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EVALUATION OF AN ANAEROBIC MBR AS PRETREATMENT FOR A CBMEM SYSTEM FOR THE PRODUCTION AND RECOVERY OF HYDROGEN FROM WINERY WASTEWATER

MEMORIA PARA OPTAR AL TÍTULO DE INGENIERA CIVIL

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RESUMEN DE LA MEMORIA PARA OPTAR AL TÍTULO
DE: INGENIERA CIVIL
POR: MACARENA ANGÉLICA ESCUDERO JIMÉNEZ
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EVALUACION DE UN MBR ANAEROBICO COMO PRETRATAMIENTO DE UN SISTEMA CBMEM PARA LA PRODUCCION Y RECUPERACIÓN DE HIDROGENO A PARTIR DE AGUAS RESIDUALES VITIVINICOLAS

Las crecientes limitaciones de recursos han cambiado la perspectiva del enfoque de las aguas residuales; hoy en día, la provisión de tratamiento es igualmente importante que la recuperación de agua, nutrientes y energía [Veluhamy et al., 2021]. La producción de vino es una de las principales industrias de bebidas en Chile, sus aguas residuales si no son tratadas pueden generar contaminación del agua y degradación del suelo Ioannou et al., 2015]. Diversas tecnologías de tratamiento ofrecen una forma de convertir los recursos de las aguas residuales en productos comercializables. Algunos autores prefieren los métodos anaeróbicos para el tratamiento de aguas residuales y la recuperación de energía. La digestión anaeróbica combina cuatro pasos bioquímicos importantes para formar biometano o biohidrógeno. En los últimos años, el enfoque de la investigación se ha desplazado del metano al hidrógeno debido a su potencial como fuente de energía limpia inagotable, de bajo coste y renovable [Ngo et al., 2020].

El objetivo de este estudio fue modelar y simular un tren de tratamiento de aguas residuales vitinícolas y de generación de hidrógeno para implementar la tecnología de membranas bioactivas compuestas (CBMem) a escala real. La CBMem consiste en membranas de fibra hueca con bacterias acetogénicas encapsuladas; demostró ventajas en el rendimiento y la eficiencia de captura de hidrógeno [Prieto et al., 2016]. El afluente corresponde al agua residual generada en todas las etapas de la elaboración del vino y los requisitos del CBMem son una DQO soluble superior a 2000 mg/L y la eliminación de los sólidos en suspensión [Prieto et al., 2016]. El investigador realizó una revisión bibliográfica de diferentes biorreactores anaeróbicos. En resumen, un biorreactor anaeróbico de membrana (AnMBR) podría tratar las aguas residuales vitivinícolas y cumplir con las restricciones de la CBMem. Además, el autor revisó los parámetros operativos y de diseño que influyen en la producción de hidrógeno, los principales son el tiempo de retención hidráulico (HRT), el tiempo de retención de sólidos (SRT) y la tasa de carga orgánica (OLR). Los sólidos suspendidos en el licor mezclado (MLSS) influyen en el rendimiento de la membrana; por lo tanto, debe oscilar entre 10 y 20 g/L.

El autor construyó el modelo utilizando el software SIMBA, y simuló para SRT entre 2 y 15 días y para OLR en el rango de 10 a 30 kg_{COD}/m^3 - d. En resumen, el pH y el hidrógeno inhibieron totalmente los procesos de oxidación anaeróbica, y el pH inhibió parcialmente la fermentación, por lo tanto, el modelo de digestión anaeróbica describió los procesos críticos para la implementación del CBMem. Los resultados demostraron que a mayor SRT, mayor producción de hidrógeno, y que el incremento de OLR promueve el mecanismo de inhibición de la actividad metanogénica. El investigador seleccionó un SRT de 7 días y un OLR de 21 kg_{COD}/m^3-d para operar el AnMBR. Las principales ventajas de la aplicación del AnMBR en la industria vitivinícola son una eliminación del 23% de la DQO y una producción de hidrógeno de 821 m^3/d. El hidrógeno producido puede transformarse en energía, y la energía disponible podría cubrir hasta el 1,4% de la demanda de la bodega.

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EVALUATION OF AN ANAEROBIC MBR AS PRETREATMENT FOR A CBMEM SYSTEM FOR THE PRODUCTION AND RECOVERY OF HYDROGEN FROM WINERY WASTEWATER

The increasing resource limitations have changed the perspective of wastewater focus; nowadays, the provision of treatment is equally essential to the recuperation of water, nutrients, energy, and other by-products [Veluhamy et al., 2021]. Wine production is one of the leading beverage industries in Chile; its wastewater generates water pollution and soil degradation if not treated [Ioannou et al., 2015]. Various treatment technologies offer a way to convert the resources from wastewater into marketable products. Some authors prefer the anaerobic methods for wastewater treatment and energy recovery. Anaerobic digestion combines four significant biochemical steps to form biomethane or biohydrogen. Over the last years, the research focus has shifted from methane to hydrogen due to its potential as an inexhaustible, low-cost, and renewable source of clean energy [Ngo et al., 2020].

The objective of this study was to model and simulate a winery wastewater treatment and hydrogen generation train to implement full-scale composite bioactive membrane technology (CBMem). The CBMem consists of hollow fiber membranes with encapsulated acetogenic bacteria; it demonstrated advantages in yield and hydrogen capture efficiency [Prieto et al., 2016]. The influent corresponded to the wastewater generated from all the stages of the winemaking, and the CBMem requirements were a soluble COD higher than 2000 mg/L and the removal of the suspended solids [Prieto et al., 2016]. The researcher performed a literature review of different anaerobic bioreactors. In summary, an anaerobic membrane bioreactor (AnMBR) could treat winery wastewater and fulfill the CBMem restrictions. Besides, the author reviewed the operational and design parameters that influence hydrogen production. The main variables are hydraulic retention time (HRT), solids retention time (SRT), and organic loading rate (OLR). The mixed liquor suspended solids (MLSS) influence the membrane performance; therefore, it should be range between 10 and 20 g/L.

The author built the model using the SIMBA software and simulated for SRT between 2 to 15 days and for OLR in the range of 10 to 30 $\text{kg}_{\text{COD}}/\text{m}^3$–d. In summary, pH and hydrogen inhibited the anaerobic oxidation processes entirely, and pH partially inhibited the fermentation; therefore, the anaerobic digestion model described the critical processes for the CBMem implementation. A high SRT allows higher hydrogen productions; therefore, operating at a higher SRT is advisable. The OLR increment promotes the inhibitory mechanism of the methanogenic activity; therefore, it is advisable to operate at a higher OLR. The researcher selected an SRT of 7 days and an OLR of 21 *kgCOD/m*3-*d* to operate the AnMBR. The principal advantages of implementing the AnMBR in the wine production industry are 23% of COD removal and hydrogen production of 821 m3/d. The hydrogen produced could be transformed into energy, and the available energy could cover up to 1.4% of the winery demand.

A mis padres -
les dedico este trabajo por siempre apoyarme,
gracias por todos los días confiar y creer en mí y en mis expectativas.

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Chapter 1

Introduction

1.1. General context

The worldwide focus is on fulfilling the 2030 Agenda for Sustainable Development. One of the targets is sustainable management and efficient use of natural resources, mainly focusing on water, energy, and food.

Water use has been increasing worldwide by about 1% per year since the 1980s, driven by a combination of population growth, socio-economic development, and changing consumption patterns [United Nations, 2019]. Climate change and fresh and clean water scarcity have led to a crisis. By 2050, more than half of the global population (57%) will live in areas that suffer water scarcity at least one month each year [Boretti & Rosa, 2019]. This concern has highlighted the importance of water as a vital resource and the need to adopt water reuse and recycling [Zarei, 2020].

Global water use for the industry will increase from 20% to 30% by 2050, and as water consumption increases, the wastewater generation will grow as well [Boretti & Rosa, 2019]. Water fulfills several roles and functions in all industries, mainly used for fabricating, processing, washing, diluting, cooling, or transporting a product [Barber, 2009]. Almost all the water used ends up as industrial wastewater, producing 300 to 400 megatons of waste every year [Boretti & Rosa, 2019; Ranade & Bhandari, 2014]. Although most of the wastewater produced is treated before disposal to protect the environment and human health, the increasing resource limitations have changed the perspective of wastewater focus. Nowadays, wastewater is considered a potential resource, and its use or recycling after suitable treatment can provide economic and financial benefits [Veluhamy et al., 2021; United Nations, 2019].

The primary concern about energy is improving energy efficiency and moving forward to renewable energy. However, the share of renewable energy in final energy consumption has only reached 17.5% in 2015 [United Nations, 2020]. Traditional energy sources are dependent on fossil fuels such as petroleum, diesel, coal, and natural gas. Its use leads to environmental degradation and greenhouse gas emissions [Sarangi & Nanda, 2020; Wang & Ying, 2017].

Over the years, there has been significant research on renewable and eco-friendly energy sources such as solar, wind, geothermal and organic biomass. Organic waste biomass is the only source that can provide biofuels with high energy content to potentially substitute fossil fuels [Sarangi & Nanda, 2020].

Resource recovery strategy includes the provision of waste treatment and recuperation of water, nutrients, energy, and other by-products simultaneously. It has been more prominent recently, mainly because it alleviates the environmental impacts of conventional wastewater treatment and brings down the cost of treatment [Estahbanati et al., 2021]. Energy can be extracted from the organic content in wastewater by anaerobic treatment and fertilizers for sustainable agriculture from the nutrients present [Song et al., 2018]. Thus, the importance of including this strategy in the industrial operation and wastewater management.

1.2. Resource recovery from industrial effluents

Between 50 to 100% lost waste resources from wastewater [Puyol et al., 2017]. Therefore, significant drivers such as the economy, environmental expertise, and industrials are pushing to regain and recover all substances inherited in the wastewater [Veluhamy et al., 2021].

In terms of resources present in industrial wastewater, water, nitrogen, phosphorus, and carbon are the principal. Both nitrogen and phosphorus are nutrients, and their requirement has increased to fulfill the food demand. Industrial wastewater contains carbon in two different forms, organic and inorganic carbon, which is considered a way for energy generation [Estahbanati et al., 2021]. In addition, there are by-products of wastewater treatment processes, such as bio-solids and biofuels with high energy content, as biomethane and biohydrogen [Sarangi & Nanda, 2020].

For energy generation purposes, researchers have utilized organically rich industrial wastes. The most utilized are beverage and food industrial wastes, such as palm oil mill, sugar-beet processing, dairy, cassava starch, brewery, and winery wastewater. The composition and concentration of different food and beverage wastewaters vary from low-medium (dairy effluents) to high strength substrates (cheese or winery wastewaters) in terms of organic matter, proteins, and available nutrients [Rajapoal et al., 2013]. For industrial effluents, low-strength wastewaters are characterized as those with COD values less than 2,000 $[mg_{COD}/L]$ [Ergüder & Demirer, 2008].

The main parameters of industrial wastewater are total suspended solids (TSS), chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP). Table 1.1 presents reference concentration values for the beverage industry, dairy, and winery wastewater.

Table 1.1: Characteristics of industrial wastewater [Carrasco, Platzer & Teichert, 2017; Rajapoal et al., 2013; Brito et al., 2007]

	Beverage Industry	Dairy	Winery
TSS [mg/L]	330-2600	900-1400	350-4600
TP [mg/L]	62-100	-	16-68
TN [mg/L]	8-62	-	19-93
COD [mg/L]	600-3400	1400-2500	1200-10200

Wine production is one of the leading beverage industries in Chile. In 2019, the cultivated area was 137,000 hectares, in contrast, *pisco* production was 9171 hectares [SAG, 2019]. The wine industry generates large wastewater volumes, mainly from several washing operations (e.g., during the crushing and pressing of the grapes and cleaning the fermentation tanks, equipment, and surfaces) [Rajapoal et al., 2013]. Each winery is unique regarding the volume of wastewater generated (highly variable, from 0.5 to 14 L per liter of wine produced) [Ioannou et al., 2015]. For example, in Chile, the wastewater production is about 8 liters per liter of wine produced. In 2015, total wine production exceeded 128 million liters, i.e., 10.3 million m^3 of wastewater [Teichert et al., 2017].

The environmental impact of wastewater from the wine industry is diverse. It goes from water pollution, soil degradation, and vegetation damage to odors and air emissions resulting from wastewater management [Ioannou et al., 2015]. Regarding disposal practices applied, each winery is unique. For example, at Viña Concha y Toro S.A., a leading wine producer in Latin America, the wastewater treatment is established depending on the characteristics of the influent and the current discharge regulations. The leading technologies applied are mixing flow reactors for neutralization, activated sludge, and aerobic membrane reactors [Concha y Toro S.A., 2020]. Most wineries and vineyards do not consider resource recovery strategies; the water treated is discharged to surface water bodies, and the sludge produced goes to landfills [Day Ltd., 2011]. Thus, it the importance to evaluate the feasibility of resource recovery, especially energy, from winery wastewater .

Various treatment technologies offer a way to concentrate and convert the resources from waste/wastewater into marketable products, which results in technological development. The techniques for recovering value-added materials from wastewater include biological, physical, and physicochemical (e.g., coagulation-flocculation, adsorption, and flotation) processes. However, biological methods offer the most robust promise to efficiently recover valuable resources [Estahbanati et al., 2021; Puyol et al., 2017].

Biological treatments mainly aim to remove the organic material present in the wastewater. These systems use microorganisms to break down organic matter and are often used as a secondary treatment process in the sanitary industry. Depending on the microorganism's metabolism, the processes can be classified into aerobic and anaerobic [Estahbanati et al., 2021; Teichert et al., 2017].

Aerobic treatment employs oxygen and other nutrients like nitrogen and phosphorus to assimilate organic matter, and it is the most widely used due to its effectiveness and ease of operation. However, it produces large amounts of bio-solid and requires energy to maintain optimal aerobic conditions (between 45 and 75% of the plant energy expenditure) [Robles et al., 2018; Longo et al., 2016]. There are different configurations for resource recovery. For example, membranes can recover ammonia in either pure or high concentrations and are also cost-effective when the initial concentration of ammonia is high. Enhanced biological phosphorus removal (EBPR) can be applied to recover phosphorus [Estahbanati et al., 2021].

