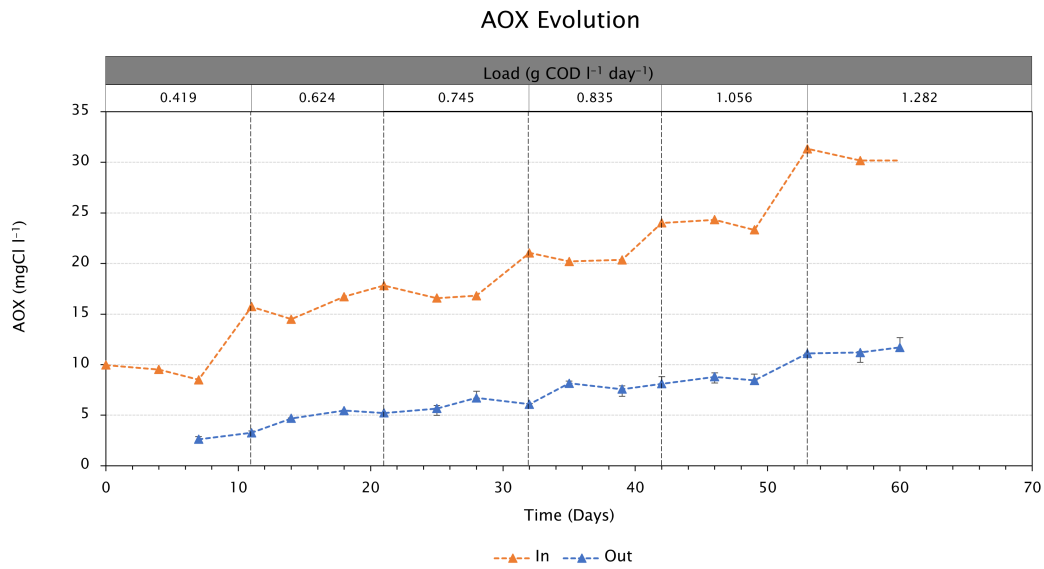


Figure 4.13: AOX evolution at pH 4

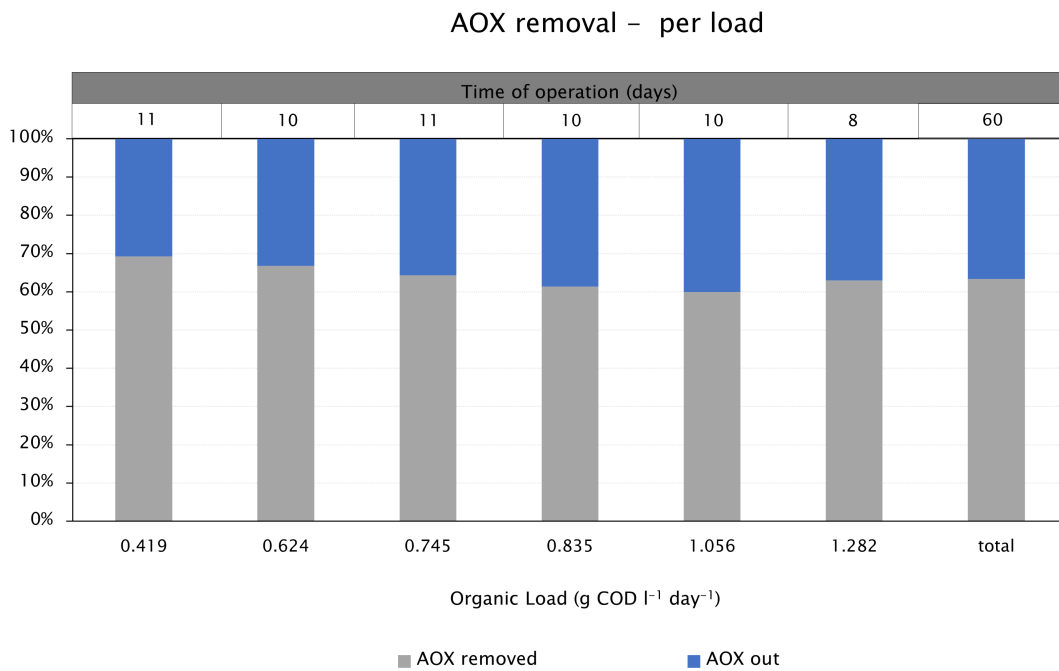


Figure 4.14: AOX balance per load at pH 4

4.2.5 Efficiencies

Figure 4.15 shows the daily removal efficiency of sCOD and AOX.

Looking at the removal efficiency of sCOD, Figure 4.15 shows that it was nearly constant throughout the entire operation, achieving a removal efficiency of around 60%, although it has a sharp drop at day 11 (31%).

The removal efficiency of AOX from the effluent was also quite regular throughout the

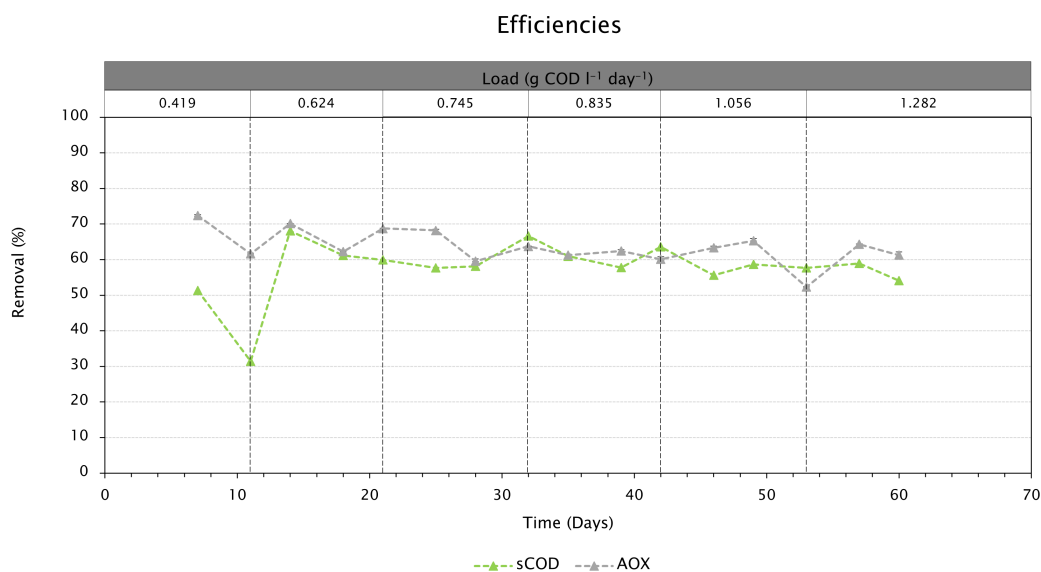


Figure 4.15: AOX and sCOD removal efficiencies at pH 4

operation and achieved a performance close to the value obtained for the removal of sCOD.

Both removal efficiencies were comparable to each other after day 14, and in both of them, a slight downward trend can be observed. The operation ended with a removal of sCOD and AOX of 52% and 61%, respectively.

4.2.6 Biogas and Volatile Fatty Acids production

Due to a problem in the measuring equipment, it was not possible to measure the volume of biogas produced. Therefore, only the methane content in the produced biogas was measured. This content is shown in **Figure 4.16**. The figure also shows the VFAs produced in the first 24 days (VFAs were not detected to between day 25 and day 57).

As can be seen in **Figure 4.16** in the first 21 days, the reactor did not produce any methane. In the last 35 days, only on day 32 the reactor did not produce methane. On days when methane was produced, with the exception of day 35, when the CH₄ concentration was 27%, the percentage of methane in the biogas was at least 50%.

When considering the VFAs production, it was only measurable in 3 days (day 10, 21 and 25), with very low values around 18 mg_{o₂}/l.

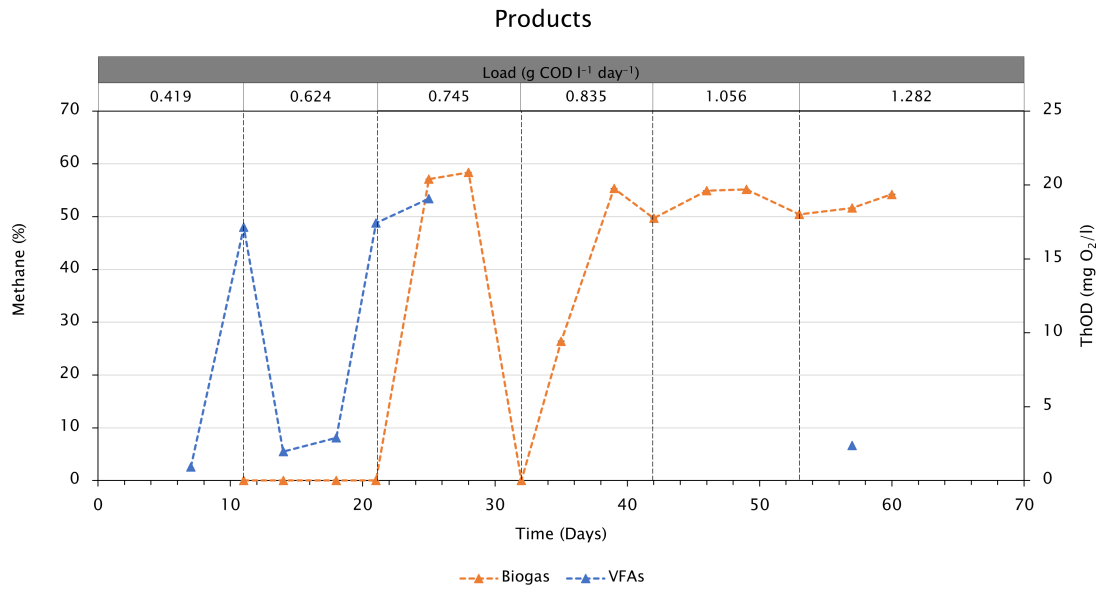


Figure 4.16: Methane and VFAs produced at pH 4

4.3 Influent pH 6

4.3.1 Operating Conditions

As mentioned earlier, in **Section 3.1**, this run was started with a concentration of anaerobic sludge of $3 \text{ g}_{VSS}/\text{l}$ and was then acclimated to 35°C with tap water. The effluent D_0 was also diluted, as in the two operations aforementioned. After this dilution, nutrient solutions were added before the pH was adjusted to 6. This run was the longest in this study, lasting 74 days, having 3 different HRTs and 6 OLRs.

As seen in **Figure 4.17**, the reactor was started with an HRT of 2.431 *days* and a load of $0.509 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$. In the first 13 days, the OLR was increased twice, to $0.774 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$ on day 7 and to $0.910 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$ on day 11. On the 19th day, the HRT was changed from 2.43 *days* to 2.03 *days*, with the corresponding load increase to $1.027 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$. On day 46, the load was changed one last time to $1.400 \text{ g}_{COD} \text{ l}^{-1} \text{ day}^{-1}$, through the alteration of the HRT, which was reduced to 1.74 *days*.

In this operation, the SRT was also changed during the second HRT used and on day 32 it was changed from 20 *days* to around 8 *days*.