Aerobic treatments are typically designed to treat low-strength wastewaters, while anaerobic systems are applied to situations where COD concentrations are higher than 4000 mg/L [Ngo et al., 2020]. Anaerobic treatment occurs in the absence of oxygen and is becoming more popular given that it generates biogas as a by-product. Another advantage is that excess sludge produced is significantly lower than aerobic treatment. However, it can present some issues depending on the operating conditions and the waste to be treated, mainly due to the low growth rate of microorganisms and their sensitivity to process dynamics [Robles et al., 2018]. Table 1.2 presents the main differences between aerobic and anaerobic treatment.

For nutrient recovery by anaerobic treatment, other technologies can facilitate it, such as chemical precipitation, adsorption, membrane processes, ion exchange, and the use of photosynthetic bioreactors [Ngo et al., 2020]. Both methods have advantages and disadvantages; however, the anaerobic methods appear to be preferred over the aerobic for winery wastewater treatment and energy recovery.

Table 1.2: Main differences between aerobic and anaerobic processes [Simate et al., 2011]

Parameter	Aerobic Treatment	Anaerobic Treatment
Application	Low to medium strength wastewater (e.g. municipal wastewater)	Medium to high strength wastewater (e.g. food and beverage industry wastewater)
Nutrient Requirement	High	Low
Energy Consumption	High	Low
Investment costs (CAPEX)	Low	High*
Operational costs (OPEX)	High	Low
* Biogas production that could be used to generate energy		

1.3. Resource recovery from winery wastewater by anaerobic digestion

Anaerobic digestion is a widely accepted and well-studied technology. This process allows the formation of a mix of gases or *biogas* and a co-product called *digestate*, which is typically high in nitrogen, phosphorus, and potassium. These nutrients can be used as organic fertilizer for soil amendment [INN, 2015]. Figure 1.1 shows a basic schematic of the anaerobic digestion process and the potential usage of the final products.

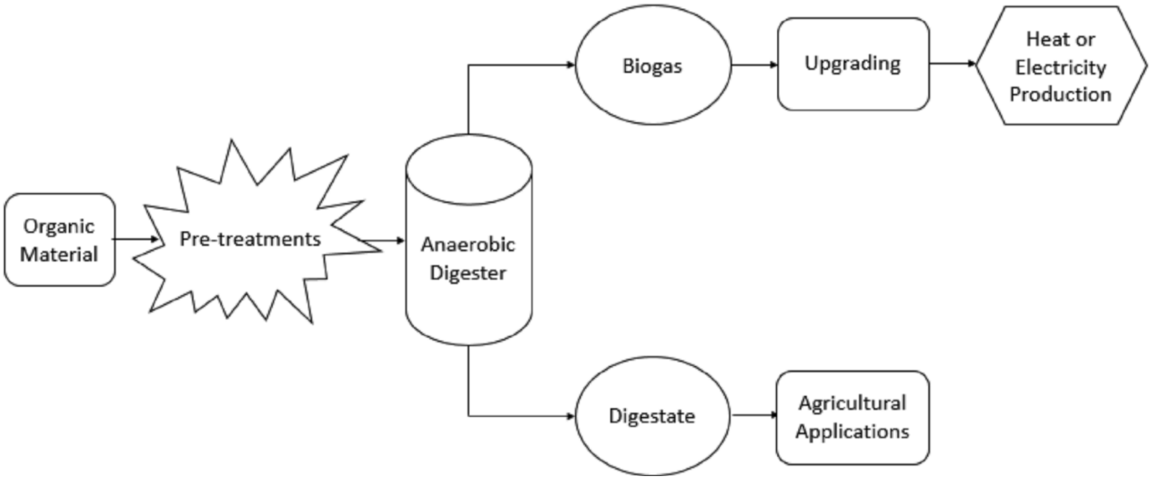


Figure 1.1: Anaerobic Digestion process diagram [Gunes et al., 2019]

Anaerobic digestion is a combination of four significant biochemical steps: bacterial hydrolysis, acidogenesis, acetogenesis, and methanogenesis, as shown in figure 1.2.

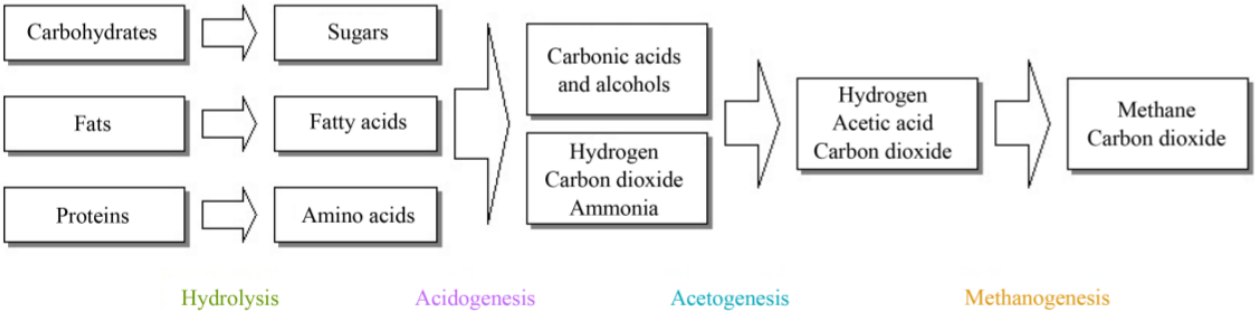


Figure 1.2: Stages of anaerobic digestion process [Adekunle & Okolie, 2015]

In the process of hydrolysis (Eq.1.1), hydrolytic bacteria convert carbohydrates, lipids, and proteins into sugars, long-chain fatty acids (LCFAs), and amino acids, respectively [Bianco et al., 2021; Meegoda et al., 2018]. Then, in the acidogenesis process (Eq.1.2), the monomers produced are taken up by different facultative and obligatory anaerobic bacteria and are degraded further into intermediate volatile fatty acids (butyric acids, propanoic acids, acetic acids), hydrogen, and carbon dioxide [Adekunle & Okolie, 2015].

In the acetogenesis process (Eq.1.3), the acetogenic bacterias reduce the organic products to acetate, hydrogen, and bicarbonate [Meegoda et al., 2018; Garcia-Mancha, 2016]. Finally, in the methanogenic phase (Eq.1.4 and 1.5), the production of methane and carbon dioxide from intermediate products is carried out by methanogenic bacterial [Adekunle & Okolie, 2015]. The AD phases are summarized in the following equations [Bianco et al., 2021]:

$$n \cdot (C_6H_{10}O_5) + n \cdot H_2O \rightarrow n \cdot C_6H_{12}O_6 + n \cdot H_2 \tag{1.1}$$

$$C_6H_{12}O_6 \leftrightarrow 2 \cdot CH_3CH_2OH + 2 \cdot CO_2 \tag{1.2}$$

$$CH_3CH_2OH \leftrightarrow CH_3COO^- + 3 \cdot H_2 + H^+ \tag{1.3}$$

$$CO_2 + 4 \cdot H_2 \rightarrow CH_4 + 2 \cdot H_2O \tag{1.4}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{1.5}$$

Over the past few years, investigations have focused mainly on methane production, an alternative to conventional fuel. However, the solubility of methane in moderate climate countries is almost 50%, which poses a serious threat as it could escape into the environment when there is an increase in temperature. Therefore, the focus shifted toward hydrogen, whose energy value is 142 kJ/g, almost three times higher than methane. More importantly, hydrogen does not produce any emissions during its conversion to energy [Ashok & Kumar, 2020; Ngo et al., 2020]. Hydrogen is considered the future energy, and it could have up to 34 % of the total renewable energy share of 69 % by 2050 [Sarangi & Nanda, 2020].

There is biohydrogen production during the acidogenesis and acetogenesis stages of anaerobic digestion. Then, it is directly consumed in the final stage of anaerobic digestion (methanogenesis) [Meegoda et al., 2018]. Consequently, it is essential to inhibit the activities of methanogens for the production of biohydrogen [Ngo et al., 2020]. Hydrogen can be used directly or converted to electricity through fuel cells [Sarangi & Nanda, 2020].

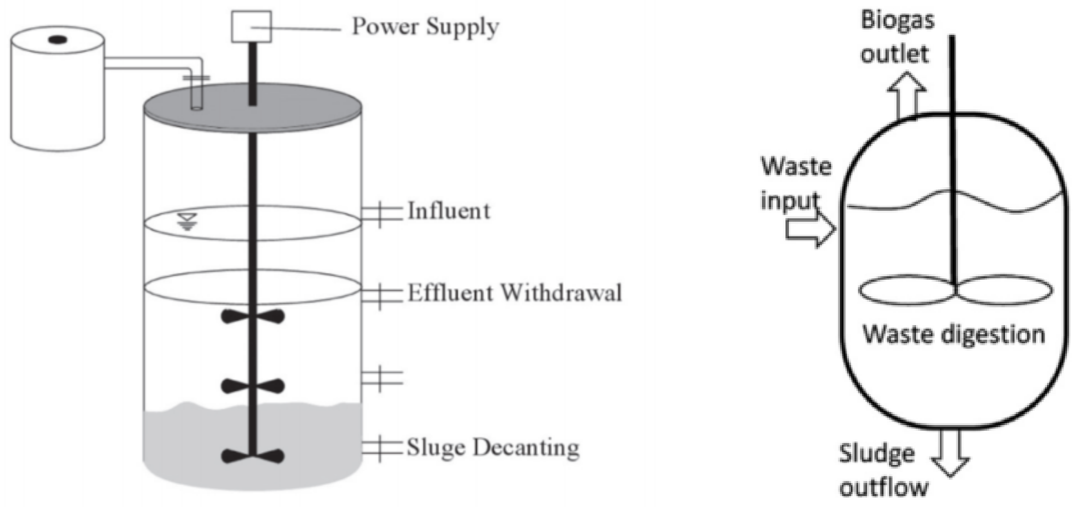
Different types of anaerobic bioreactors have been tested and applied for biohydrogen production. They can be categorized based on their orientation (vertical, horizontal), mode of operation (batch, continuous, semi-continuous), and operating temperature [Bianco et al., 2021]. The most utilized bioreactors are anaerobic sequential batch reactor (ASBR), continuously stirred batch reactor (CSTR), anaerobic fluidized-bed reactor (AFBR), up-flow anaerobic sludge blanket reactor (UASB), and anaerobic membrane bioreactor (AnMBR).

1.3.1. Anaerobic sequential batch reactor (ASBR)

Anaerobic sequential batch reactors are operationally simple; the reactor is filled and operates as a batch reactor for a certain time. ASBR requires less operating and maintenance cost than other anaerobic digesters, but good mixing and retention time determine the system performance [Aziz et al., 2019; Gunes et al., 2019]. Figure 1.3 a) shows a schematic diagram of an ASBR.

1.3.2. Continuously stirred batch reactor (CSTR)

Continuously stirred batch reactors are considered a first-generation high rate anaerobic digestion bioreactor. The substrate requires constantly mixing to facilitate good contact with the biomass for a certain period. Its application has proven to be suitable for treating high levels of suspended solids. It can operate as either single and two-stage or in plug flow or semi-continuous mode. However, it requires long retention times, and the continuous mixing could account for about 54% of the total energy required [Bianco et al., 2021; Gunes et al., 2019]. Figure 1.3 b) shows a schematic diagram of a CSTR.



(a) ASBR - Aziz et al., 2019

(b) CSTR - Bianco et al., 2021

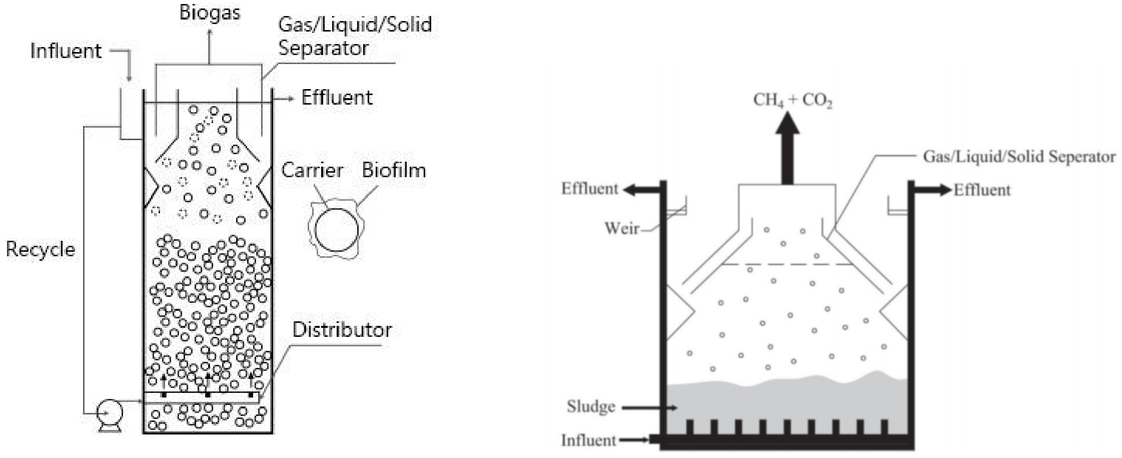
Figure 1.3: Schematic diagram of an anaerobic sequencing batch reactor and continuously stirred batch reactor

1.3.3. Anaerobic fluidized-bed reactor (AFBR)

Anaerobic fluidized-bed reactors have been implemented largely in the treatment of high-strength wastewater. In these reactors, the microorganisms are attached to the filter media (natural or synthetic), so when the wastewater passes through the filter, it comes in contact with large active biomass. AFBRs require a lower retention time than CSTRs, allowing high COD removal. However, the possibility of clogging during treatment of high suspended solids containing waste can lead to failure of the system [Bianco et al., 2021, Gunes et al., 2019, Aziz et al., 2019, Young & McCarty, 1969]. Figure 1.4 a) shows a schematic diagram of an AFR.

1.3.4. Up-flow anaerobic sludge blanket reactor (UASB)

Up-flow anaerobic sludge blanket reactors are one of the most popular high rate anaerobic digester configurations. In UASBs, the water enters from the bottom upwards through a dense sludge bed, allowing the biomass contained in the sludge to contact the wastewater substrates. UASBs can handle high organic loading rates and achieve high COD removal. However, the performance is highly attached to the liquid flow velocity and requires a gas-liquid-solid separator to ensure that solid sludge is retained in the system while gas and liquid effluent are removed [Bianco et al., 2021; Aziz et al., 2019; Gunes et al., 2019; Rajagopal et al., 2013; Simate et al., 2011]. Figure 1.4 b) shows a schematic diagram of an UASB.



(a) AFBR - Bianco et al., 2021

(b) UASB - Aziz et al., 2019

Figure 1.4: Schematic diagram of an anaerobic fluidized bed reactor and an up-flow anaerobic sludge blanked reactor

1.3.5. Anaerobic membrane bioreactor (AnMBR)

Anaerobic membrane bioreactor combines membrane filtration with an anaerobic bioreactor, allowing the treatment of high and low strength wastewater. AnMBRs require lower HRT than conventional bioreactors (e.g., CSTR and UASB) by enhancing biomass retention. These reactors achieve high COD removal and enhanced biogas production. However, one of the most challenging operational problems is membrane fouling resulting from the adsorption and precipitation of organic and inorganic matter onto the membrane [Bokhary et al., 2020; Gunes et al., 2019; Simate G., 2015; Simate et al., 2011]. Figure 1.5 shows a schematic diagram of an AnMBR.

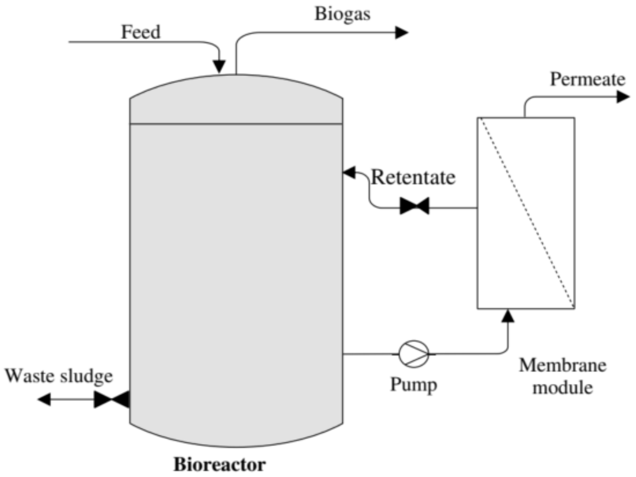


Figure 1.5: Schematic diagram of an anaerobic membrane bioreactor [Bokhary et al., 2020]

1.4. Novel approaches/strategies for biohydrogen production

Although anaerobic digestion is a viable process to produce hydrogen, it has limitations, such as low hydrogen yield due to inefficient conversion of substrates to hydrogen or accumulation of acid-rich organics in the treated effluent. Many novel strategies have been developed to increase biohydrogen's production rate and yield. Integrated biorefineries (two-stage fermentation), microbial electrolysis cell (MEC), and the development of immobilized cell systems are some of the strategies developed [Banu et al., 2020].

Two-stage fermentation processes combine two sequential reactors for biohydrogen and methane production. In the first stage, the dominant bacterial population is acidogens; therefore, there is biohydrogen production. Then, methanogens utilize the treated effluent for methane production. This process can increase the organic removal efficiency and energy recovery from industrial wastewater [Banu et al., 2020].

The microbial electrolysis cells (MECs) are a novel strategy developed to generate hydrogen under external potential application. The operation of MEC relies on the inoculum nature, electrodes, membrane, employed potential, wastewater (substrate) nature, and the OLR. This process has proved less energy requirement and effective substrate utilization when compared to water electrolysis or conventional anaerobic digestion [Banu et al., 2020].

Immobilized cells have been effectively employed in wastewater treatment in different biodigesters [Banu et al., 2020]. Novel technology is the composite bioactive membrane (CBMem) developed by Prieto et al. (2016). CBMem consists of hollow fiber membranes with encapsulated acetogenic bacteria (Figure 1.6) for biohydrogen production from high-strength synthetic and real wastewaters.

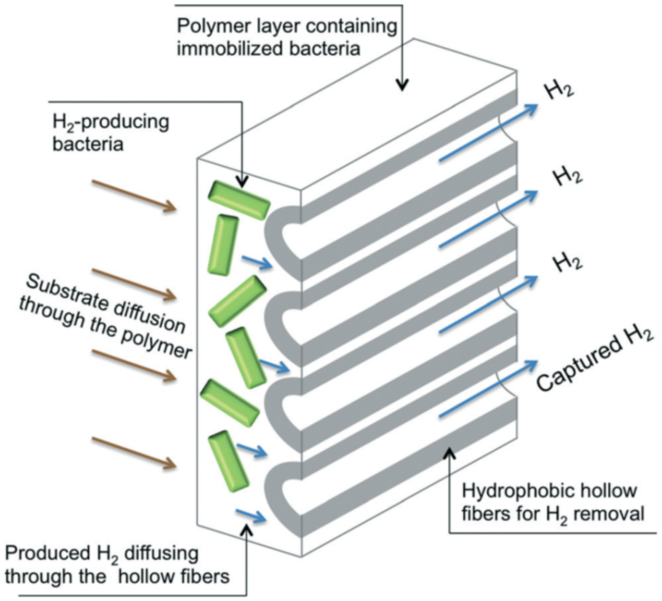


Figure 1.6: Conceptual schematic of the composite bioactive membrane [Prieto et al., 2016]

The CBMem modules could produce and capture H_2, providing another technological opportunity to explore energy-generating wastewater treatment. The importance of this novel approach is that the CBMem modules demonstrated advantages in yield and H_2 capture efficiency. In addition, the proposed design could be suitable for scale-up, and it could overcome many of the problems previously encountered in reactors, such as inhibition of the acetogenic community by H_2 partial pressure. However, the CBMem technology requires specific requirements (COD and solids) for its implementation [Prieto et al., 2016].

1.5. Objectives

This work aims to model and simulate a winery wastewater treatment and hydrogen (H_2) generation train to implement full-scale composite bioactive membrane technology (CBMem). For this purpose, the researcher proposed the following specific objectives:

SO1: Define the winery wastewater characteristics and the CBMem technology requirements for its implementation.

SO2: Define a technical solution that allows hydrogen based on the influent and effluent characteristics.

SO3: Define the size of the technical solution selected using the simulation software Simba.

SO4: Discuss the advantages and disadvantages of implementing the technology in the wine production industry.

Chapter 2

Methodology

2.1. SO1: Define the high-strength wastewater characteristics and the CBMem technology requirements for its implementation.

2.1.1. Task 1: Characterization of the influent.

In order to characterize the winery wastewater, understanding the sources of different quality waste streams is essential. Figure 2.1 presents a diagram of typical processes in winemaking, typical winery wastes, and their sources.

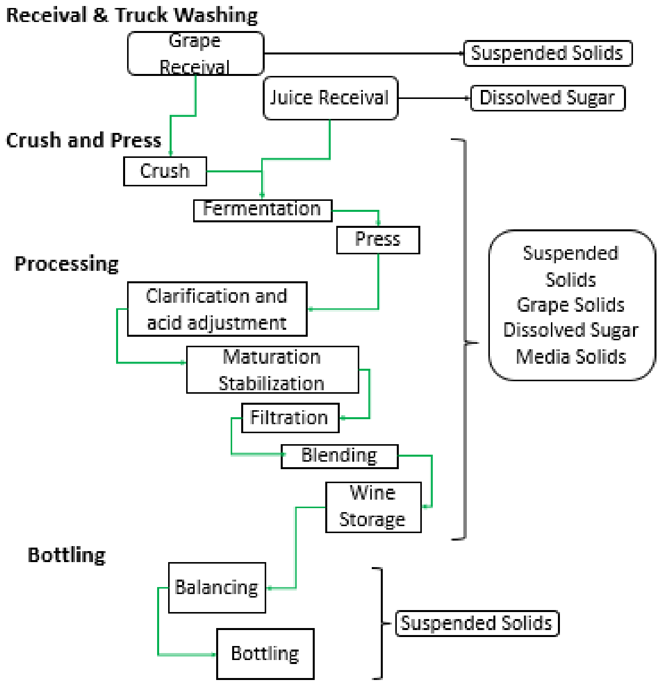


Figure 2.1: Typical processes in wine making, typical winery wastes and their sources [adapted from Day et al., 2011]

The process starts with harvesting the grapes from March to May in the southern hemisphere. Then, the grapes received are destemmed and selected in the winery, which generates the stalk. The cleaning of this waste generates the first liquid waste. It follows crushing and pressing. The juice and the solids go to fermentation for a period. Finally, the wine is filtrated and bottled [Day et al., 2011].

Most suspended solids and organic matter are generated during crushing, pressing, processing, and cleaning (primarily floors and walls and equipment). For this study, the influent corresponds to the wastewater generated in the winery *Chimbarongo* belonging to Viña Concha y Toro S.A. The wastewater corresponds to the produced from all the stages previously mentioned. First, it goes through physical separation; then, it is stored in aerated tanks for pH adjustment and to ensure that the flux-to-be treated is constant during the year. For modeling and sizing, it was used the water quality mean values. Viña Concha y Toro S.A. does not measure alkalinity regularly; thus, its value could change [SEIA, 2017]. Table 2.1 shows the characteristics of the winery wastewater for the samples analyzed between 01 March 2020 and 28 February 2021 by the manager of Viña Concha y Toro S.A.

Table 2.1: Main characteristics of the influent

Parameter	Unit	Harvesting	No Harvesting	Mean (σ)
COD	mg/L	18522	3030	8240 (3030)
TP	mg/L	15	15	15 (0)
TKN	mg/L	80	80	80 (0)
TSS	mg/L	5520	1833	3601 (908)
pH	-	8.9	6.4	7 (0.36)
Alkalinity	mg/L as CaCO3	-	-	477.5
# samples: 228				

2.1.2. Task 2: Define the CBMem technology requirements.

The influent should not have suspended solids before entering the CBMem system, and the COD must be soluble [Prieto et al., 2016]. Besides, an acid effluent helps the process Table 2.2 shows the CBMem technology requirements.

Table 2.2: CBMem requirements [Prieto et al., 2016]

	Unit	Concentration
COD	mg/L	Soluble and preferable higher than 2000
TSS	mg/L	≈ 0

2.2. SO2: Define a technical solution that allows hydrogen based on the influent and effluent characteristics.

2.2.1. Task 3: Perform a literature review of anaerobic bioreactors for wastewater to biohydrogen conversion.

As was previously mentioned, different types of anaerobic bioreactors have been tested and applied for industrial applications. In particular, the anaerobic sequential batch reactor (ASBR), continuously stirred batch reactor (CSTR), anaerobic fluidized bed reactors (AFBR), up-flow anaerobic sludge blanket reactor (UASB), and anaerobic membrane bioreactor (AnMBR) are the most used. This section focuses on the advantages, disadvantages, and performance of these anaerobic bioreactors for biohydrogen production.

Regarding the operation, batch reactors (e.g., an ASBR) are mainly employed for research purposes, whereas at industrial-scale, the continuous types of bioreactors are more employed [Saratale et al., 2019]. In addition, feedstocks with a high solid content are usually best converted to biogas in continuously stirred tank reactors and plug flow reactors [Stamatelatou et al., 2014].

The ASBR and CSTR are the most used for biohydrogen production. The advantages of the ASBR are high efficiency for COD removal and gas production, no need for primary and secondary settles, and flexible control [Kim, 2011]. However, it has high maintenance costs and is challenging to escalate [Gunaskaran et al., 2019]. The CSTR is easy to operate and has a simple design. Compared to other reactor configurations, it has better mass transfer with a short hydraulic retention time (HRT) [Banu et al., 2020]. However, it has biomass washout and has a high operating cost due to stirring [Banu et al., 2020; Usman et al., 2019].

Similarly, AFBRs are suitable at low HRT and high OLR and easy to scale up [Gunaskaran et al., 2019]. However, the capital cost is higher and requires media for biomass separation [Bianco et al., 2021; Usman et al., 2019; Aziz et al., 2019; Gunes et al., 2019]. The UASB reactor is one of the most popular configurations for treating high-strength wastewater due to its high substrate conversion efficiency, less biomass out, and longer solids retention time (SRT) [Banu et al., 2020; Aziz et al., 2019]. Excess biomass formation and the presence of suspended solids in the effluent are the downsides of this system [Usman et al., 2019].

The advantages of a CSTR with a membrane module (i.e., an AnMBR) are high biomass concentration, lower HRT than conventional bioreactors, enhanced biogas production, and high effluent quality (without solids or bacteria) [Bokhary et al., 2020; Gunes et al., 2019; Dvořák et al., 2016; Simate G., 2015]. However, the main limitations of this technology are membrane fouling and high costs due to the membrane [Usman et al., 2019].

Table 2.3 presents the main advantages and disadvantages of the reactors employed for biohydrogen production.