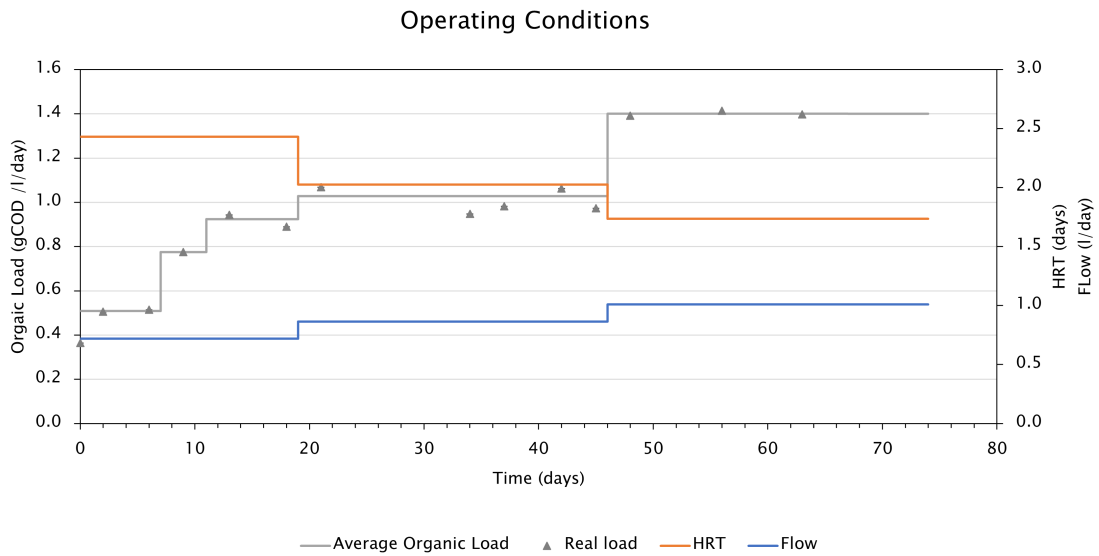


Figure 4.17: Operating conditions at pH 6

4.3.2 pH

Figure 4.18 shows the pH evolution of the run. As expected, the influent pH was around 6 throughout the run. When considering the

reactor pH, the graph shows that, throughout the run, it was around 7 having reached a peak on day 32 (at 7.9). Looking at the sludge pH, **Figure 4.18** shows that it was also around 7, having two peaks at two different times, on day 32 and day 65, with a pH of 7.93 and 7.91, respectively. When considering the treated effluent pH, it is possible to see that, although it started in the range of 7.5, it increased, and on day 34 it was around 8.2. For the

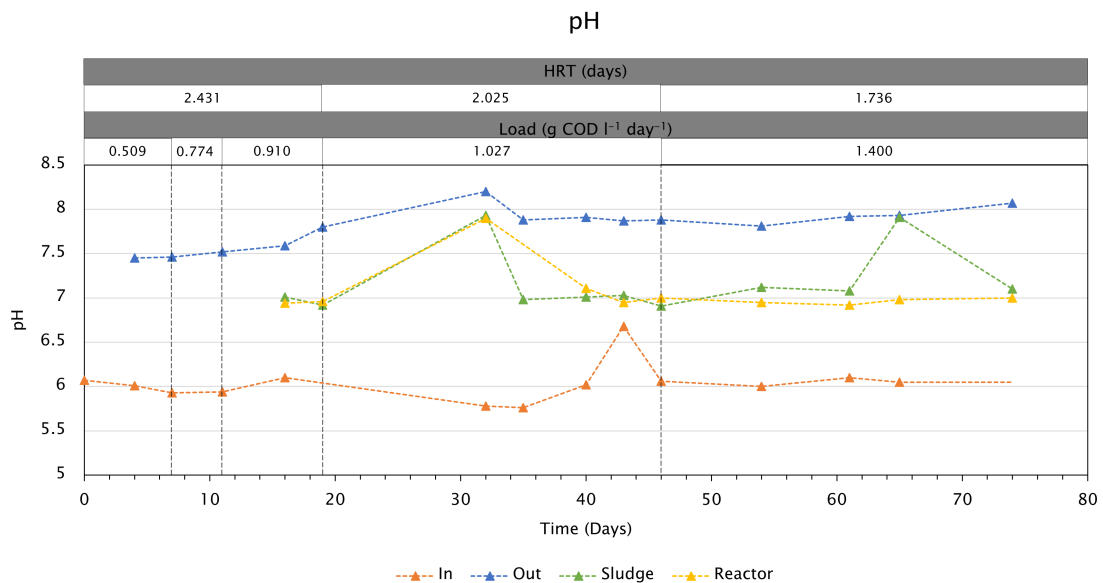


Figure 4.18: pH evolution at pH 6

rest of the operation, the treated effluent pH was around 8.

4.3.3 Chemical Oxygen Demand

In **Figure 4.19** the sCOD evolution of the run is shown. As shown in the graph, the run was started with a sCOD concentration of $1.2 \text{ g}_{\text{COD}}/\text{l}$. The influent concentration was raised (on day 7) to around $1.900 \text{ g}_{\text{COD}}/\text{l}$ and again on day 11 to around $2.100 \text{ g}_{\text{COD}}/\text{l}$. The influent concentration remained around this value until day 46, when it was increased one last time to $2.4 \text{ g}_{\text{COD}}/\text{l}$ until the end of the run.

When considering the treated effluent sCOD concentration, **Figure 4.19** shows that it started at $0.193 \text{ g}_{\text{COD}}/\text{l}$ and increased in the following days, reaching $0.838 \text{ g}_{\text{COD}}/\text{l}$ on day 19. The effluent sCOD concentration remained constant until day 40 when it started increasing again. On day 46, the effluent concentration was $1.318 \text{ g}_{\text{COD}}/\text{l}$. Over the next 22 days, the concentration of the treated effluent did not change significantly.

Figure 4.20 shows the reactor's performance in the different OLRs used. As can be seen in the graph, the first pair of loads, $0.509 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$ and $0.774 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, the reactor had a similar performance, removing around 65% of the influent sCOD. While in the next two loads, at 0.910 and $1.027 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, performance dropped and removal efficiency was 58% (although having different HRTs). In the last OLR ($1.400 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$) and HRT used (1.736 days) the digester had its worst performance, removing only 48% of the sCOD that entered the reactor. When considering the overall performance of the reactor, **Figure 4.20** shows that the reactor removed more than half of the total sCOD fed (54%). This means that, of the total $143 \text{ g}_{\text{COD}}$ fed into the digester, $77 \text{ g}_{\text{COD}}$ were removed.

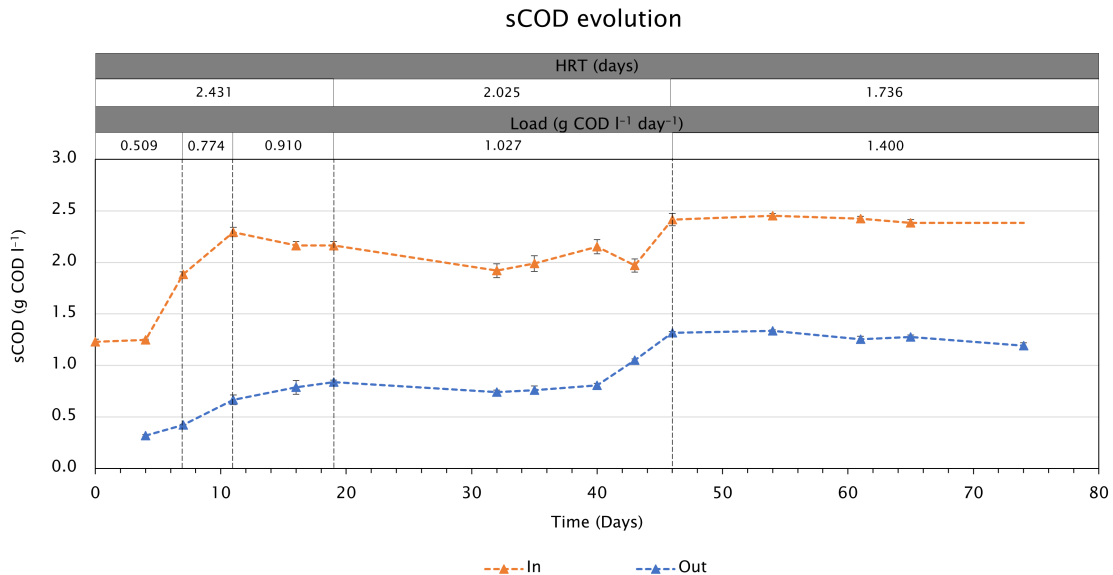


Figure 4.19: sCOD evolution at pH 6

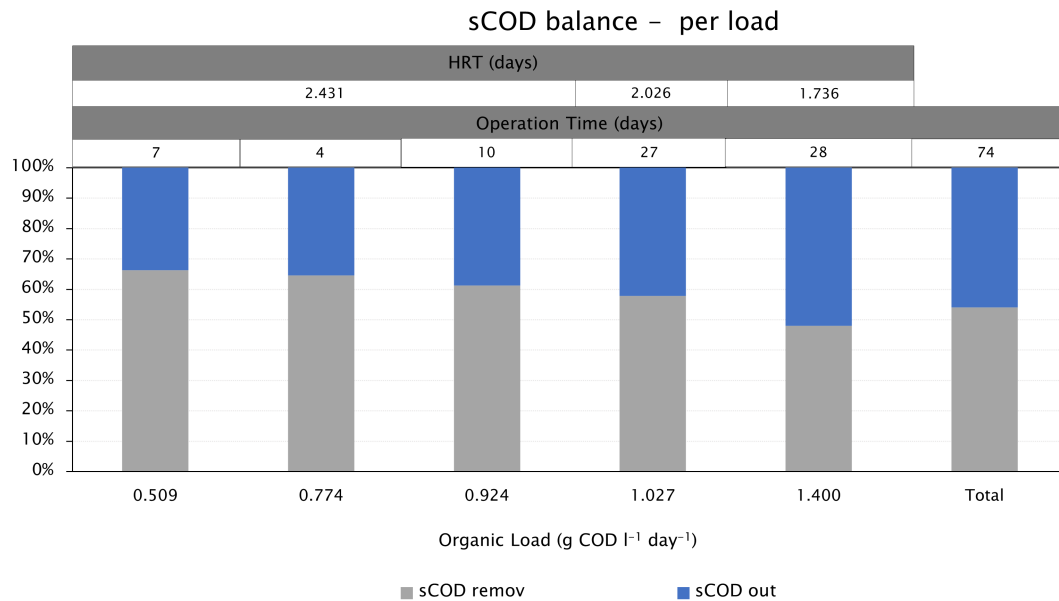


Figure 4.20: sCOD balance per load at pH 6

4.3.4 Adsorbable Organically Bound Halogens

In **Figure 4.21** the daily evolution of AOX of the run is presented. As shown in the graph, the reactor was started with an influent with an AOX concentration of 23.01 $mgCl/l$. This concentration was increased until day 40, when it was at 48.21 $mgCl/l$. Over the next 21 days, AOX was around 45 $mgCl/l$ before being raised for the last time on day 67 to 51.13 $mgCl/l$.