Table 2.3: Main advantages and disadvantages of the reactors more used for biohydrogen production [Gunaskaran et al., 2019]

Reactor Type	Advantage	Disadvantage
Anaerobic sequential batch reactor (ASBR)	• Higher COD removal rate and gas production • Higher SRT	• Higher Maintenance • Difficult to escalate
Continuously stirred batch reactor (CSTR)	• Frequently used for production of hydrogen • Hydrogen-producing bacteria are well suspended in mixed liquor • Simple design and easy to operate	• Wash out of the biomass • Long HRT • High requirement of energy for stirring
Anaerobic fluidized bed reactors (AFBR)	• Higher OLR • Suitable at low HRT • Retain high of biomass by supporting medium • Easy to scale up	• Requirement of media for biomass separation • Higher capital cost
Up-flow anaerobic sludge blanked reactor (UASB)	• High OLR • Suitable at low HRT • High biomass concentration	• Excess biomass formation • Long start-up phase • Uncleaned biogas • Foaming issue
Anaerobic membrane bioreactor (AnMBR)	• Wastewater of low or high concentration • Eliminate most of the pathogens • High biomass concentration • Low generation of excess sludge	• Membrane fouling issue • High membrane cost

Various authors have studied the application of ASBR at the lab scale. Prasertsan et al. (2009) examined biohydrogen production from palm oil mill effluent using an ASBR. The results showed 55% H_2 in the biogas and a maximum H_2 yield of 0.27 L_{H_2}/g_{COD}. Buitron & Carvajal (2010) obtained 29% H_2 in the biogas and a maximum H_2 yield of 48 $mmol_{H_2}/L-d$ using tequila vinasees. On the other hand, Sivagurunathan et al. (2015) examined biohydrogen production from beverage wastewater using an anaerobic CSTR. The results showed 43.7% of H_2 in the biogas with a maximum production of 55.44 $L_{H_2}/L-d$. In addition, using molasses wastewater, Qin et al. (2014) obtained 37% of H_2 in the biogas and maximum production of 27.1 L_{H_2}/d using a CSTR.

Ramos & Silva (2016) investigated the biohydrogen production from sugarcane vinasse and cheese whey on two AFBRs, the maximum values for hydrogen production rate (HPR) and H_2% were 5.36 L_{H_2}/hL and 50% for cheese whey, and 0.71 L_{H_2}/hL and 42% for vinasse. Mahmod et al. (2019) analyzed the biohydrogen production using a UASB, the results for H_2% and H_2 yield were 52% and 2.65 mol_{H_2}/mol_{sugar}. In addition, using a two-stage UASB and cassava wastewater, Chavadej et al. (2019) obtained 42.3% of H_2 in the biogas and a maximum H_2 yield of 15 mL/g_{COD}.

Villanueva (2020) evaluate the feasibility of implementing an AnMBR in the wine industry, the results for maximum H_2 % and biogas production were 33.9 % and 133.8 $L_{biogas}/m^3_{treated}$. Using glucose as substrate, Noblecourt et al. (2017) obtained 51% of H_2 in the biogas, a maximum H_2 yield of 1.85 $mol_{H_2}/mol_{glucose}$ and a maximal productivity of 2.46 $L_{H_2}/L-h$. In addition, Bakonyi et al. (2017) results showed 59–60% H_2 in the biogas and a maximum H_2 yield of 1.91 $mol_{H_2}/mol_{glucose}$.

Table 2.4 shows a resume of biohydrogen production reported, including operational parameters (such as pH, HRT, temperature), the substrate, and reactor type.

Table 2.4: Experimental conditions and main results of studies of the production of biohydrogen using different wastewater

Reactor type	Substrate	Operational Parameters	Results	Reference
ASBR	Palm oil mill effluent	pH 5.5; Temperature 60°C; HRT 2d; OLR 60 gCOD/L-d	55% H2 in biogas, maximum H2 yield 0.27 LH2/gCOD	Prasertsan et al., 2009
ASBR	Tequila vinasses	Temperature 25-35 °C; HRT 24h; CODin 29.9 - 30.5 gCOD/L	29.2% H2 in biogas and maximum production of 48 mmol H2/L-d	Buitrón & Carvajal, 2010
CSTR	Molasses wastewater	OLR 21 kgCOD/m3-d; pH 4.7 - 4.9	37% H2 in biogas; maximum production of 27.1 LH2/d	Qin et al., 2014
CSTR (inmobilized cell CSTR)	Beverage wastewater	HRT 1.5 - 8h; OLR 60-320 gCOD/L-d; Temperature 37 °C; without pH control	43.7% H2 in biogas; maximum production of 55.44 LH2/L-d	Sivagurunathan et al., 2015
AFBR	Cheese whey	HRT 4h; Temperature 65 °C; CODinf 11 gCOD/L	50% H2 in biogas; maximum production 5.36 LH2/h-L	Ramos & Silva, 2016
AFBR	Viansse	HRT 4h; Temperature 55 °C; CODinf 28 gCOD/L	42% H2 in biogas; maximum production 0.7 LH2/h-L	Ramos & Silva, 2016
Two stage UASB	Cassava wastewater with added casava residue	Working volume 24L; Temperature 55°C; COD loading rate 10.29 [kg/m3*d]; System operated for 1 year; pH 5.5; COD 10.6 [g/L]	42.3% H2; highest H2 yield 15 mL/gCOD	Chavadej et al., 2019
UASB	Pre-teated palm oil mill effluent (POME)	CODin 53.19 [g/L]; pH 5.2 to 6.0; working volume 20L; Temperature 55°C; HRT 6 to 48h for 70 days	52% H2 in biogas; maximum H2 yield 2.65 molH2/molsugar at 6h	Mahmod et al., 2019
Subsumerged AnMBR	Artifitial	Feed solution contained 60 [g/L] glucose; Working volume 5L; Temperature 35°C; pH 6; HRT 35h	51% H2; maximum H2 yield 1.85 molH2/molglucose; Maximal productivities 2.46 LH2/L-h	Noblecourt et al., 2017
CSTR to Gas Separation AnMBR system	Artifitial (glucose as substrate in 20 g/L concentration)	Feed solution contained 20 [g/L] glucose; CSTR with 0.9L working volume; Temperature 35°C; pH 5.5; HRT 12h	59–60 vol.% H2; highest H2 yield 1.91 molH2/molglucose	Bakonyi et al., 2017
AnMBR	Artificial winery wastewaters	CODin 278 [mg/L]; Temperature 24°C; pH 4.5-5.5; HRT 53d	33.9% H2 maximum; biogas production rate 133.8 Lbiogas/m3treated	Villanueva, 2020

2.2.2. Task 4: Select the solution to implement, that permits fulfilling the restrictions and hydrogen production.

For the selection of the reactor type, the researcher considered that the reactor must allow the treatment of the high-strength wastewater (i.e., winery wastewater), the effluent must fulfill the requirements for the CBMem, and the system should allow hydrogen production. The objective of hydrogen production is to convert it into energy and thus use it within the production line.

Each reactor reviewed could treat winery wastewater. However, considering the CBMem requirements, the UASB would not be applicable. Regarding hydrogen production, the CSTR has been more used. However, the AFBR is more efficient. Some authors indicate that the AFBR high energy requirements make it unsuitable for the proposed objective because most of the hydrogen produced would be used for stirring [Aziz et al., 2019; Gunaskaran et al., 2019]. Many authors have used CSTRs for hydrogen production. The application of the AnMBR has proven to overcome the washout limitations of the CSTR [Bokhary et al., 2020; Gunes et al., 2019]. The AnMBR as pretreatment of the CBmem would fulfill the restrictions and allow hydrogen production.

There are two basic AnMBR configurations depending on the location of the membrane in the system. The membranes can be located either in a secondary and separate membrane bioreactor (side-stream configuration) or in the primary bioreactor (submerged configuration) as shown in figure 2.2.

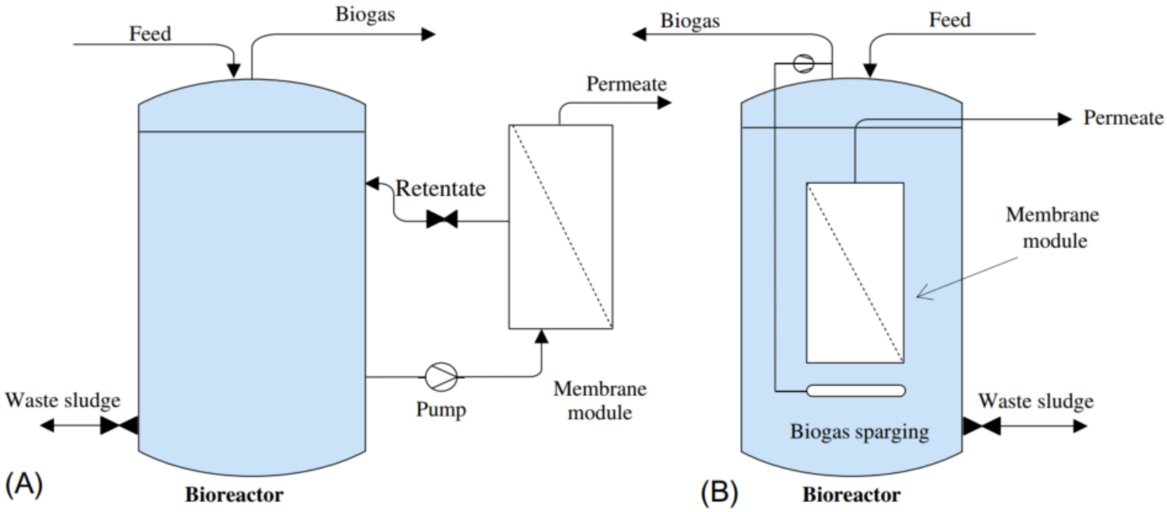


Figure 2.2: Illustration of AnMBR configurations: (A) side-stream configuration, (B) submerged configuration [Bokhary et al., 2020]

The side-stream AnMBR's main advantage is that the cross-flow could physically clean the surface of the membranes. In submerged AnMBRs, the membranes are directly immersed in the mixed liquor, involving lower energy requirements than side-stream configurations. However, there will be difficulty cleaning and replacing the membrane modules [Ashok & Kumar, 2020; Robles et al., 2018].

Currently, the AnMBR's modeling considers a primary anaerobic bioreactor (CSTR) and a secondary membrane bioreactor. The primary anaerobic bioreactor contains microorganisms that convert organic carbon into biogas. The biogas, produced in the primary anaerobic bioreactor, can be converted to electricity, heat, or fuel for vehicles. The secondary membrane bioreactor contains membranes that separate the microorganisms and other suspended solids from the treated effluent (permeate) [Shin et al., 2021; Evans, 2018].

The application of anaerobic membrane bioreactors has shown that large-size particles, such as sands, rocks, hairs, and plastics, must be removed before the influent enters the membrane. Besides, it is advisable to have a regulation tank in which the influent is homogenized. In addition, the tank serves to dampen the variations in the influent load throughout the day. [Kong et al., 2021; Evans, 2018; Zuluaga et al., 2015; Giménez, 2014; Robles et al., 2012].

Finally, the researcher considered a permeate storage tank because the treatment train will serve as a pre-treatment for implementing the CBMem. Figure 2.3 shows the proposed process flow diagram for the winery wastewater treatment plant (WWTP).

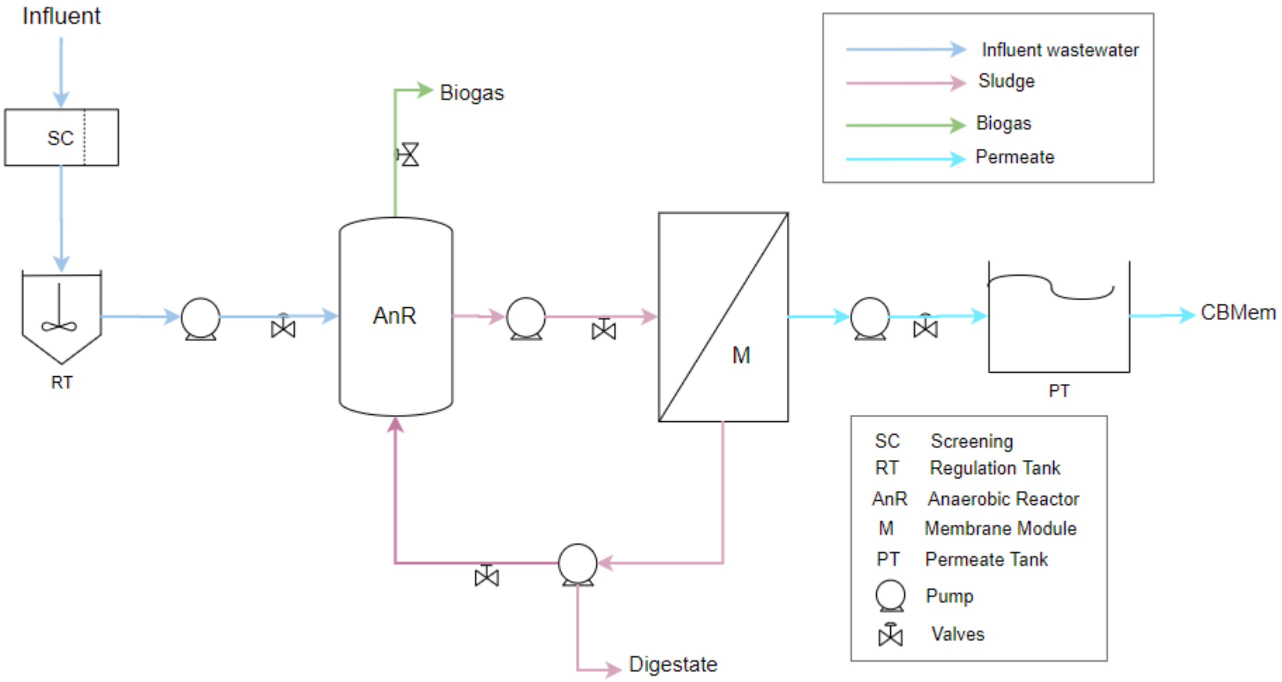


Figure 2.3: Process flow diagram for the proposed AnMBR WWTP

2.2.3. Task 5: Perform a literature review of the operational and design parameters that influence hydrogen production.

For the treatment train's design, the researcher considered the influent characteristics and operational parameters found in the literature. The main variables are influent flow (Q), temperature, pH, hydraulic retention time (HRT), solids retention time (SRT), and organic loading rate (OLR). Table 2.5 shows values found in the literature for the main design and operation variables of anaerobic membrane reactors.

The anaerobic digestion could operate under psychrophilic (0 - 20°C), mesophilic (20 - 45°C), and thermophilic (42 - 75°C) conditions [Bianco et al., 2021; Deowan et al., 2015]. Authors have reported optimal conditions for biogas production. For mesophilic conditions, the optimum temperature found was 35°C. For thermophilic conditions, it was 55 °C [Hamzah et al., 2019; Ince et al., 2017; Ghimireet al., 2015].

The pH is one of the most critical parameters that affect the performance of an anaerobic digestion system. The pH usually decreases during the acidogenic phase ($\sim$ 6.0). Afterward, it increases during the methanogenic phase to $\sim$ 8.0 due to alkalinity production [Bianco et al., 2021]. Several studies presented that pH from 4.5 to 6.0 were suitable for hydrogen production, however, a pH range of 5.0–5.7 was observed to be optimum [Dareli et al., 2021; Chavadej et al., 2019; Ghimire et al., 2015; Hernández & Rodríguez, 2013].

The hydraulic retention time (HRT) affects the biogas generation and the digester's stability during long-term operation. HRT reflects the digester volume and depends on the digester type [Bianco et al., 2021]. Generally, a low HRT is preferred because it reduces the tank volume and enhances hydrogen production [Banu et al., 2020; Ghimire et al., 2015].

Organic Loading Rate (OLR) is an essential monitoring parameter to enhance the hydrogen production rate (HPR). The total conversion of carbohydrates is inversely proportional to OLR in the reactor. For AnMBRs, the substrate concentration range may vary with the substrate composition and inoculum characteristics, and there is no universal optimum substrate concentration [Banu et al., 2020; Aslam et al., 2018].

Similarly, the solids retention time (SRT) is related to the microbial diversity in the system. Changes in SRT may accelerate the proliferation of hydrogen-producing bacteria or the proliferation of competitive-hydrogen-consuming microbes. For AnMBRs, there is no universal solids retention time, and it is necessary to determine appropriate SRT for the system and case-specific considering all operational variables. However, studies have demonstrated that maintaining longer SRT and shorter HRT might improve the bioH_2 generation efficiency [Usman et al., 2019; Aslam et al., 2018; Bakonyi et al., 2014].

Table 2.5: Operational Parameters for AnMBR

Variable	Value(s)	Reference
T [°C]	35 or 55	Ghimire et al., 2015
pH [-]	5.0 - 5.7	Banu et al., 2020
HRT [d]	0.15-15; 1-7; 0.5 - 1	Metcalf&Eddy, 2014; Bianco et al., 2021; Aslam et al., 2019
SRT [d]	30-160; 6-270; 2.7	Metcalf&Eddy, 2014; Bokhary et al., 2020; Villanueva, 2020
OLR [kgCOD/m$^3 - d$]	5-15; 1.5-20; 10-30	Metcalf&Eddy, 2014; Bianco et al., 2021; Aslam et al., 2018

Finally, the mixed liquor suspended solids (MLSS) influence the membrane performance (membrane clogging) and, sequentially, biogas sparging efficiency. The relationship between MLSS and membrane fouling is complex, and there is a discrepancy in the data obtained in different studies. However, according to the literature, the researcher considered MLVSS between 10 and 20 g/L for long-term AnMBR operation and industrial wastewater treatment [Bokhary et al., 2020].

2.3. SO3: Define the size of the technical solution selected using the simulation software Simba.

2.3.1. Task 6: Build the model of the selected solution using the Simba software.

The Simba software developer is the Institute for Automation and Communication (IFAK), Germany. According to the developer, the SIMBA program is a versatile software for modeling and dynamic simulation in wastewater technology. It allows the integration of simulation of wastewater treatment processes with state-of-the-art activated sludge models or own model developments, including the mechanical equipment of sludge treatment plants and control options. The software focuses on biological processes; therefore, it does not include screening and homogenization.

Regarding anaerobic processes, Simba includes a dedicated library, in which could be found anaerobic reactor blocks with gaseous phase and interface models for linking with activated sludge models. Besides, the anaerobic models allow the prognosis of COD, TS degradation, gas production, gas synthesis (carbon dioxide, methane, hydrogen), nitrogen release, organic acids, and pH [Ifak, 1994].

The model used was *admsieg02* based on Siegrist et al. (2002). It is a mathematical model developed to describe the dynamic behavior of both mesophilic and thermophilic digestion. The model's approach is similar to the IWA activated sludge models. A stoichiometric matrix describes the model's physical, biological, and chemical processes (see Annexed A for stoichiometric matrix). The model allows the variation of digested sludge and biogas composition. Besides, the biogas composition is described by the partial pressures of methane (p_{CH4}), carbon dioxide (p_{CO2}) and hydrogen (p_{H2}) [Siegrist et al., 2002].

The model considers seven processes (Figure 2.4), which describe the hydrolysis of particulate organic matter (carbohydrates, proteins, and lipids) into amino acids, sugars, and long-chain fatty acids (process 2), fermentation of amino acids and sugars (processes 3 and 4), anaerobic oxidation of long-chain fatty acids (process 5) and propionate (process 6), and methanogenesis (processes 7 and 8). The reaction kinetics of the processes are of first-order for hydrolysis and Monod type for the remaining six processes of microorganism growth (see Annexed A for process rates and kinetic expressions).

Besides, it considers inhibition due to pH, free ammonia, hydrogen, and acetate. Inhibition due to pH affects fermentation and anaerobic oxidation. Inhibition by hydrogen and acetate affects the anaerobic oxidation of LCFA and propionate in a non-competitive way. Finally, inhibition due to free ammonia affects the anaerobic oxidation of propionate (see Annexed A for inhibition expressions).

The CBMem consists of hollow fiber membranes with encapsulated acetogenic bacteria. Therefore, the processes essential for its implementation are the hydrolysis of particulate degradable COD and amino acids and sugars fermentation. The results were analyzed to ensure that the model describes the key processes.

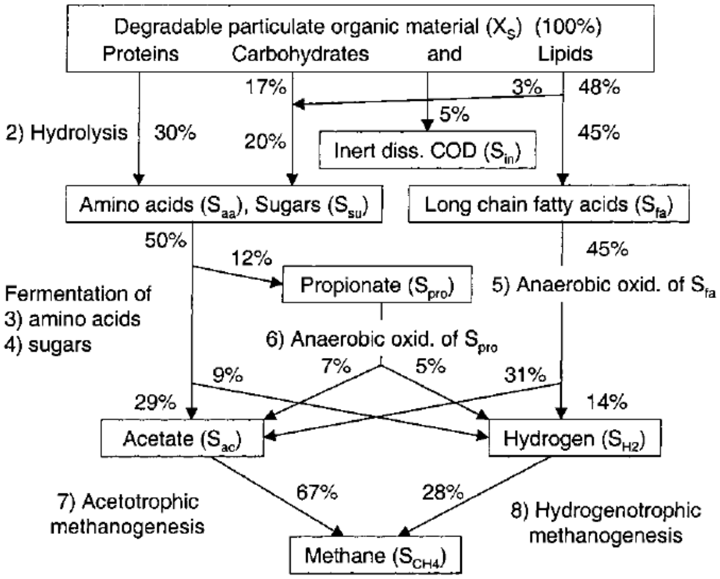


Figure 2.4: Reaction scheme for anaerobic digestion [Siegriest et al., 2002]

The AnMBR system consists of a CSTR coupled with a membrane module [Shin et al., 2021]. The CSTR module is included in the blocks library (as Digestion), and the membrane module is modeled as an ideal clarifier, as shown in figure 2.5.

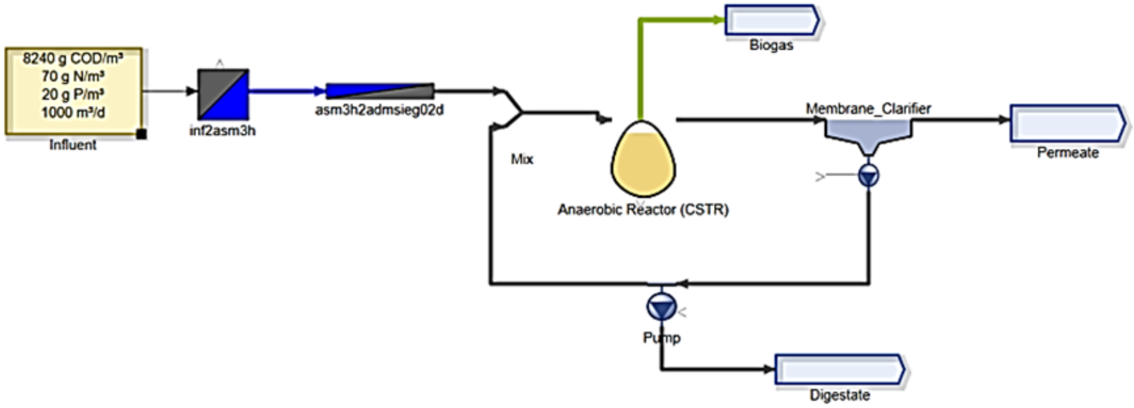
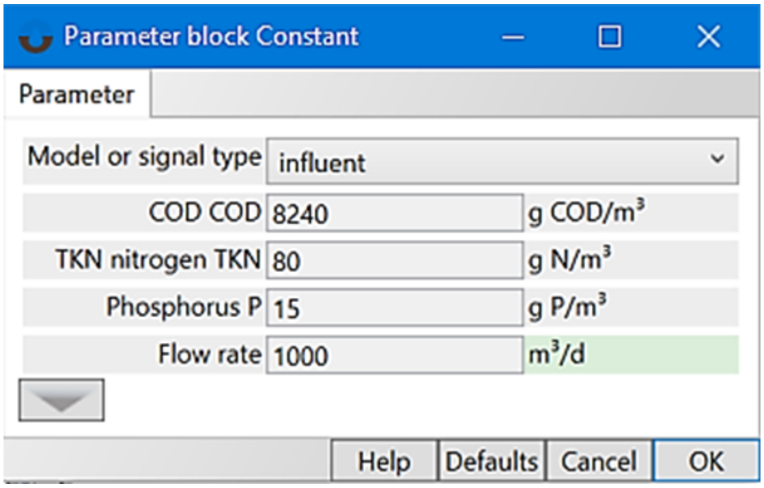


Figure 2.5: Process flow diagram

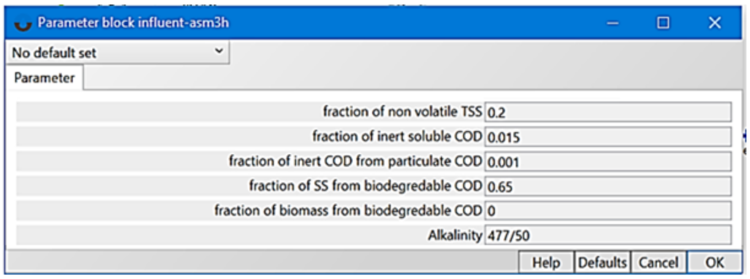
The model requires three modules (Influent, inf2asm3h, and asm3h2admsieg02d) to characterize the influent. The first module (*Influent*) contains a description of the influent by a vector of 4 values, as presented in figure 2.6.



Model or signal type: influent
COD COD: 8240 g COD/m³
TKN nitrogen TKN: 80 g N/m³
Phosphorus P: 15 g P/m³
Flow rate: 1000 m³/d

Figure 2.6: Influent characterization - influent module

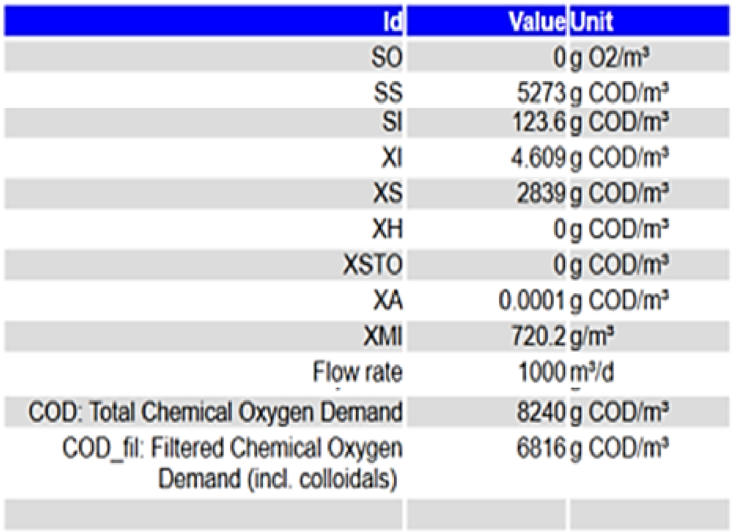
The module *inf2asm3h* is primarily for COD fractionation; it uses a vector regarding the activated sludge model asm3h, as presented in figure 2.7.



fraction of non volatile TSS	0.2
fraction of inert soluble COD	0.015
fraction of inert COD from particulate COD	0.001
fraction of SS from biodegredable COD	0.65
fraction of biomass from biodegredable COD	0
Alkalinity	477/50

Figure 2.7: COD fractionation input - inf2asm3h module

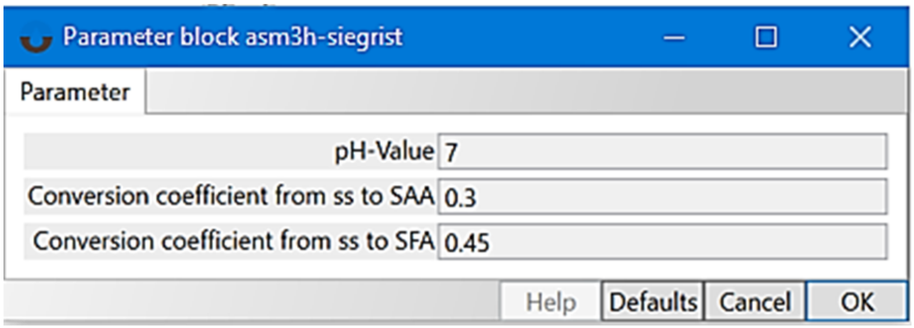
The COD fractionation was based on Avaria (2019) and considered COD of soluble readily biodegradable substrates (S_S), inert soluble organic substrates (S_I), particulate slowly biodegradable substrates (X_S), inert particulate organic substrates (X_I), autotrophic biomass (X_A), heterotrophic biomass (X_H) and internal organic storage products of heterotrophic biomass (X_{STO}). The developers based the calculation model and parameters on the German design guideline A131, appendix COD model [Ifak, 2020], figure 2.8 presents the values after the conversion.