Looking at the AOX concentration in the treated effluent, **Figure 4.21** shows that on the

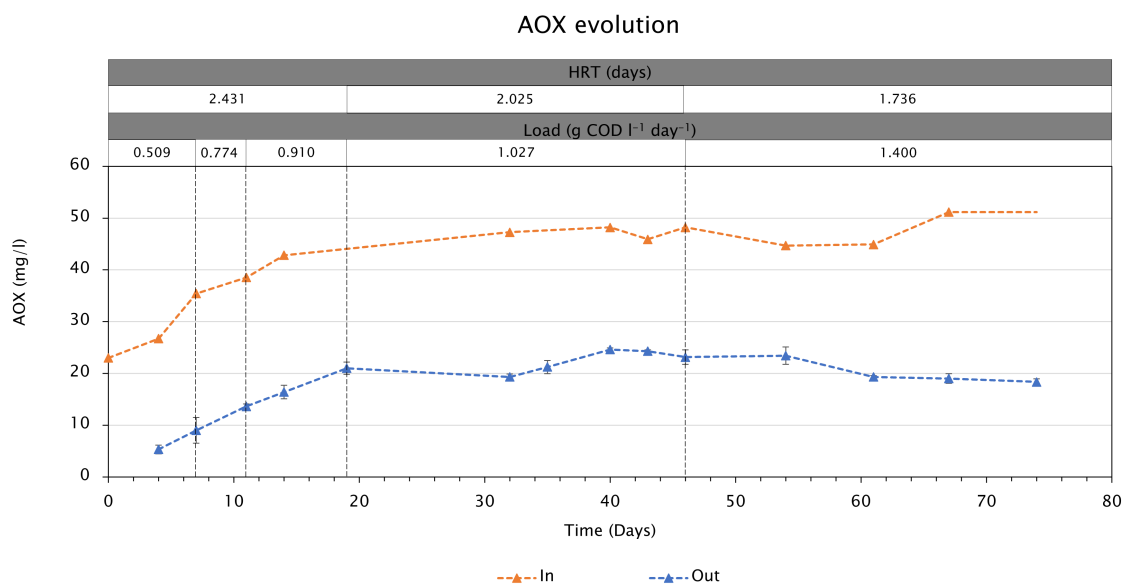


Figure 4.21: AOX evolution at pH 6

first day analyzed, day 4, this concentration was quite low (at 5.32 mgCl/l). From that day onwards, the effluent concentration increased until day 19, when it reached 21.00 mgCl/l . The treated effluent AOX concentration remained around this value for the rest of the operation, although with a small increase between days 35 and 61.

Figure 4.22 shows the digester’s performance at the different loads and HRTs used. As can be seen in the graph, like as with the removal of sCOD, the removal efficiency of AOX at $0.509 \text{ gCOD l}^{-1} \text{ day}^{-1}$ and $0.774 \text{ gCOD l}^{-1} \text{ day}^{-1}$ was similar, removing 66% and 62%, respectively. In the last load used for the HRT of 2.431 days ($0.910 \text{ gCOD l}^{-1} \text{ day}^{-1}$), the reactor had its worst performance, with an efficiency below 50% (47%). With the HRT decreasing to 2.025 days and the load increasing to $1.027 \text{ gCOD l}^{-1} \text{ day}^{-1}$, the reactor responded favorably, having achieved a removal efficiency of 52%. In the third decrease in HRT (1.736 days), and with a load of $1.400 \text{ gCOD l}^{-1} \text{ day}^{-1}$, the reactor had an even better performance, having removed 57% of the AOX present in the influent. With regard to the overall operation, the reactor was capable of producing a treated effluent with 56% less AOX than the total amount fed.

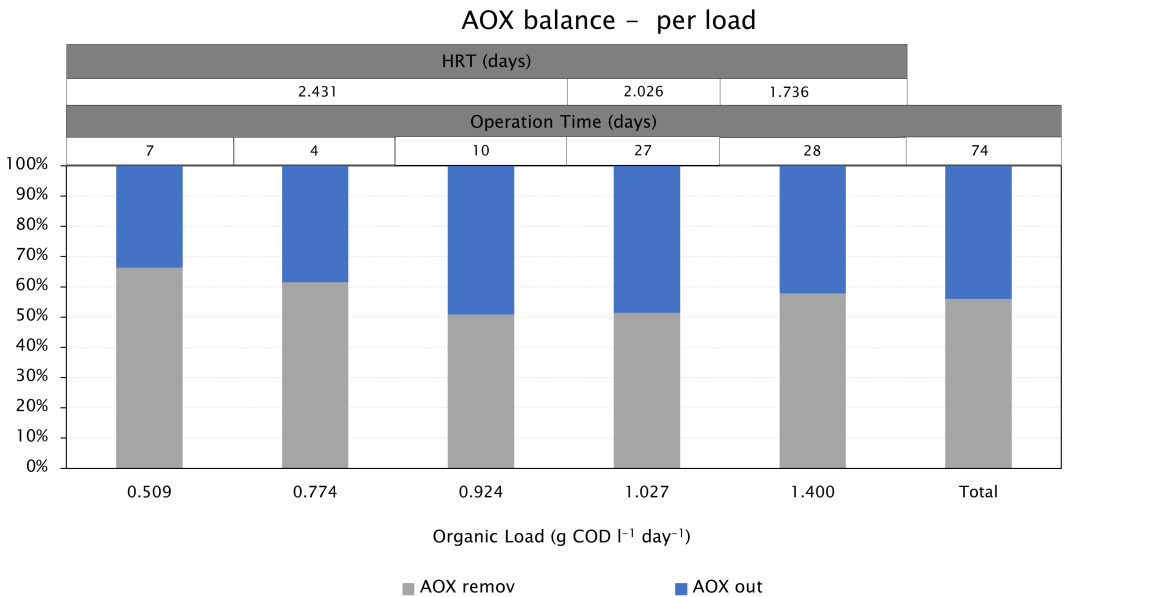


Figure 4.22: AOX balance per load at pH 6

4.3.5 Efficiencies

The removal efficiency throughout the run is presented in **Figure 4.23**.

The removal efficiency of sCOD started at 74% and decreased in the following days. After the 7th day, the efficiency remained somewhat constant until day 40, when it started to decrease, hitting a minimum on day 48 (with 33%). This drop in efficiency could be due to the change in SRT done at day 32. On day 56, the removal efficiency started increasing again, and by the end of the run it was 50%.

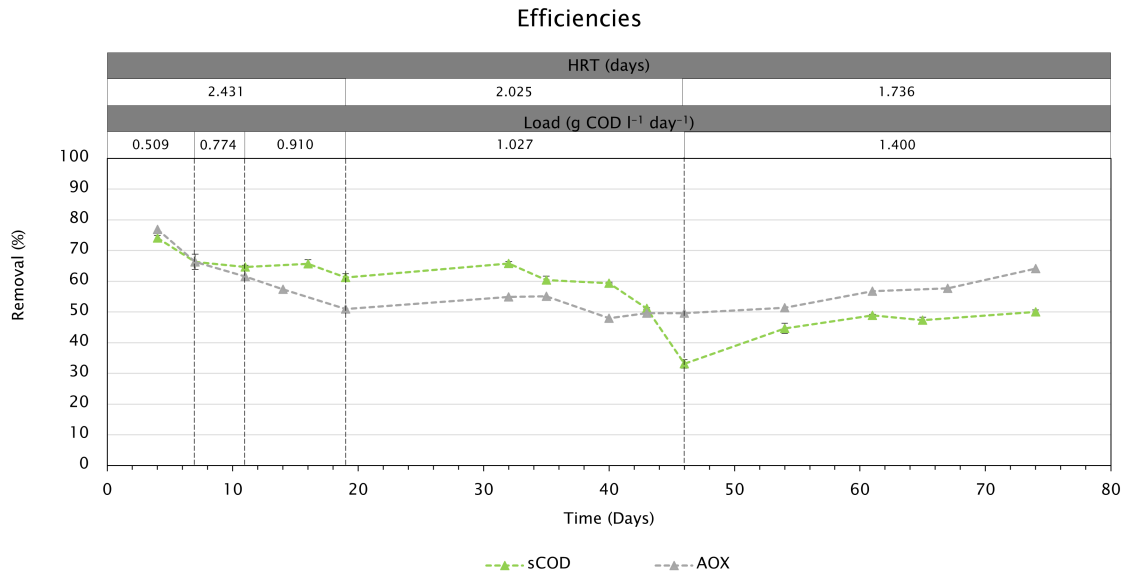


Figure 4.23: AOX and sCOD removal efficiencies at pH 6

When considering AOX removal, **Figure 4.23** shows that the reactor started with a removal efficiency of 77% of AOX. This performance decreased in the following days and, on day 19 it was at 51%. Until day 56 the removal efficiency of AOX stabilized around 50%. In the last 13 days the digester increased its performance and the run was ended with a removal efficiency of 64%. Although there was a slight drop in the AOX removal efficiency on day 36, it turns out that the AOX removal efficiency was not as severely affected as that of sCOD when the SRT was lowered (at day 32).

Contrary to what happened before, after day 48, the sCOD removal performance did not surpass AOX, and it did not even achieve a 50% removal efficiency in the rest of the operation, although it had a good response to the change of HRT and OLR done on day 48.

4.3.6 Biogas and Volatile Fatty Acids production

Due to an equipment problem, the methane percentage in the biogas was not quantified between days 34 and 56. Nonetheless, on the other days, the biogas produced did not contain methane. Therefore, **Figure 4.24** represents only the VFAs produced in this operation. The VFAs produced in the first 21 days of the run, had a concentration around $20 \text{ mg}_{\text{O}_2}/\text{l}$ (having a peak on day 9 with $77 \text{ mg}_{\text{O}_2}/\text{l}$). After the 22nd day, the VFAs production decreased and reached a historic low on day 42 (with a concentration of $5 \text{ mg}_{\text{O}_2}/\text{l}$). The concentration of these compounds increased in the following days, reaching a maximum of $76 \text{ mg}_{\text{O}_2}/\text{l}$ on day 48, although it rapidly decreased again. The run ended with an increasing trend in the last days of operation, ending at $37 \text{ mg}_{\text{O}_2}/\text{l}$.

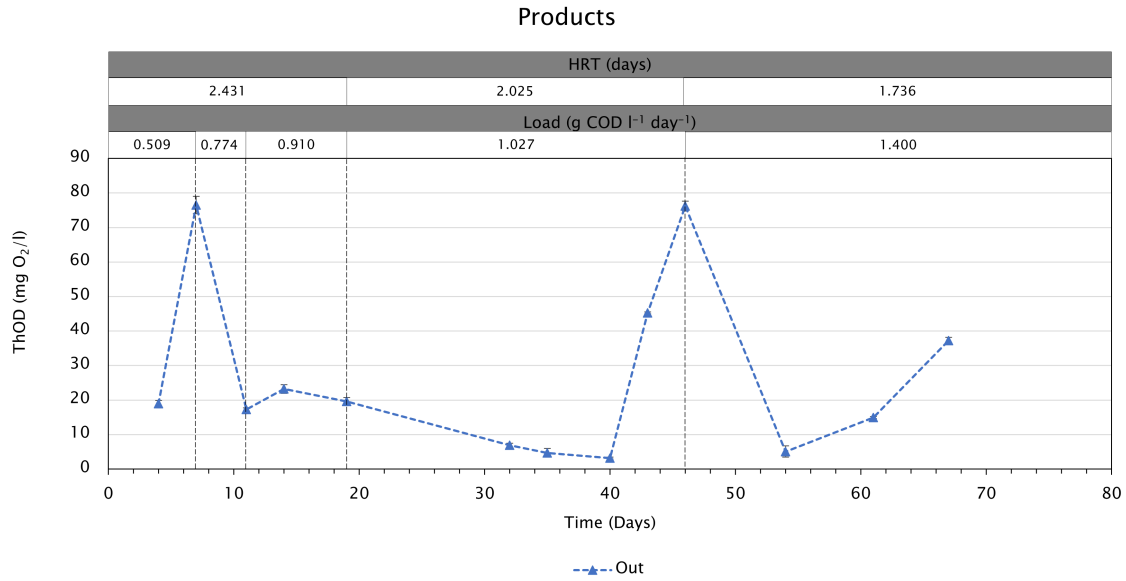


Figure 4.24: VFAs produced at pH 6

4.4 Influent pH 7

4.4.1 Operating Conditions

Like the runs done with pH 3 and pH 6, this run was also started with 3 g_{VSS}/l of anaerobic sludge. The industrial effluent (D_0) was diluted and, after the nutrients were added, it's pH was adjusted to 7 before being fed into the digester. The reactor was operated during 26 days with 3 different OLRs, and its operation was interrupted due to the low biomass inside.