Id	Value	Unit
SO	0	g O2/m^3
SS	5273	g COD/m^3
SI	123.6	g COD/m^3
XI	4.609	g COD/m^3
XS	2839	g COD/m^3
XH	0	g COD/m^3
XSTO	0	g COD/m^3
XA	0.0001	g COD/m^3
XMI	720.2	g/m^3
Flow rate	1000	m^3/d
COD: Total Chemical Oxygen Demand	8240	g COD/m^3
COD_fil: Filtered Chemical Oxygen Demand (incl. colloidals)	6816	g COD/m^3

Figure 2.8: COD fractionation results - inf2asm3h module

Finally, the module *asm3h2admsieg02d* contains a description of the wastewater using a vector of 3 values regarding the admsieg02 model (Siegrist et al.), as presented in figure 2.9. The pH value was set based on the characterization of the influent (Table 2.1), and the other values as default.



pH-Value 7

Conversion coefficient from ss to SAA 0.3

Conversion coefficient from ss to SFA 0.45

Figure 2.9: Influent characterization - asm3h2admsieg02d module

2.3.2. Task 7: Using the developed model, size the unit processes and analyze the effect of the reviewed parameters on the response of the system.

Regarding sizing, the *anaerobic reactor* module consists of a sludge and a gas phase. As input, it requires the volume of the sludge phase, the maximum volume of the reactor, the temperature, the recycle and waste rate. The volume of the sludge phase (V_{sf}) was calculated using equation 2.1, where COD_{in} corresponds to the influent COD (8240 g/m^3), Q to the flow (1000 m^3/d) and OLR to the organic loading rate (Table 2.5). In the case of the reactor volume (V_R), it was calculated as the volume of sludge phase plus 10 m^3 to ensure that the hydrogen produced was removed from the reactor continuously. Thus, the process was thermodynamically feasible [Ashok & Kumar, 2020].

$$V_{sf} = \frac{COD_{in} \cdot Q}{OLR} \quad [m^3] \qquad \& \qquad V_R = V_{sf} + 10 \quad [m^3] \tag{2.1}$$

The process temperature and the recycle ratio were set at 35 °C and 1, respectively. Equation 2.2 present the relationship between waste flow and SRT, where V_R corresponds to the reactor volume $[m^3]$, Q_w to the waste flow $[m^3/d]$, Q_p to the permeate flow $[m^3/d]$ and VSS_{react}, VSS_w, VSS_p to the volatile suspended solids in the reactor, digestate and permeate in g/m^3, respectively.

$$SRT = \frac{V_R \cdot VSS_{react}}{Q_w \cdot VSS_w + Q_P \cdot VSS_p} \tag{2.2}$$

Equation 2.3 presents the relationship between the reactor volume (V_R), influent flow (Q), and hydraulic retention time (HRT).

$$HRT = \frac{V_{sf}}{Q} \tag{2.3}$$

The author analyzed the effect of the hydraulic retention time (HRT), solids retention time (SRT), and organic loading rate (OLR) on the quality of the permeate, reactor pH, MLVSS, and hydrogen production. As was previously mentioned, the literature is not consistent regarding the optimal set of SRT and OLR. The researcher simulated for SRT between 2 to 15 days and OLR in the range of 10 to 30 $kg_{COD}/m^3 - d$ [Bokhary et al., 2020; Villanueva, 2020; Aslam et al., 2018].

Besides, the researcher calculated the hydrogen production using equation 2.4, where H_2 corresponds to the hydrogen produced in mol/m^3 and Q_{bio} to the biogas produced in m^3/d. Then, in terms of volume (m^3/d) at standard condition (20°C and 1 atm) and mass (kg) using the molar weight of H_2 (2.01588 grams).

$$V_{H_2} = H_2 \cdot Q_{bio} \tag{2.4}$$

For the determination of the operational conditions (SRT-HRT), the researcher selected a range of OLR for each SRT that ensured the fulfillment of the following criteria:

1. Soluble permeate COD must be higher than 2000 mg/L.
2. The reactor should operate with a pH above 5.0.
3. The mixed liquor volatile suspended solids must be in the range of 10 to 20 g/L.

Afterward, the researcher selected the operational condition with which the AnMBR would operate by considering three design criteria. The MVLSS should be between 15 to 18 g/L, the reactor volume should be small, and the hydrogen production should be the highest possible.

Finally, the effect of alkalinity in the system response was analyzed. The operational conditions were the ones previously selected, and the values adopted were based in other studies. The values for alkalinity selected were 400, 477 and 550 mg/L as $CaCO_3$ [Villanueva, 2020; Avaria, 2019; Brito et al., 2007].

2.4. SO4: Perform an advantages and disadvantages discussion of the implementation of the technology in the wine production industry.

2.4.1. Task 8: Discuss the advantages and disadvantages of the implementation of the technology, focusing on the energy generation potential.

As was previously mentioned, at the wine industry (Viña Cocha y Toro S.A.), the wastewater treatment is established depending on the characteristics of the influent and the current discharge regulations. The principal technologies applied are mixing flow reactors for neutralization, conventional activated sludge, and aerobic membrane reactors (MBR).

The application of MBR has proven to be more effective than conventional activated sludge. However, it is a negative energy system due to the lack of energy recovery and high energy demand, which is approximately two kWh/m^3 of wastewater treated [Ashok & Kumar, 2020; Valderrama et al., 2012]. On the contrary, anaerobic MBRs can facilitate energy recovery, it produces less sludge when compared to the MBR, and there is no requirement of oxygen supply. However, a wide variation in energy demand (0.03 to 2.5 kWh/m^3) was founded in the literature, principally because its application is not widespread as aerobic processes [Zhen et al., 2019; Martin et al., 2011].

The main disadvantages considered were the requirement of a long time to stabilize the microbial culture within the reactor and constant monitoring of the process parameters. The AnMBR has a high investment cost primarily because the membrane and fouling are perennial issues [Pramodbabu et al., 2021; Náthia-Neves et al., 2018].

The principal advantages considered were energy recovery, COD removal, and that it could be a compact system [Pramodbabu et al., 2021]. For the evaluation, the researcher considered that the discharge flow varies according to the seasonality of the production process, 650 m^3/d during the harvest (March to July) and 375 m^3/d during the non-harvest period (August to February) [SEIA, 2017]. The energy demand of *Bodega Chimbarongo* was 3819 MWh in 2021, and 1 kg of hydrogen contains 33.33 kWh of usable energy [Viña Concha y Toro, 2022; Sarangi & Nanda, 2020]. Researchers have used fuel cells for hydrogen to energy conversion, achieving an efficiency of 79.3% to 82.7% for $H_2 - O_2$ fuel cell and 75.7% to 82.7% for H_2-air fuel cell [Haseli, 2018].

Chapter 3

Results and Discussion

3.1. Anaerobic digestion model evaluation

The *admsieg02* model considers seven processes, from hydrolysis to methanogenesis (Figure 2.4). The soluble readily biodegradable substrates (S_S) are divided into 45% long-chain fatty acids (LCFA), 30% sugars, 20% amino acids, and 5% inert, as presented in Table 3.1.

Table 3.1: Influent amino acids, sugar and fatty acids concentration

Amino Acids $[g_{COD}/m^3]$	Sugar $[g_{COD}/m^3]$	LC Fatty acids $[g_{COD}/m^3]$	Inert $[g_{COD}/m^3]$
1582	1318	2373	124

Besides, the model considers initial values for the substrates and biomass in the digester, as presented in table 3.2.

Table 3.2: Initial default values for substrates and biomass set in the digester

	Value $[g_{COD}/m^3]$	Description
SAA	10	Amino acids
SSU	10	Sugars
SFA	120	Long chain fatty acids (LCFA)
XBAA	300	Biomass fermenting amino acids
XBSU	300	Biomass fermenting sugars
XBFA	500	Biomass degrading LCFA
XBPRO	400	Biomass transforming propionate into acetate
XBAC	500	Biomass undergoing acetotrophic methanogenesis
XBH2	400	Biomass undergoing hydrogenotrophic methanogenesis
SAC	30	Acetate
SPRO	20	Propionate

The researcher evaluated the performance of the anaerobic digestion model by observing the methane, hydrogen, biomass, sugar, amino acids, LCFA, acetate, propionate, and pH profiles.

Figure 3.1 presents the results for hydrogen, methane, and reactor pH as a function of time. The profile for the digester pH shows that it started at pH 7.0, then it reached 8.1 at 0.18 hrs. It decreased afterward until the seventh day when it remained constant until the twentieth day.

The curves show that in the period of 0 to 1.5 days, there is methane production. The methane production increases until 0.19 days when the pH is 6.8, which marks the start of the inhibition of the anaerobic oxidation of LCFA and propionate [Siegriest et al., 2002]. Afterward, as the inhibition increases, the methane production rate decreases and, therefore, the hydrogen consumption decreases. The profile for hydrogen indicates that its consumption ends at 1.5 days; then, its production rate increases until achieving a constant production rate of 821.5 m^3/d on the seventh day.

The dissolved hydrogen also affects anaerobic oxidation; a concentration of 1 mg_{COD}/m^3 generates total inhibition [Siegriest et al., 2002]. At 1.5 days, the concentration was 20.1 mg_{COD}/m^3. Therefore, there is inhibition of the processes by dissolved hydrogen as well.

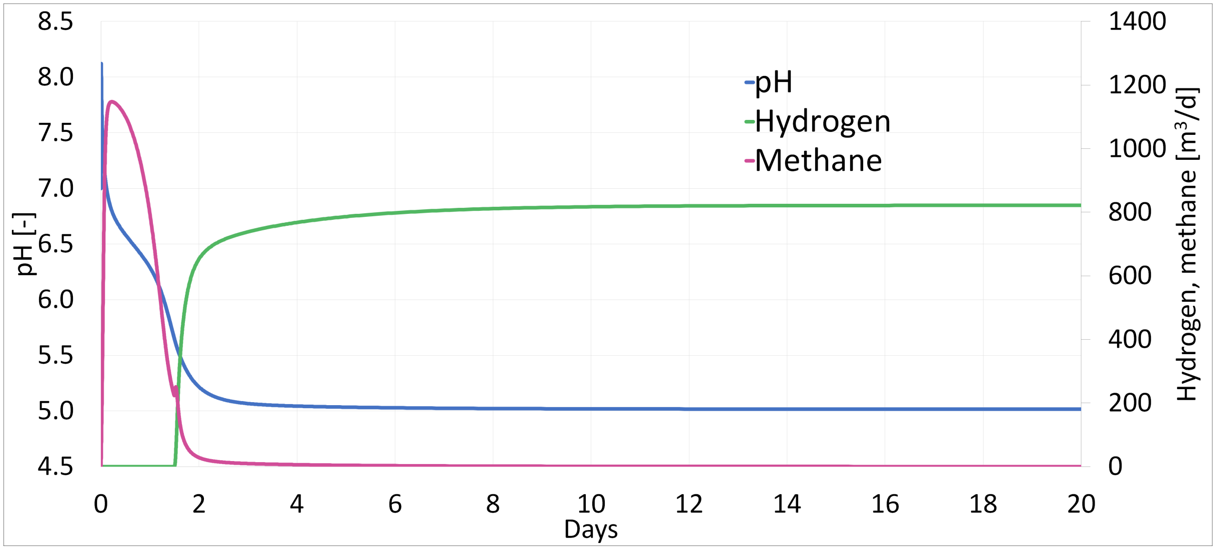


Figure 3.1: Results for hydrogen, methane and pH as function of time for SRT of 7 days and OLR of 21 $kg_{COD}/m^3 - d$

Figure 3.2 presents the results for the fermenters of amino acids and sugar along with the degraders of LCFA and propionate as a function of time. The profiles for the fermenters show a fast growth until day two; then, the rate decreases until its concentration does not experience variations from the eighth day.

The profiles for the degraders show that their concentration does not vary until day one. Then, the concentration decreases exponentially. It is important to mention that even though the process is been inhibited, the kinetic expressions of the decay processes are of first-order ($\rho_j = k_{d,j} \cdot X_i$) and the decay rate ($k_{d,j} = 0.06\ d^{-1}$) is constant.