As shown in **Figure 4.25**, the flow was the same throughout the reactor's operation (0.72 l/day) and therefore the HRT was also constant (2.431 $days$). The reactor was started with an OLR of 0.356 $g_{COD} l^{-1} day^{-1}$ until day 8, when it was increased to 0.533 $g_{COD} l^{-1} day^{-1}$. The load was raised to 0.614 $g_{COD} l^{-1} day^{-1}$ on the 13th day, where remained until the end of the run.

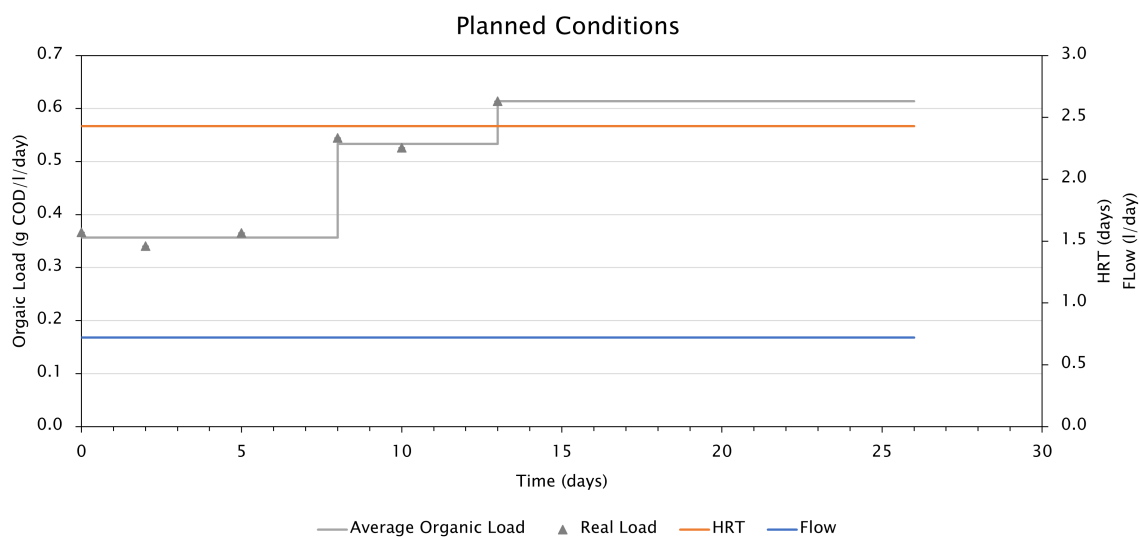


Figure 4.25: Operating conditions at pH 7

4.4.2 pH

Figure 4.26 shows the pH evolution of the reactor during its operation. As said in Section 4.4.1, the influent pH was adjusted to 7 before feeding, which is clear in Figure 4.26, though having its minimum pH in the 1st day of operation (6.65). When considering the treated effluent's pH, the graph shows that on day 2, the pH was around 8. The effluent's pH on the 5th and 8th dropped, but rapidly returned to range 8.

The pH of the sludge and reactor was also analyzed. The sludge's pH was 7.06 and 7.22 on day 13 and day 26, respectively and at the end of the run (day 26), the reactor had a pH of 7.5.

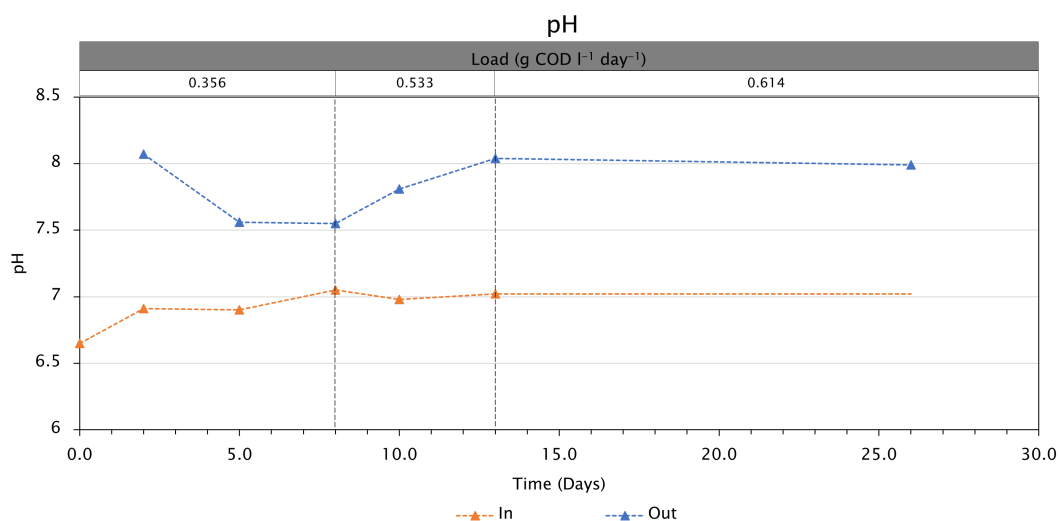


Figure 4.26: pH evolution at pH 7

4.4.3 Chemical Oxygen Demand

As shown in **Figure 4.27**, the reactor was started with a sCOD concentration of around 0.9 gCOD/l and after 8 days of operation it was changed to 1.3 gCOD/l . The reactor continued to operate in this range of values until day 13, when it was changed to 1.5 gCOD/l .

When considering the treated effluent sCOD concentration, on the 2nd day it was 0.317 gCOD/l . The concentration in the effluent decreased over the next two days of sampling and on day 8, it was 0.213 gCOD/l . After the increase in load, on day 8, the effluent increased its sCOD concentration as can be seen in the sample done on the 10th day, where the sCOD concentration was 0.747 gCOD/l . After this increase, the sCOD concentration decreased on day 13 to 0.581 gCOD/l and by the end of the run the concentration was almost the same (0.587 gCOD/l).

Figure 4.28 shows the sCOD removal efficiency in the different loads used, as well as the overall performance of the reactor.

As shown in **Figure 4.28**, the removal efficiency started at 73% in the first OLR used ($0.356 \text{ gCOD l}^{-1} \text{ day}^{-1}$), whereas at $0.533 \text{ gCOD l}^{-1} \text{ day}^{-1}$, the reactor had its worst performance removing only half of the influent's sCOD. At the last OLR used ($0.617 \text{ gCOD l}^{-1} \text{ day}^{-1}$), though, the efficiency removal of sCOD was of 60%. Finally, when considering the overall performance of the digester, it is possible to see in **Figure 4.28** that the reactor removed 61% (14.33 g of sCOD) of the total sCOD fed to it (23.43 g of sCOD).

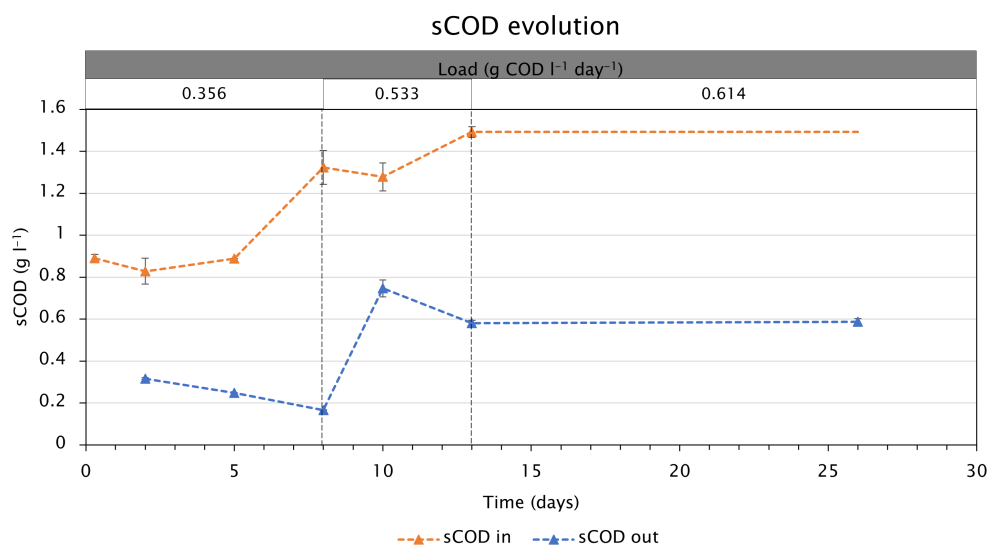


Figure 4.27: sCOD evolution at pH 7

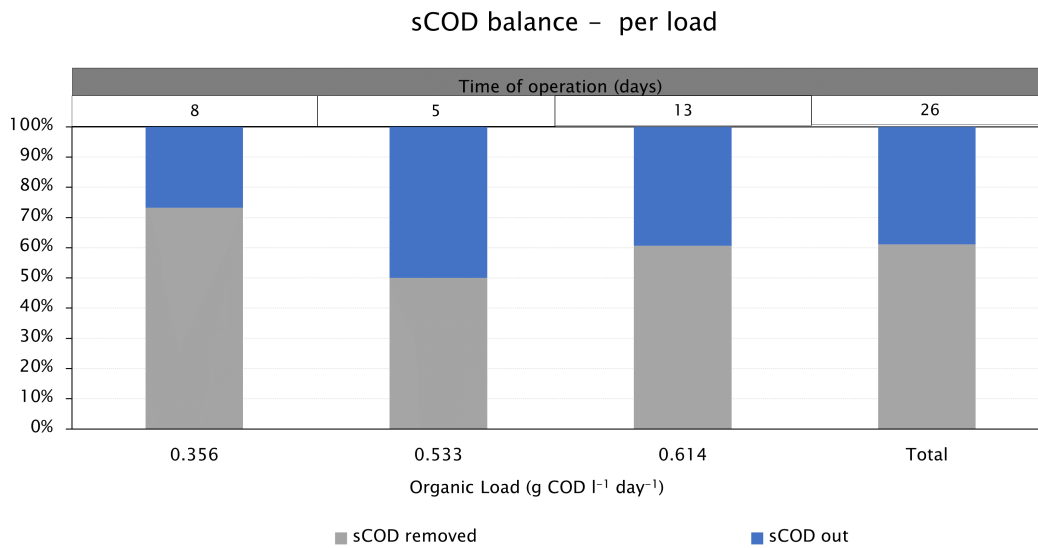


Figure 4.28: sCOD balance per load at pH 7

4.4.4 Adsorbable Organically Bound Halogens

In Figure 4.29 the AOX evolution throughout the run is represented. As shown in the graph, the influent at the beginning of the operation had a concentration around 18 mgCl/l. This concentration was kept for the next 8 days, when it was increased to around 24 mgCl/l which continued until day 13. Afterwards, the AOX concentration was changed to 30 mgCl/l.