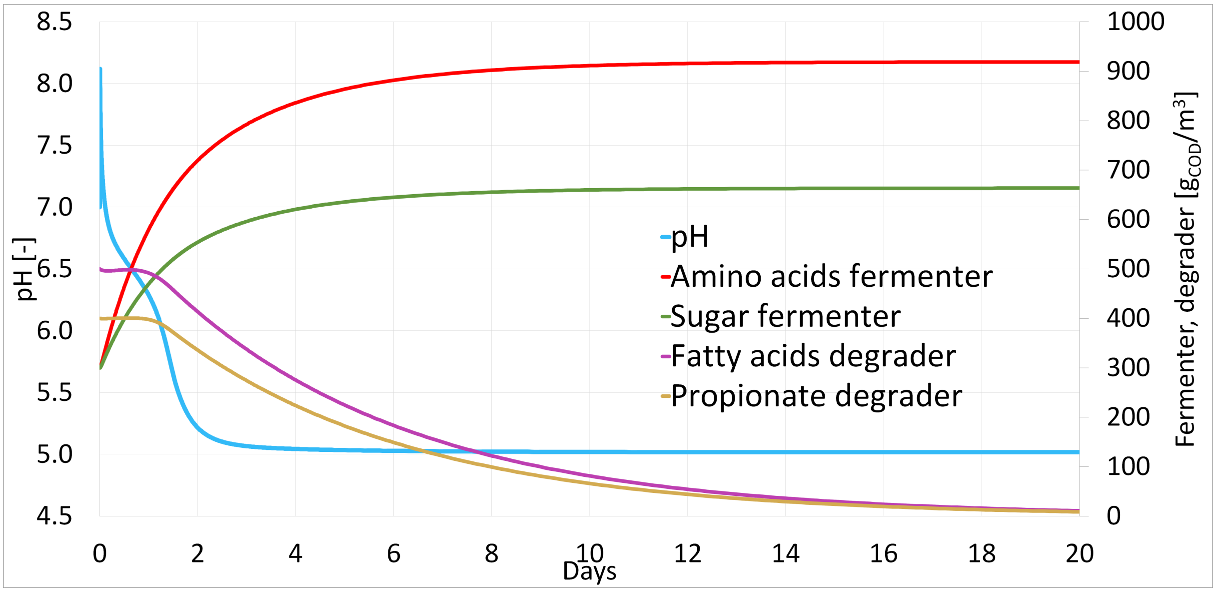
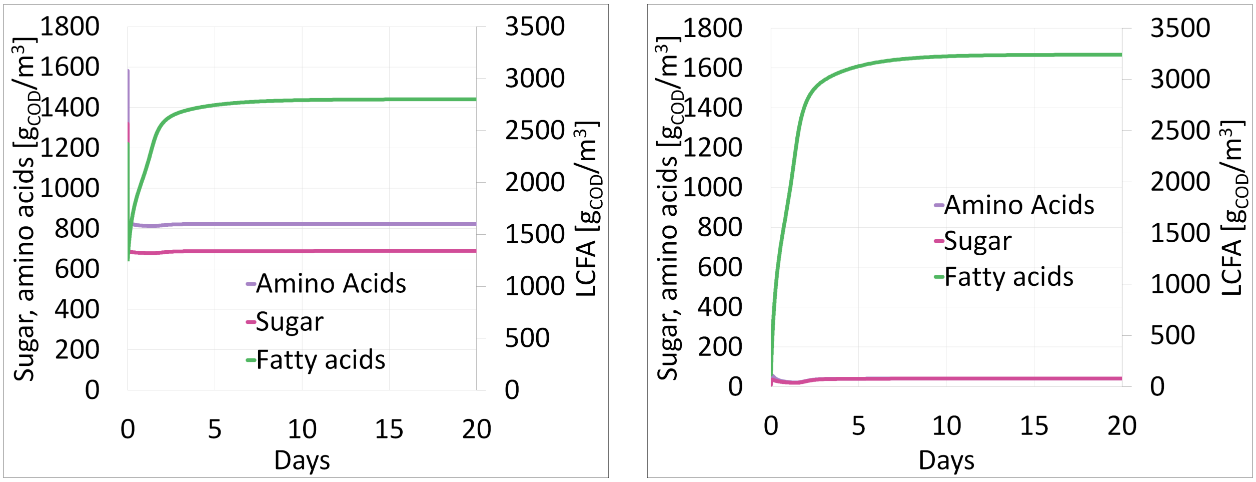


Figure 3.2: Results for fermenters and degraders as function of time for SRT of 7 days and OLR of 21 $kg_{COD}/m^3 - d$

Figure 3.3 presents the results of sugars, amino acids, and long-chain fatty acids measured before and after the digester, as a function of time. The concentration before the digester corresponds to the measured after mixing the influent with the recycle stream. The difference between the initial concentrations (Tables 3.1 and 3.2) generates a decrease in the substrate concentration, which is observed as a decay at 0 days in the profiles for before the digester.

The profiles for sugars and amino acids show that its concentration after the digester is lower than before the digester because both substrates are being fermented. The profile for LCFA shows that between 0 and 1.5 days its concentration increases but remains lower than before the digester because it is being consumed. Then, as the only process is the hydrolysis of lipids, the concentration of LCFA increases. Finally, from the seventh day, there is no more variation of the concentration.



(a) Results measured before the digester (b) Results mesured after the digester

Figure 3.3: Results for sugar and amino acids as a function of time for SRT of 7 days and OLR of 21 $kg_{COD}/m^3 - d$

Figure 3.4 presents the results for amino acids and sugar for the period of 0 to 5 days. The curves show a peak between 0 and 1.6 hours, which could be the start-up period. Afterward, there is substrate consumption (fermentation). The pH affects the fermentation process as well. The inhibition starts at a pH of 5.5, which occurred on day 1.5, and increases as the pH decreases. The fermentation occurs with a constant inhibition of 48% from day seven.

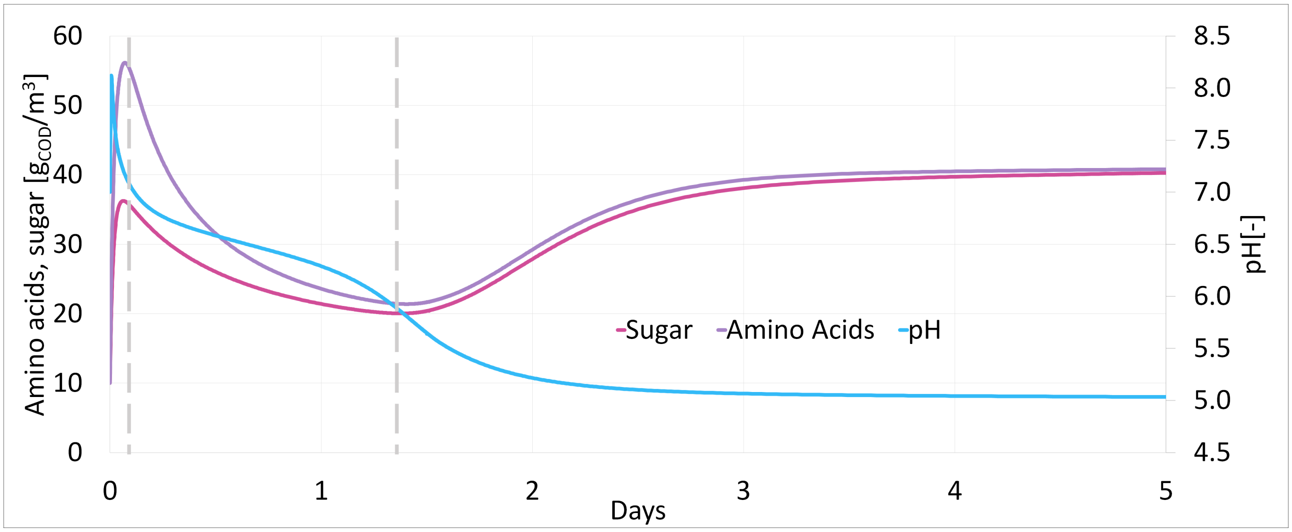
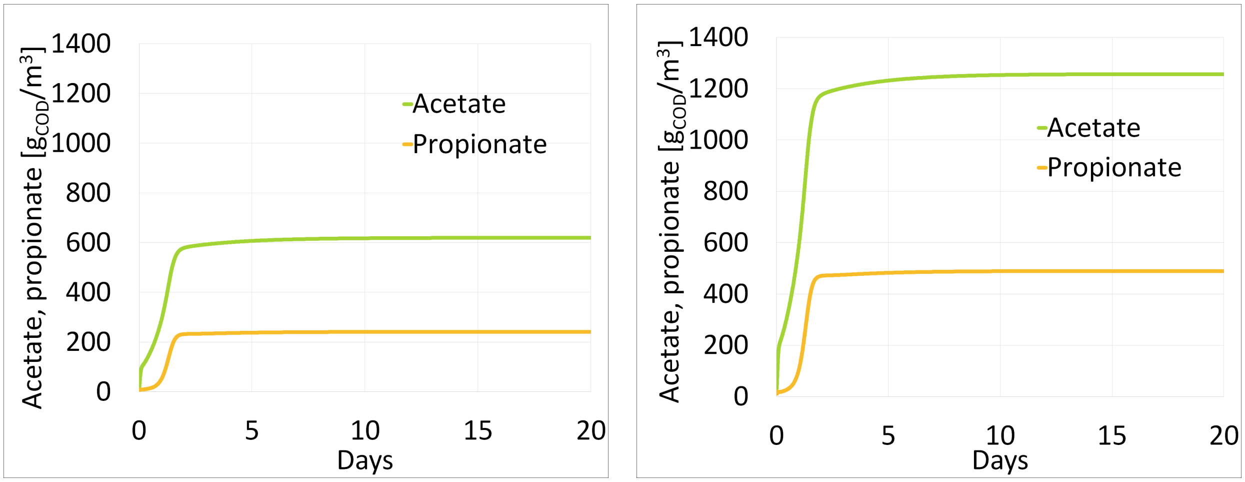


Figure 3.4: Results for sugar and amino acids for period between 0 to 5 days

Figure 3.5 presents the results for acetate, propionate as a function of time. The curves illustrates an increasing production until 1.5 days. Then, the production rate remains constant, which corroborate the inhibition of the processes. Besides, the concentration of acetate and propionate after the digester is higher than before the digester, which confirm the fermentation of amino acids and sugars.



(a) Results measured before the digester

(b) Results mesured after the digester

Figure 3.5: Results for acetate and propionate as a function of time for SRT of 7 days and OLR of 21 $kg_{COD}/m^3 - d$

In summary, after the seventh day there were no more variation in the pH, hydrogen production and substrate concentration. The processes that occurred were hydrolysis, fermentation, anaerobic oxidation and methanogenesis. The pH partially inhibited the fermentation (48%). Meanwhile, the anaerobic oxidation of propionate and LCFA was entirely inhibited by pH and hydrogen from the second day. These results allowed the researcher to conclude that the model achieved to describe the key processes for the CBMem implementation (hydrolysis and fermentation).

3.2. Overall operation of AnMBR under OLR and SRT changes

The AnMBR was started with an OLR of 10 $kg_{COD}/m^3 - d$. Then, the volumetric OLR was increased in a stepwise manner to $30 kg_{COD}/m^3 - d$. The reactor and sludge phase volume were adjusted to achieve the OLR changes. The SRT was gradually increased from 2 to 15 days as well. The bioreactor temperature was constant at 35 °C for the complete study, and each OLR was maintained for 20 days to ensure no further changes in the sludge composition.

Figure 3.6 shows the stepwise increase in OLR and its corresponding HRT. The profile shows the inverse relationship between HRT and OLR as in equation 3.6. As the organic loading rate increments, a lower hydraulic retention time is required.

The OLR also is inversely proportional to the reactor volume and SRT, as in equation 2.1. Therefore, to achieve smaller volumes, higher organic loading rates are required. In addition, at an SRT fixed, to achieve higher OLR, the waste flow should decrease as in equation 2.2.

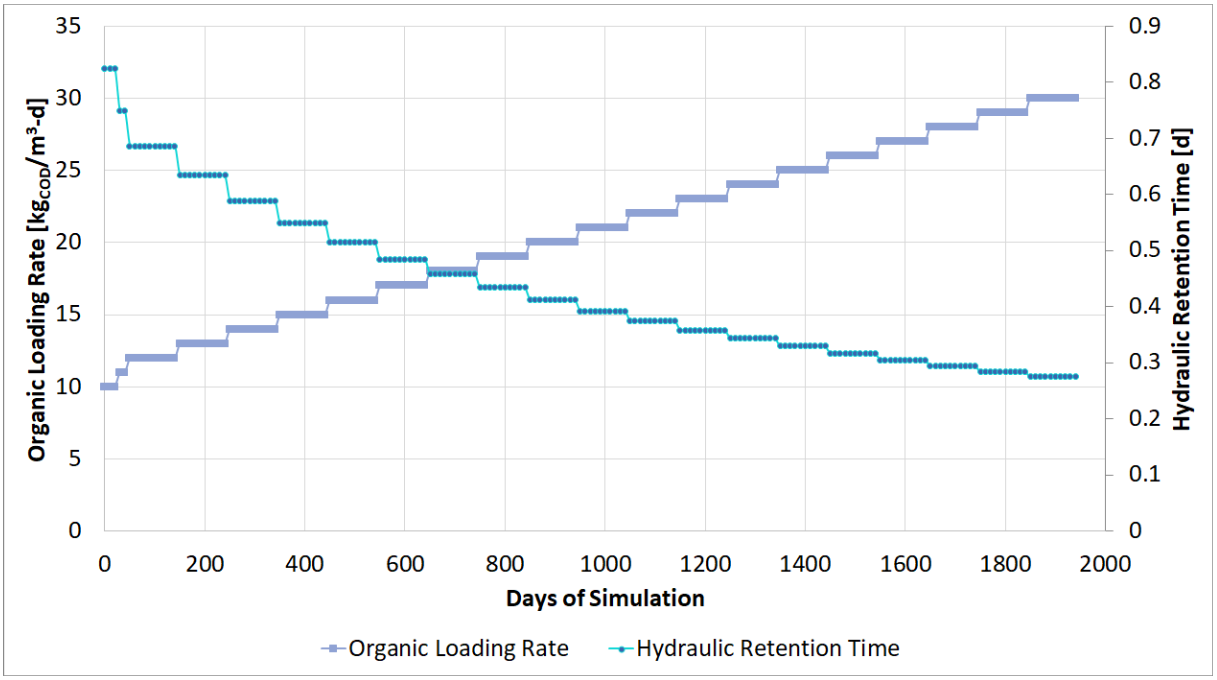
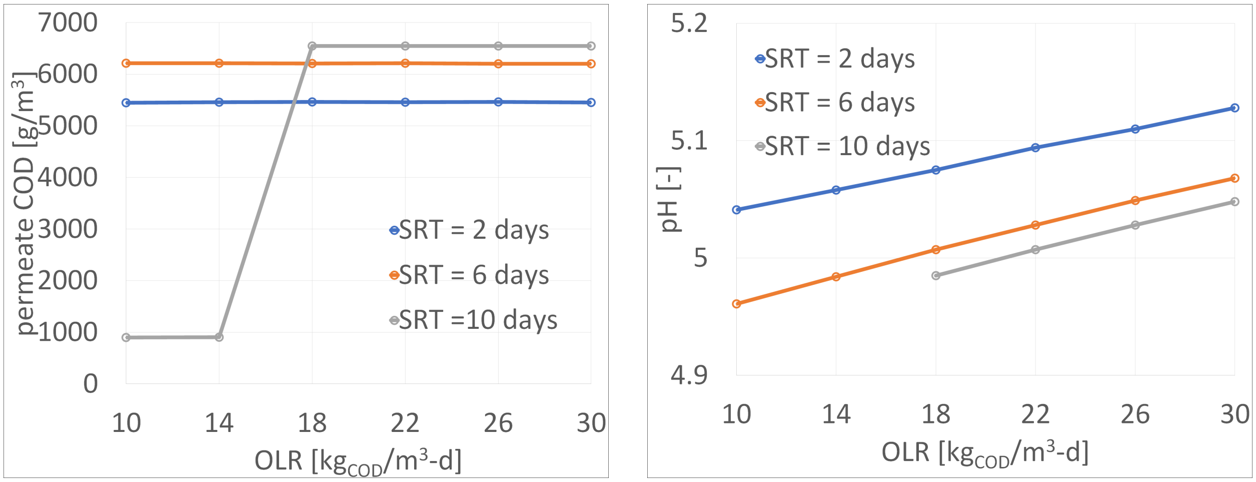