When considering the treated effluent, Figure 4.29 shows that on day 2, it had an AOX concentration of 1.84 mgCl/l. This concentration continued to increase in the following days

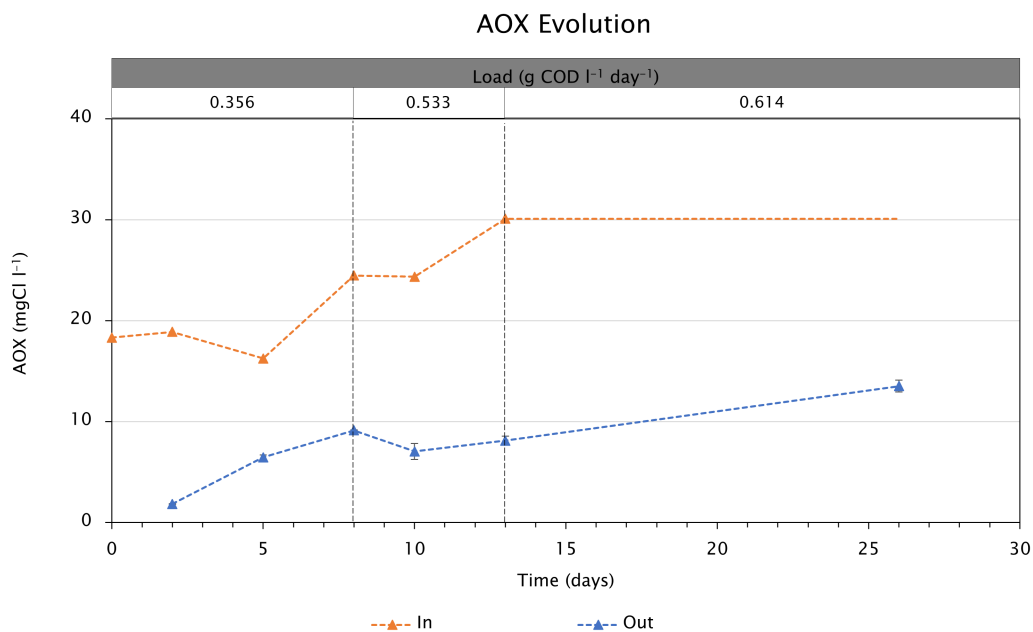


Figure 4.29: AOX evolution at pH 7

(on day 8 it was $9.13 \text{ mg}_{\text{Cl}}/\text{l}$), however, after the first increase in OLR it decreased to $7.04 \text{ mg}_{\text{Cl}}/\text{l}$. After day 10, the AOX concentration in the treated effluent continued to increase and at the end of the operation it was $13.51 \text{ mg}_{\text{Cl}}/\text{l}$.

Figure 4.30 shows the performance of the reactor at the different loads used. The graph shows that, in the first pair of OLRs used ($0.356 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$ and $0.533 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$), the digester had a similar performance, removing 64% and 68%, respectively, of the AOX present in the influent. In the third load used, $0.614 \text{ g}_{\text{COD}} \text{ l}^{-1} \text{ day}^{-1}$, the removal efficiency of AOX from the influent was of 55%. Overall, of the $471.89 \text{ mg}_{\text{Cl}}$ fed to the reactor, only $190.51 \text{ mg}_{\text{Cl}}$ were not removed, which means that, the reactor removed 60% of the AOX fed.

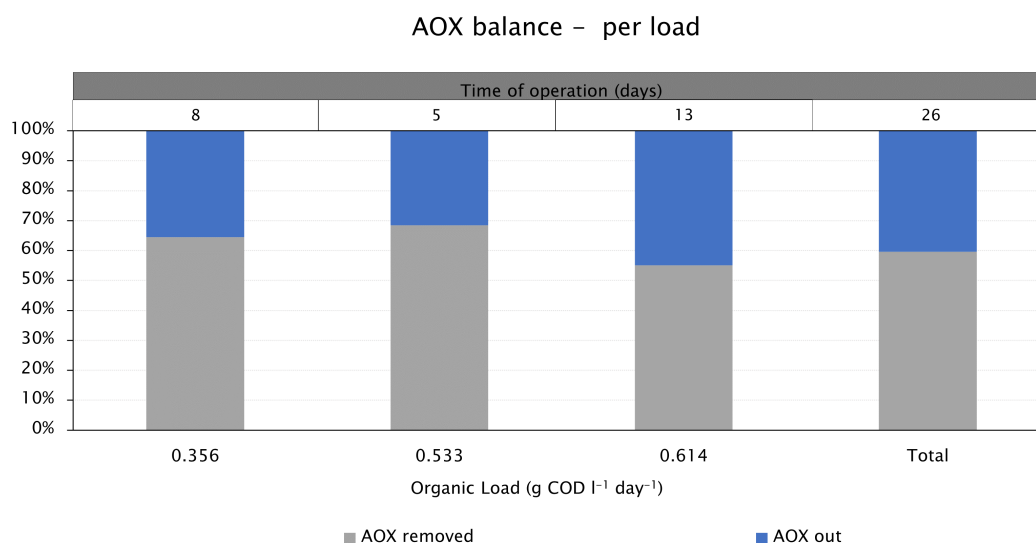


Figure 4.30: AOX balance per load at pH 7

4.4.5 Efficiencies

Figure 4.31 represents the removal efficiency of sCOD and AOX. On day 2, the removal efficiency of the first one was 64%. This efficiency increased in the next days and on day 8 it was at 81%. When the load was increased, the removal efficiency decreased by almost half (44%) the value of the 8th day, but increased again in the following days. On the last day of operation (day 27) the removal efficiency of sCOD was 61%.

When looking at the removal efficiency of AOX, **Figure 4.31** shows that on the 2nd day of operation, the reactor had a removal efficiency of AOX of 90%. The efficiency latter dropped and on day 8 it was 44%. On day 10, however, the performance of the reactor improved and the removal of AOX was 71% before dropping again, finishing the run with a removal efficiency of 55%.

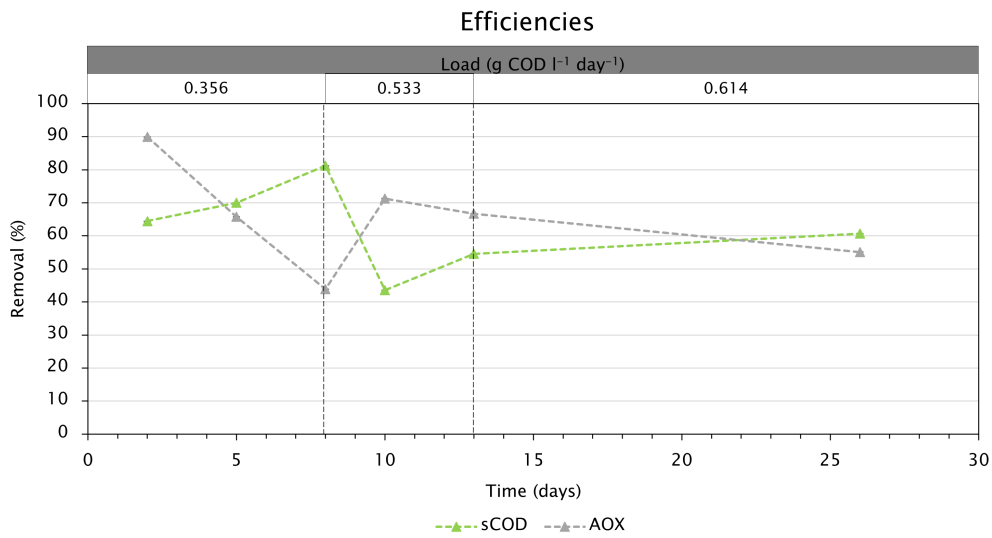


Figure 4.31: AOX and sCOD removal efficiencies at pH 7

4.4.6 Biogas and Volatile Fatty Acids production

In this operation, there was no methane in the biogas. Again, the products presented in Figure 4.32 only show the production of VFAs in this run. The concentration of these compounds started at $49 \text{ mg}_{\text{O}_2}/\text{l}$ and on the next sampling day was already at $112 \text{ mg}_{\text{O}_2}/\text{l}$. Although it dropped on days 8 and 10 to around $30 \text{ mg}_{\text{O}_2}/\text{l}$, it later increased again to $114 \text{ mg}_{\text{O}_2}/\text{l}$ on day 13 and the run ended around the same amount.

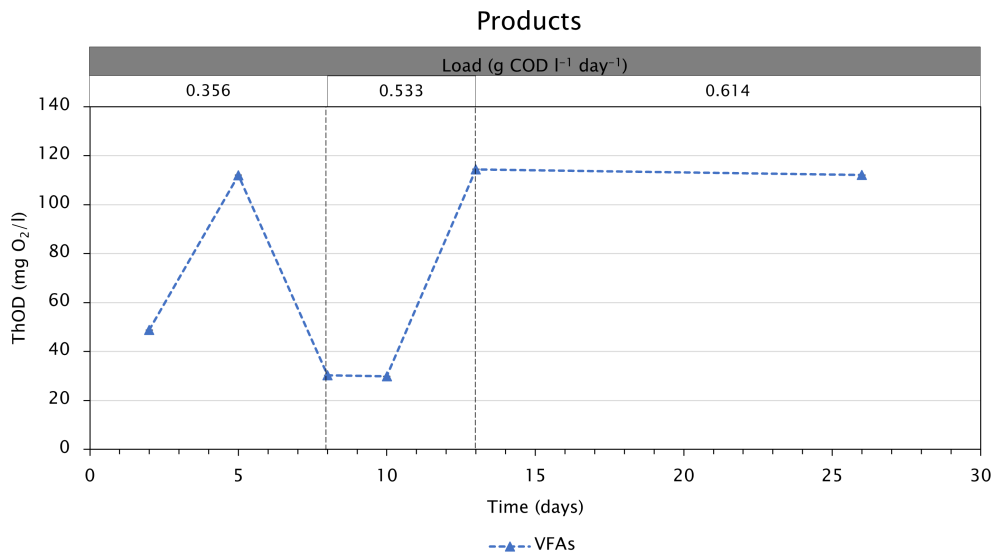


Figure 4.32: VFAs produced at pH 7

4.5 Comparisons between runs

Figure 4.33 shows the sCOD removal for all organic loads tested at different feed pH conditions.

The graph shows that operations at pH 3 and pH 7 were carried out with lower organic loads, while those carried out at pH 4 and pH 7 were higher. **Figure 4.33** also reveals that, for higher OLRs the removal efficiency of sCOD was more constant, even when decreases were made in the HRTs of the reactors, as occurred at pH 6. The same was not true for the lower organic loads, such as the occurred when the HRT in the case of pH 3 was reduced, where the removal of sCOD was greatly affected.

Because of this, the reactors fed with diluted D_0 effluent and adjusted to pH 4 and pH 6 had a more regular and higher sCOD removal efficiency than the other two, with the feed adjusted to pH 3 and 7. In conclusion, it is considered that the operation with a feed using diluted D_0 effluent and adjusted to pH 4 allows obtaining sCOD removal efficiencies between 50% and 60% at higher loads (0.6 to 1.2 $g_{COD} l^{-1} day^{-1}$) and lower HRT (1.5 days), which leads to having smaller reactors, with the consequent financial and energy savings.

Figure 4.34 shows the AOX removal in the different operations (different feed pH) and for all organic loads tested.

Figure 4.34 shows that the variation in the removal of AOX was not as small at higher organic loads as that observed for sCOD removal, even in cases where there was no change

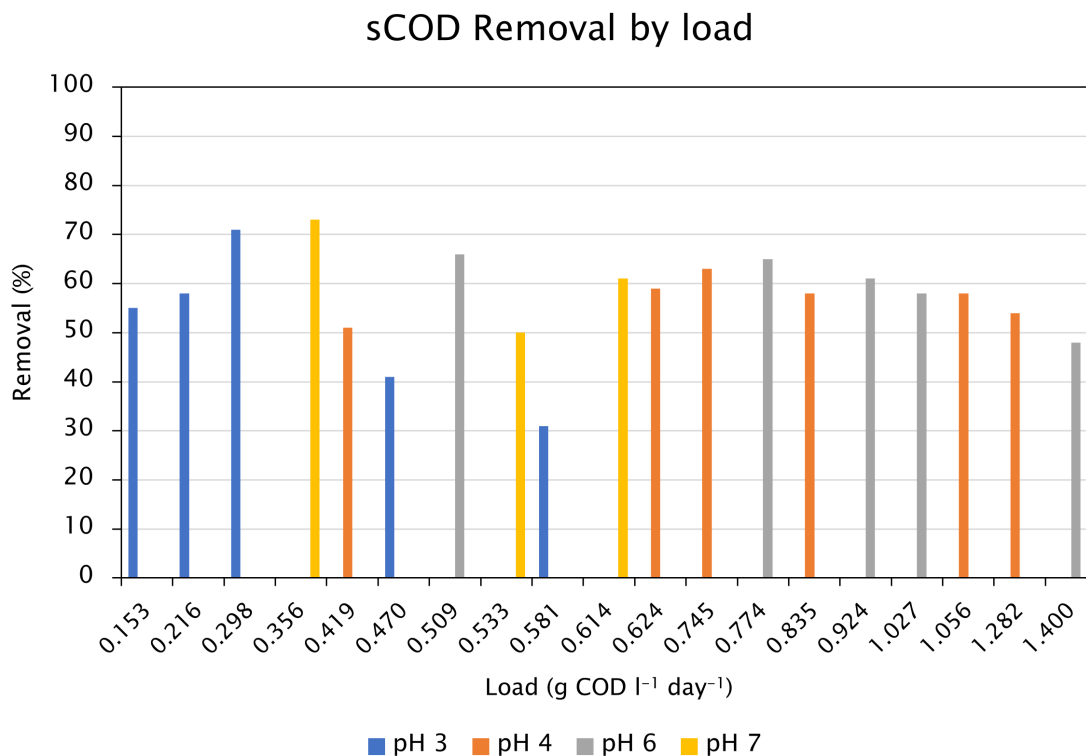


Figure 4.33: sCOD removal in the different loads used

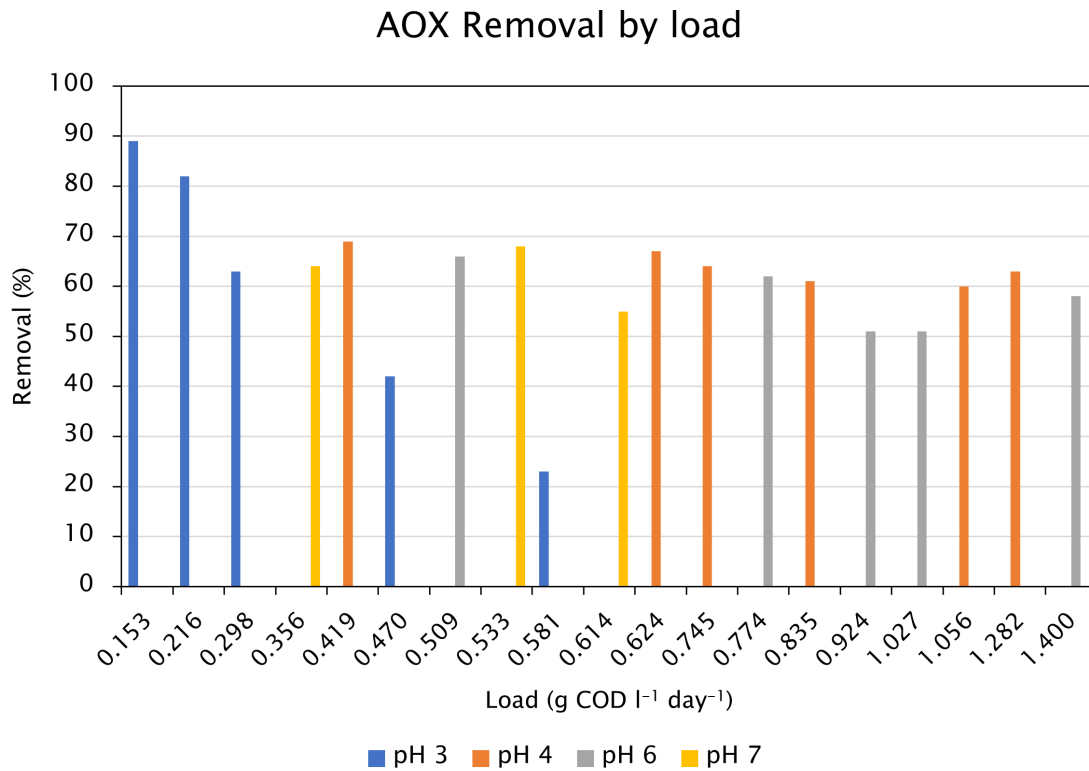


Figure 4.34: AOX removal in the different loads used

in HRT. However, the study carried out at pH 4 had the most regular removal efficiency of all the operations carried out, with a variation of less than 10%, even having operated at lower HRT values (1.461 *days*). The effect of HRT reduction on AOX removal observed at pH 3 was even more drastic than that seen for sCOD removal. In conclusion, it is considered that the operation with a feed using diluted D_0 effluent and adjusted to pH 4 also allows to obtain a slightly higher AOX removal efficiencies than for sCOD, between 60% and 65%, at higher loads (0.6 to 1.2 $g_{COD} l^{-1} day^{-1}$) and lower HRT (1.5 *days*), which also leads to having smaller reactors, with the consequent financial and energy savings.

In **Table 4.1**, a summary of the four runs tested is shown. As stated earlier, in the tests with pH 3 and pH 7 lower organic loads were applied. These tests were also done with higher HRTs and the reactors were operated for a shorter period of time. Tests at pH 4 and pH 6, on the other hand, had lower HRTs and higher applied organic loads. Both reactors were operated for longer periods of time.

The overall sCOD and AOX removal efficiencies were obtained considering all material flows entering and leaving the reactor during the entire operating period of a given reactor. The overall efficiencies of sCOD and AOX removal, regardless of the operating conditions considered, were always similar to each other. The operation performed with feed adjusted to pH 4 had the highest removal efficiency of AOX of all other operational conditions performed. On the other hand, looking at the removal efficiency of sCOD, the operation carried out with the feed adjusted to pH 7 showed the best removal efficiency. The operation carried out at

Table 4.1: Overall performance of the four operations

Run	Load (gCOD/l/day)	HRT (days)	Operation Time (days)	Overall Removal (%)	
				sCOD	AOX
pH 3	0.153~0.581	6.076~3.739	43	47	49
pH 4	0.419~1.282	1.461	60	58	63
pH 6	0.509~1.400	2.431~1.736	74	54	55
pH 7	0.356~0.614	2.431	27	61	60

pH 3 had the worst performance in terms of both sCOD and AOX removal.

In conclusion, considering the global operation in each operating condition, it appears that, depending on the treatment objective (either of sCOD or AOX removal), the choice of operating conditions can be different. However, considering that the biggest problem in the treatment of chlorine bleaching effluents from kraft pulp mills is the presence of recalcitrant and potentially toxic compounds such as AOX, the chosen condition is that of a feed adjusted to pH 4. Under these conditions, adequate AOX and sCOD removal efficiencies (approximately 60%) are obtained and smaller amounts of chemicals to adjust the pH of the feed are used.

In **Figure 4.35** is presented the BOD evolution of all operations performed.

As shown in **Figure 4.35**, in all runs, the Soluble Biochemical Oxygen Demand (sBOD) of D_0 (blue lines) was decreased after treatment (other color lines). The ultimate BOD of the treated effluent from the operations carried out at pH 3, pH 4 and pH 7 were very close to each other (around $225 \text{ mgO}_2/l$), while the effluent treated anaerobically at pH 6 had a concentration slightly higher of $276 \text{ mgO}_2/l$.

The ultimate BOD was used to calculate the aerobic biodegradability of the treated effluent. Biodegradability is given by the ratio of sBOD and sCOD concentrations.

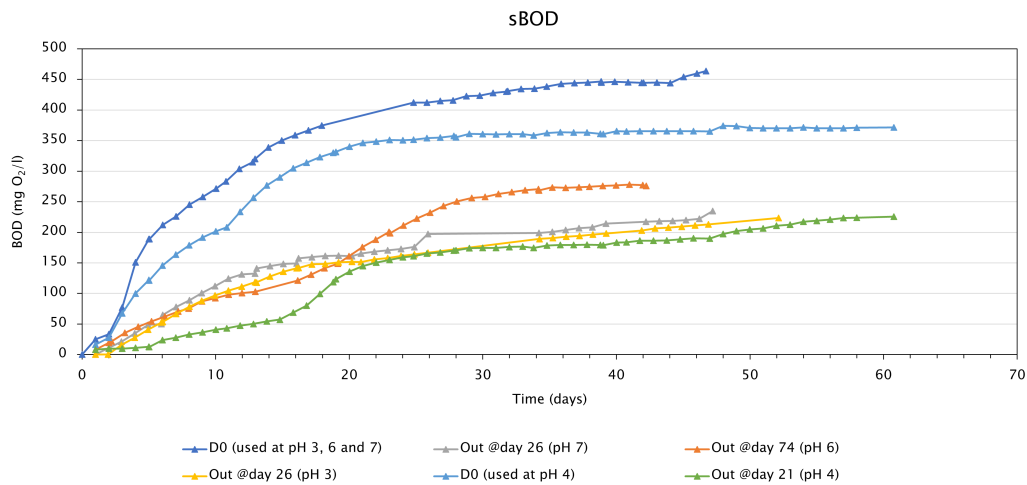


Figure 4.35: sBOD evolution of all operations

The biodegradability results are presented in **Table 4.2**. As shown in **Table 4.2**, the biodegradability of the bleaching effluent (D_0) increased with each operation performed. Operating at pH 4 had the best improvement of the four conditions tested (4.5 times increase), while operating at pH 6 increased biodegradability by only 1.3 times. Operating at pH 3 or pH 7 had an increased biodegradability of 2.2 - 2.3 times.

When looking at which operation is best suited to treat the bleaching effluent from the Kraft pulp production process, some priorities need to be defined. In this case, and since the AD treatment would be followed by an aerobic digestion treatment (activated sludge), the main evaluation parameter considered was the removal of AOX. As shown in **Table 4.1**, the best removal efficiency of these contaminants was achieved at pH 4.

Nonetheless, operating at pH 4 seems to be the best pH range to treat this type of effluent (bleaching effluent from a kraft pulping industry), as it was also able to produce methane more consistently. Operating at this pH, also allows for higher OLRs and lower HRTs applied to the anaerobic reactors. This means that smaller reactors can be used at this operational condition (feeding pH at 4). Operating in this range also proved capable of producing the most biodegradable treated effluent with a neutral pH to be fed to the activated sludge process. It also requires less amount of NaOH (alkaline compound) to set the effluent's pH to the desired value, leading to lower operating costs.

Table 4.2: Biodegradability gained in the different runs

Run		Biodegradability (g sBOD/g sCOD)
pH 3	D0	0.180
	Out @ day 26	0.421
pH 4	D0	0.141
	Out @ day 21	0.633
pH 6	D0	0.180
	Out @ day 74	0.231
pH 7	D0	0.180
	Out @ day 26	0.400

Conclusions and Recommendations

The main objective of this study was to study the acidogenic and methanogenic anaerobic processes applied to an industrial effluent with low biodegradability and with potentially inhibitory compounds for the production of materials, such as VFAs, and energy (methane), respectively. The effluent under study was the bleaching effluent from the Kraft pulp production process, denominated D_0 , which contains, among other recalcitrant materials, AOX compounds.

D_0 is a very acidic effluent with low solids content and high concentration of AOX (between 40 - 50 mg_{Cl}/l). This effluent also has a low biodegradability (under 0.2) and COD concentrations of around 2.5 g_{COD}/l .

Four reactors with different operational conditions were carried out to study the methanogenic and acidogenic processes applied to this type of effluents. The main difference of the reactors operations was the adjusted pH of the influent: pH 3, pH 4, pH 6 and pH 7. The pH adjustment of the feed was carried out, not only because this parameter is crucial in anaerobic processes, but also because in this specific case the possibility of adding less alkalinizing compounds to raise the pH of the effluent should be considered. All reactors were operated with a successive increase in the organic load obtained by increasing the concentration of COD and AOX (lower dilution of D_0) or increasing the flow rate.

The first reactor (influent pH 3), the operation with the lowest NaOH addition, was operated for 43 days, and applied five low OLRs between 0.153 $g_{COD} l^{-1} day^{-1}$ and 0.581 $g_{COD} l^{-1} day^{-1}$ and two high HRTs of 6.076 *days* and 3.739 *days* (the highest of all operations). This run had sCOD and AOX global removal efficiencies below 50% (47% and 49%, respectively). It was unable to produce methane and the VFAs produced were low. In this operation, the reduction of HRT by half had a drastic effect on the pH of the treated effluent, which decreased a lot, which was reflected in the low removal efficiency of sCOD and AOX under these conditions.

The reactor with an influent at pH 4 was operated for 60 days with a constant HRT of 1.461 *days* (the lowest of all operations) and with six different organic loads, varying from 0.419

$g_{COD} l^{-1} day^{-1}$ to $1.282 g_{COD} l^{-1} day^{-1}$. This operation had the best removal efficiency of AOX (63%) and the second best removal efficiency of sCOD (58%). This reactor had the most constant behaviour of the four, performing similarly across all 6 OLRs. It was also the only reactor to consistently produce methane (percentage in biogas greater than 50%), given the problems with the biogas measuring equipment, it was not possible to determine the biogas production. As for the production of VFAs, this analysis was only carried out 7 times, and only at the beginning, so their values were very low, thus not being representative of the entire period of operation.

The third reactor operated at an influent pH of 6 for 74 days. This run had 3 increasing flow rates, corresponding to HRTs between 2.431 *days* and 1.736 *days* and 5 organic loads in total comprehended between $0.509 g_{COD} l^{-1} day^{-1}$ and $1.400 g_{COD} l^{-1} day^{-1}$. This run removed 54% and 55% of the sCOD and AOX, respectively, of the total fed to the reactor. The changes in HRT in this operation affected sCOD removal efficiency more than AOX removal efficiency. As for products, this reactor did not produce any methane and the VFAs produced were very low during most of the run.

In the last run, an influent with a neutral pH (7) was used for 27 days with a constant HRT of 2.431 *days* and 3 increasing OLRs between $0.356 g_{COD} l^{-1} day^{-1}$ and $0.614 g_{COD} l^{-1} day^{-1}$. In this run, the best overall removal efficiency of sCOD, 61%, was achieved, although it varies greatly across the loads tested. AOX removal was not as influenced by changes in organic load having achieved an overall removal efficiency of 60%. This reactor did not produce methane, although it produced VFAs above $100 mg_{O_2}/l$.

Under all operating conditions, the sBOD concentration of the treated effluent significantly decreased as expected after a biological treatment process. However, and most importantly, the aerobic biodegradability of the treated effluent has increased, which is an advantage when this effluent is fed to an activated sludge system (aerobic biological process existing in most waste water treatment plants). The highest improvement in aerobic biodegradability of the four conditions tested was achieved in the operation at pH 4 (4.5 times increase). The operation carried out at influent pH 6 provided the smallest increase in the aerobic biodegradability of the treated effluent, in just 1.3 times. The operation at influent pH 3 or pH 7 had an intermediate increased biodegradability of 2.2 – 2.3 times.

For all of the above, the best value for the feed pH to carry out the AD for the treatment of this type of effluent (D_0) is 4, as it removes more AOX and produces methane more consistently. Operating at this pH in feed also allows for higher organic loads ($0.8 - 1.2 g_{COD} l^{-1} day^{-1}$) and lower HRTs (1.5 *days*). Under these conditions, the effluent produced has a pH of 7 and needs less NaOH to adjust the influent pH to the desired value (when compared to the tests at pH 6 and pH 7).

Further studies with an influent with pH 4 should be carried out to evaluate whether the HRT can be lowered. It should also be studied whether the reactor can achieve higher efficiencies with other organic loads and others HRTs. It would also be beneficial to further study the operation at pH 3 in the feed, once this run failed when the HRT was halved.

References

- Abbasi T. and Abbasi S. (2011). Renewable energy sources: Their impact on global warming and pollution. PHI Learning Pvt. Ltd.
- Abbasi T. and Abbasi S. (2012). Formation and impact of granules in fostering clean energy production and wastewater treatment in upflow anaerobic sludge blanket (uasb) reactors. *Renewable and Sustainable Energy Reviews*, 16(3):1696–1708.
- Abbasi T., Tauseef S. and Abbasi S. (2012). Anaerobic digestion for global warming control and energy generation—an overview. *Renewable and Sustainable Energy Reviews*, 16(5):3228–3242.
- Ahn J.H. and Forster C. (2002). A comparison of mesophilic and thermophilic anaerobic upflow filters treating paper–pulp–liquors. *Process Biochemistry*, 38(2):256–261.
- Akunna J.C. (2018). Anaerobic waste-wastewater treatment and biogas plants: a practical handbook. CRC Press.
- Appels L., Baeyens J., Degrève J. and Dewil R. (2008). Principles and potential of the anaerobic digestion of waste-activated sludge. *Progress in energy and combustion science*, 34(6):755–781.
- Aquino S.F. and Stuckey D.C. (2008). Integrated model of the production of soluble microbial products (smp) and extracellular polymeric substances (eps) in anaerobic chemostats during transient conditions. *Biochemical Engineering Journal*, 38(2):138–146.
- Asumadu-Sarkodie S. and Owusu P.A. (2016). Feasibility of biomass heating system in middle east technical university, northern cyprus campus. *Cogent Engineering*, 3(1):1134304.
- Balat M. (2005). Usage of energy sources and environmental problems. *Energy exploration & exploitation*, 23(2):141–167.
- Barber W.P. and Stuckey D.C. (1999). The use of the anaerobic baffled reactor (abr) for wastewater treatment: a review. *Water Research*, 33(7):1559–1578.
- Bodkhe S. (2008). Development of an improved anaerobic filter for municipal wastewater treatment. *Bioresource technology*, 99(1):222–226.
- Boe K. and Angelidaki I. (2009). Serial cstr digester configuration for improving biogas production from manure. *Water research*, 43(1):166–172.
- Bolzonella D., Cavinato C., Fatone F., Pavan P. and Cecchi F. (2012). High rate mesophilic, thermophilic, and temperature phased anaerobic digestion of waste activated sludge: a pilot scale study. *Waste management*, 32(6):1196–1201.
- Bowen E.J., Dolfing J., Davenport R.J., Read F.L. and Curtis T.P. (2014). Low-temperature limitation of bioreactor sludge in anaerobic treatment of domestic wastewater. *Water Science and Technology*, 69(5):1004–1013.
- Braguglia C.M., Gallipoli A., Gianico A. and Pagliaccia P. (2017). Anaerobic bioconversion of food waste into energy: A critical review. *Bioresource technology*, 248(Pt A):37–56.
- Chakar F.S. and Ragauskas A.J. (2004). Review of current and future softwood kraft lignin process chemistry. *Industrial Crops and Products*, 20(2):131–141.
- Chelliapan S., Mahat S.B., Din M.F.M., Yuzir A. and Othman N. (2012). Anaerobic digestion of paper mill wastewater. *Iran. J. Energy Environ*, 3:85–90.

- Chen L. and Neibling H. (2014). Anaerobic digestion basics. University of Idaho Extension CIS, 1215.
- Chen Y., Cheng J.J. and Creamer K.S. (2008). Inhibition of anaerobic digestion process: a review. *Bioresource technology*, 99(10):4044–4064.
- de Lemos Chernicharo C.A. (2007). Anaerobic reactors. IWA publishing.
- De Mes T., Stams A., Reith J. and Zeeman G. (2003). Methane production by anaerobic digestion of wastewater and solid wastes. *Bio-methane & Bio-hydrogen*, 58–102.
- Demirbas M.F. and Balat M. (2009). Progress and recent trends in biogas processing. *International Journal of Green Energy*, 6(2):117–142.
- Ekstrand E.M., Hedenström M., Svensson B.H., Yekta S.S. and Björn A. (2020). Methane potentials and organic matter characterization of wood fibres from pulp and paper mills: The influence of raw material, pulping process and bleaching technique. *Biomass and Bioenergy*, 143:105824.
- El-Hadj T.B., Dosta J., Torres R. and Mata-Alvarez J. (2007). Pcb and aox removal in mesophilic and thermophilic sewage sludge digestion. *Biochemical Engineering Journal*, 36(3):281–287.
- Federation W.E., Association A.P.H. et al. (2005). Standard methods for the examination of water and wastewater. American Public Health Association (APHA): Washington, DC, USA.
- Ferguson J.F. (1994). Anaerobic and aerobic treatment for aox removal. *Water Science and Technology*, 29(5-6):149–162.
- Habets L. and Driessen W. (2007). Anaerobic treatment of pulp and paper mill effluents—status quo and new developments. *Water Science and Technology*, 55(6):223–230.
- Habets L., Engelaar A. and Groeneveld N. (1997). Anaerobic treatment of inuline effluent in an internal circulation reactor. *Water Science and Technology*, 35(10):189–197.
- Hakulinen R. et al. (1982). Treatment of pulp and paper industry wastewaters in an anaerobic fluidised bed reactor.
- Hansen K.H., Angelidaki I. and Ahring B.K. (1998). Anaerobic digestion of swine manure: inhibition by ammonia. *Water research*, 32(1):5–12.
- Hill D. and Bolte J. (1989). Digester stress as related to iso-butyric and iso-valeric acids. *Biological Wastes*, 28(1):33–37.
- Hwang M.H., Jang N.J., Hyun S.H. and Kim I.S. (2004). Anaerobic bio-hydrogen production from ethanol fermentation: the role of ph. *Journal of Biotechnology*, 111(3):297–309.
- Jeison D. and Chamy R. (1999). Comparison of the behaviour of expanded granular sludge bed (egsb) and upflow anaerobic sludge blanket (uasb) reactors in dilute and concentrated wastewater treatment. *Water Science and Technology*, 40(8):91–97.
- Kallas J. and Munter R. (1994). Post-treatment of pulp and paper industry wastewaters using oxidation and adsorption processes. *Water Science and Technology*, 29(5-6):259–272.
- Kamali M., Gameiro T., Costa M.E.V. and Capela I. (2016). Anaerobic digestion of pulp and paper mill wastes—an overview of the developments and improvement opportunities. *Chemical Engineering Journal*, 298:162–182.
- Kayhanian M. (1994). Performance of a high-solids anaerobic digestion process under various ammonia concentrations. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental AND Clean Technology*, 59(4):349–352.
- Kelleher B., Leahy J., Henihan A., O’dwyer T., Sutton D. and Leahy M. (2002). Advances in poultry litter disposal technology—a review. *Bioresource technology*, 83(1):27–36.
- Kim J., Park C., Kim T.H., Lee M., Kim S., Kim S.W. and Lee J. (2003). Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. *Journal of bioscience and bioengineering*, 95(3):271–275.

- Larsson M., Truong X.B., Björn A., Ejlertsson J., Bastviken D., Svensson B.H. and Karlsson A. (2015). Anaerobic digestion of alkaline bleaching wastewater from a kraft pulp and paper mill using uasb technique. *Environmental technology*, 36(12):1489–1498.
- Lee D.H., Behera S.K., Kim J.W. and Park H.S. (2009). Methane production potential of leachate generated from Korean food waste recycling facilities: a lab-scale study. *Waste Management*, 29(2):876–882.
- Lesteur M., Bellon-Maurel V., Gonzalez C., Latrille E., Roger J., Junqua G. and Steyer J.P. (2010). Alternative methods for determining anaerobic biodegradability: a review. *Process biochemistry*, 45(4):431–440.
- Lettinga G., Field J., Van Lier J., Zeeman G. and Pol L.H. (1997). Advanced anaerobic wastewater treatment in the near future. *Water Science and Technology*, 35(10):5–12.
- Li Y.Y. and Noike T. (1992). Upgrading of anaerobic digestion of waste activated sludge by thermal pretreatment. *Water Science and Technology*, 26(3-4):857–866.
- Mao C., Feng Y., Wang X. and Ren G. (2015). Review on research achievements of biogas from anaerobic digestion. *Renewable and sustainable energy reviews*, 45:540–555.
- Mata-Alvarez J. (2003). Fundamentals of the anaerobic digestion process. *Biomethanization of the organic fraction of municipal solid wastes*, 1–20.
- Mateos-Espejel E., Savulescu L., Maréchal F. and Paris J. (2010). Systems interactions analysis for the energy efficiency improvement of a kraft process. *Energy*, 35(12):5132–5142.
- Mechichi T. and Sayadi S. (2005). Evaluating process imbalance of anaerobic digestion of olive mill wastewaters. *Process Biochemistry*, 40(1):139–145.
- Meyer T. and Edwards E.A. (2014). Anaerobic digestion of pulp and paper mill wastewater and sludge. *Water research*, 65:321–349.
- Müller G. (2003). Sense or no-sense of the sum parameter for water soluble “adsorbable organic halogens” (aox) and “absorbed organic halogens”(aox-s18) for the assessment of organohalogenes in sludges and sediments. *Chemosphere*, 52(2):371–379.
- Nagarathnamma R., Bajpai P. and Bajpai P.K. (1999). Studies on decolourization, degradation and detoxification of chlorinated lignin compounds in kraft bleaching effluents by *Ceriporiopsis subvermispora*. *Process Biochemistry*, 34(9):939–948.
- Owusu P.A. and Asumadu-Sarkodie S. (2016). A review of renewable energy sources, sustainability issues and climate change mitigation. *Cogent Engineering*, 3(1):1167990.
- Palmisano A.C. and Barlaz M.A. (1996). *Microbiology of solid waste*, Vol. 3. CRC press.
- Pavlostathis S.G. and Giraldo-Gomez E. (1991). Kinetics of anaerobic treatment. *Water science and Technology*, 24(8):35–59.
- Rintala J.A. and Puhakka J.A. (1994). Anaerobic treatment in pulp-and paper-mill waste management: a review. *Bioresource technology*, 47(1):1–18.
- Salkinoja-Salonen M., Uotila J., Jokela J., Laine M. and Sasaki E. (1995). Organic halogens in the environment: studies of environmental biodegradability and human exposure. *Environmental health perspectives*, 103(suppl 5):63–69.
- Savant D., Abdul-Rahman R. and Ranade D. (2006). Anaerobic degradation of adsorbable organic halides (aox) from pulp and paper industry wastewater. *Bioresource Technology*, 97(9):1092–1104.
- Şentürk E., İnce M. and Engin G.O. (2010). Kinetic evaluation and performance of a mesophilic anaerobic contact reactor treating medium-strength food-processing wastewater. *Bioresource technology*, 101(11):3970–3977.
- Şentürk E., İnce M. and Engin G.O. (2013). The effect of transient loading on the performance of a mesophilic anaerobic contact reactor at constant feed strength. *Journal of biotechnology*, 164(2):232–237.
- Smook G.A., Kocurek M.J. et al. (1982). *Handbook for pulp & paper technologists*. Canadian Pulp and Paper Association.

- Switzenbaum M. (1983). A comparison of the anaerobic filter and the anaerobic expanded/fluidized bed processes. *Water Science and Technology*, 15(8-9):345–358.
- Tauseef S., Abbasi T. and Abbasi S. (2013). Energy recovery from wastewaters with high-rate anaerobic digesters. *Renewable and Sustainable Energy Reviews*, 19:704–741.
- Thompson G., Swain J., Kay M. and Forster C. (2001). The treatment of pulp and paper mill effluent: a review. *Bioresource technology*, 77(3):275–286.
- Tran H. and Vakkilainen E.K. (2008). The kraft chemical recovery process. *Tappi Kraft Pulping Short Course*, 1–8.
- Turovskiy I.S. and Mathai P. (2006). *Wastewater sludge processing*. John Wiley & Sons.
- Vidal G., Soto M., Field J., Méndez-Pampín R. and Lema J. (1997). Anaerobic biodegradability and toxicity of wastewaters from chlorine and total chlorine-free bleaching of eucalyptus kraft pulps. *Water Research*, 31(10):2487–2494.
- Vidal G., Videla S. and Diez M. (2001). Molecular weight distribution of pinus radiata kraft mill wastewater treated by anaerobic digestion. *Bioresource technology*, 77(2):183–191.
- Wang Q., Kuninobu M., Ogawa H.I. and Kato Y. (1999). Degradation of volatile fatty acids in highly efficient anaerobic digestion. *Biomass and Bioenergy*, 16(6):407–416.
- Wang Z. and Banks C. (2000). Accelerated hydrolysis and acidification of municipal solid waste (msw) in a flushing anaerobic bio-reactor using treated leachate recirculation. *Waste Management and Research*, 18(3):215–223.
- Wilkinson K.G. (2011). A comparison of the drivers influencing adoption of on-farm anaerobic digestion in germany and australia. *Biomass and bioenergy*, 35(5):1613–1622.
- Yenigün O. and Demirel B. (2013). Ammonia inhibition in anaerobic digestion: a review. *Process Biochemistry*, 48(5-6):901–911.
- Yu P. and Welander T. (1996). Toxicity of kraft bleaching plant effluent to aceticlastic methanogens. *Journal of fermentation and bioengineering*, 82(3):286–290.
- Zaiat M., Rodrigues J., Ratusznei S., De Camargo E. and Borzani W. (2001). Anaerobic sequencing batch reactors for wastewater treatment: a developing technology. *Applied microbiology and biotechnology*, 55(1):29–35.
- Zhang C., Su H., Baeyens J. and Tan T. (2014). Reviewing the anaerobic digestion of food waste for biogas production. *Renewable and Sustainable Energy Reviews*, 38:383–392.
- Zhang T., Liu L., Song Z., Ren G., Feng Y., Han X. and Yang G. (2013). Biogas production by co-digestion of goat manure with three crop residues. *PloS one*, 8(6):e66845.
- Zhang Z.P., Tay J.H., Show K.Y., Yan R., Liang D.T., Lee D.J. and Jiang W.J. (2007). Biohydrogen production in a granular activated carbon anaerobic fluidized bed reactor. *International Journal of Hydrogen Energy*, 32(2):185–191.
- Zhao D., Zhu Q. and Dubbeldam J. (2015). Terminal sliding mode control for continuous stirred tank reactor. *Chemical engineering research and design*, 94:266–274.

Appendices

Appendix A: Nutrient Solutions

	Compound	Concentration (g/l)
Macro-nutrients solution 1	NH_4Cl	165,77
	KH_2PO_4	36,15
Macro-nutrients solution 2	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	7,79
	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	8,79
Micro-nutrients solution	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0,9753
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0,9749
	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0,2432
	$\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$	0,0148
	ZnCl_2	0,024
	H_3BO_3	0,0257
	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	0,042
	EDTA	0,488
	$\text{NiCl} \cdot 6\text{H}_2\text{O}$	0,0243

Appendix B: Standard solutions used to obtain the calibration curves of the different VFAs analyzed

ID	Volume of stock solution (mL)	H-Ac (mg/L)	H-Prop (mg/L)	H-i-But (mg/L)	H-n-But (mg/L)	H-i-Val (mg/L)	H-n-Val (mg/L)	H-n-Cap (mg/L)
P#1	0.125	52.5	49.0	48.0	47.5	46.0	46.0	47.0
P#2	0.25	105.0	98.0	96.0	95.0	92.1	92.1	94.1
P#3	0.5	210.0	196.0	192.1	190.1	184.1	184.1	188.1
P#4	1.5	630.0	588.1	576.2	570.2	552.4	552.4	564.3
P#5	2.5	1 050.0	980.1	960.3	950.4	920.7	920.7	940.5
P#6	5	2100.0	1960.2	1920.6	1900.8	1841.4	1841.4	1881.0
P#7	7.5	3150.0	2940.3	2880.9	2851.2	2762.1	2 762.1	2 821.5
P#8	10	4200.0	3920.4	3841.2	3801.6	3682.8	3682.8	3762.0
P#9	20	8400.0	7840.8	7682.4	7603.2	7365.6	7365.6	7524.0
P#10	25	10500.0	9801.0	9603.0	9504.0	9207.0	9207.0	9405.0

**Appendix C: Theoretical oxygen demand (thOD)
for the acidic species analyzed**

VFA specie	M (g/mol)	thOD (gO ₂ /g)
H-Ac	60.05	1.066
H-Prop	74.08	1.512
H-i-But	88.11	1.816
H-n-But	88.11	1.816
H-i-Val	102.13	2.037
H-n-Val	102.13	2.037
H-n-Cap	116.16	2.204

Appendix D: Retention time and slop of calibration lines for each acidic specie

	H-Ac	H-Prop	H-i-But	H-n-But	H-i-Val	H-n-Val	H-n-Cap
Retention time (min)	2.571	3.502	4.461	5.037	6.199	7.098	9.160
m	945.4	1515.5	1683.3	1632.3	1782.3	1457.3	933.0
r²	0.9964	0.9960	0.9954	0.9917	0.9958	0.9875	0.9837