Figure 3.6: Organic Loading Rate and corresponding hydraulic retention time

The performance of the AnMBR in terms of permeate COD, reactor pH, MLVSS, and hydrogen production was analyzed. Figure 3.7 (a) presents the results obtained for permeate COD as a function of SRT and OLR. The profile for SRT of 10 days shows that at smaller OLR (higher volumes), there was consumption of the majority of the organic matter. This phenom is due to the occurrence of the four stages of anaerobic digestion; hence, there was methane production. Therefore, the OLR promotes the inhibitory mechanism of the methanogenic activity, as suggested by López-Escobar et al. (2014). For the analyses, only the conditions that ensured hydrogen production were considered.

The curves show that the permeate COD is directly proportional to the SRT. Besides, at a fixed SRT, it is noted that changes in the OLR or reactor volume do not generate significant changes in the permeate COD.



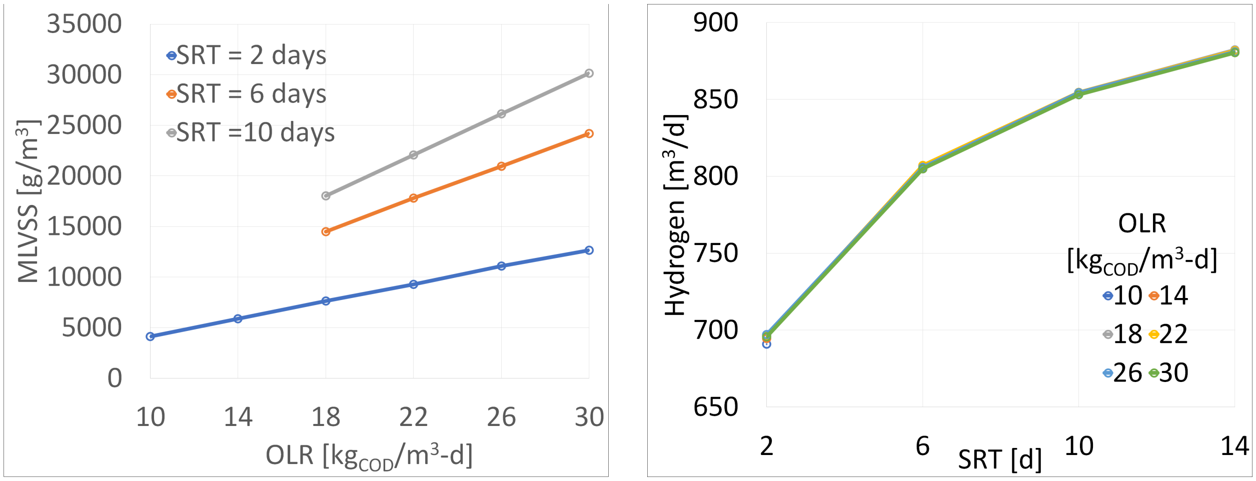
(a) Permeate COD as function of OLR and SRT

(b) Reactor pH as function of OLR and SRT

Figure 3.7: Results for permeate COD and reactor pH as a function of SRT and OLR

The results obtained for reactor pH are presented in figure 3.7 (b). The curves show that the pH is inversely proportional to the SRT. Besides, there is a slight increase in the reactor pH with the OLR increment (for example, at SRT of 6 days, the increment is 0.1).

The curves for MLVSS show that the MLVSS is directly proportional to the OLR and the SRT, as illustrated in figure 3.8 (a). Figure 3.8(b) presents the results for hydrogen production in terms of m^3/d. The profile shows that hydrogen production is directly proportional to SRT, and that the increment rate decreases as the SRT increases. Besides, the curves overlap, indicating that the OLR does not generate significant changes in the hydrogen production.

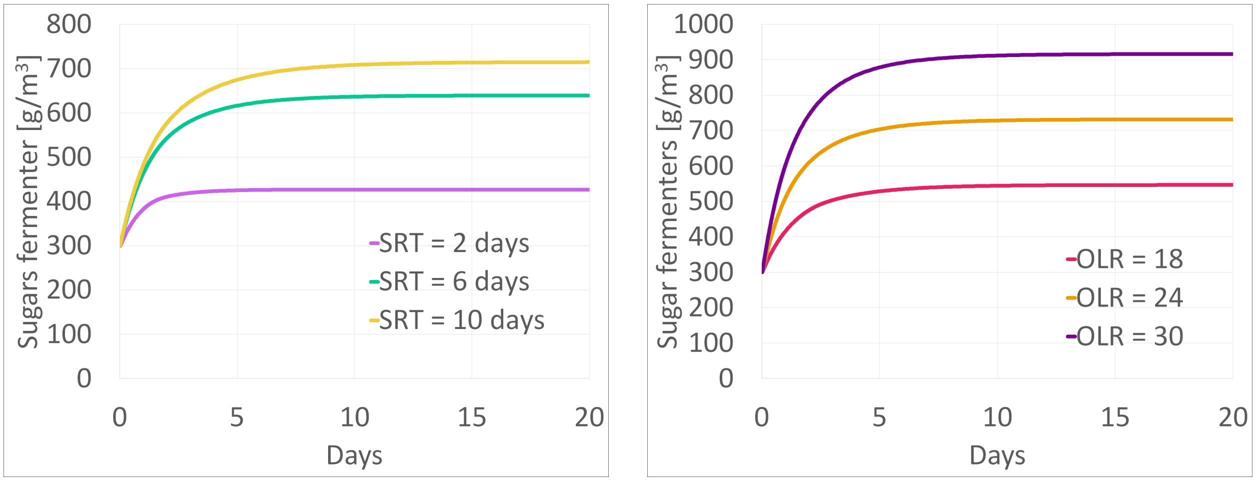


(a) MLVSS as function of OLR and SRT

(b) Hydrogen production as function of OLR and SRT

Figure 3.8: Results mixed liquor volatile suspended solid (MLVSS) and hydrogen production as function of OLR and SRT

The researcher considered the results for sugar, amino acids, fatty acids, acetate, and biomass to analyze these outcomes. The principal bacterial community present corresponds to sugar and amino acid fermenters. Figure 3.9 presents the results for sugar fermenter as a function of time. The amino acid fermenter concentration behavior is similar to the one presented. As discussed, the fatty acids degrader concentration decreases with time until reaching 0 at 20 days (see Annexed B for amino acid fermenter and fatty acids degrader curves).



(a) Results for SRT of 2, 6 and 10 days, and OLR of 21 $kg_{COD}/m^3 - d$

(b) Results for OLR of 18, 24 and 30 $kg_{COD}/m^3 - d$, and SRT of 6 days

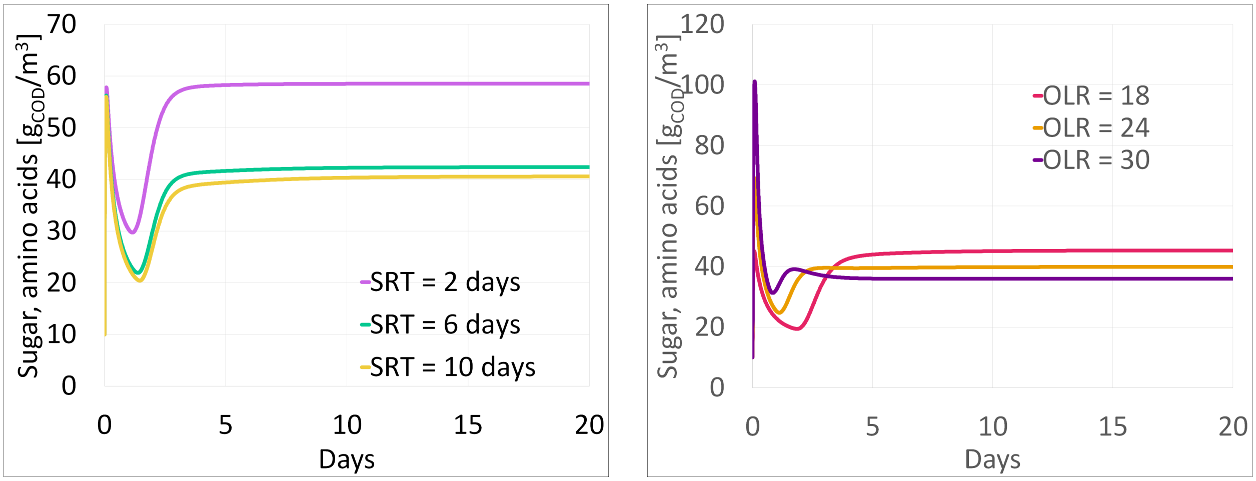
Figure 3.9: Results for sugar fermenters as a function of SRT and OLR

The curves show that the biomass concentration increases with the SRT. This is because the solids retention time controls the concentration of bacteria throughout the system. Therefore, a higher SRT contributes to a higher bacterial concentration in the reactor [Wong et al., 2003].

Besides, the profile shows that the biomass concentration increases with OLR. This phenom is because more carbon sources are available for the biomass to grow, as suggested in the literature [Roopnarain et al., 2021]. However, high substrate concentrations may generate inhibitions in the system or even changes in the microbial pathways [Grangeiro et al., 2019]. Therefore, it is fundamental to determine appropriate conditions for the system and case-specific considering all operational variables.

The MLVSS is used to measure or indicate the microorganisms present. Therefore, as discussed for the biomass concentration (Figure 3.9), the MLVSS increases with the SRT and OLR increment.

Figures 3.10 and 3.11 present the results for sugar, amino acids and long-chain fatty acids measured immediately after the digester.



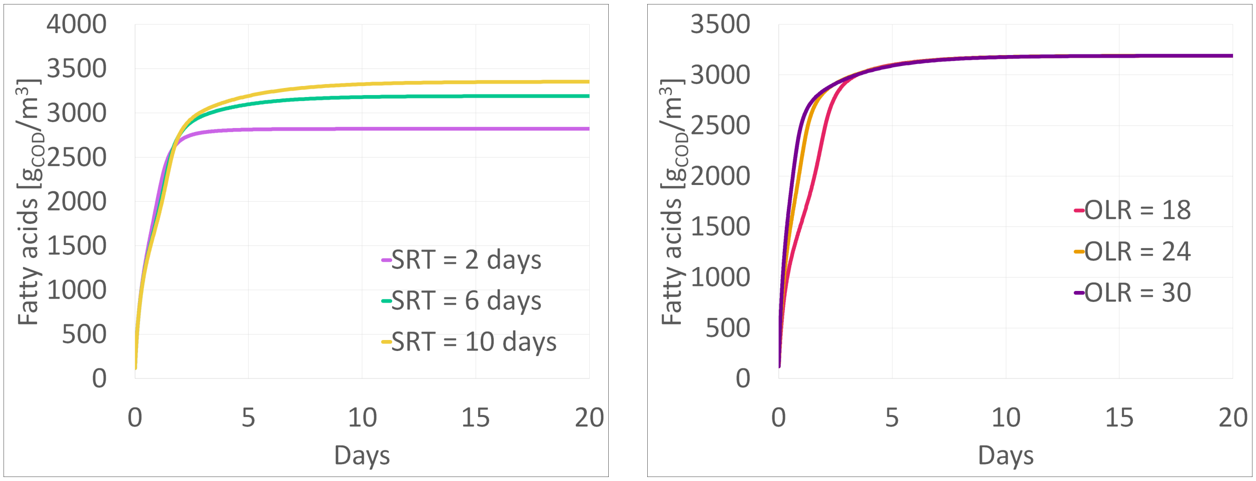
(a) Results for SRT of 2, 6 and 10 days, and OLR of 21 $kg_{COD}/m^3 - d$

(b) Results for OLR of 18, 24 and 30 $kg_{COD}/m^3 - d$, and SRT of 6 days

Figure 3.10: Results for sugar and amino acids as a function of SRT and OLR

The curves show that the sugar and amino acids concentration decrease with the solid retention time increment. This outcome is because there is more fermenters concentration, there is more substrate consumption. Similarly, there is more sugar and amino acids fermentation as the OLR increases.

As discussed before, the degradation of fatty acids is inhibited by pH. Therefore, the hydrolysis of lipids is the only process occurring, as illustrated in figure 3.11. The curves show that the hydrolysis of lipids increased with increasing SRT, as suggested by the literature [Miron et al., 2000]. On the contrary, the OLR (or volume) changes does not generate changes in the final fatty acids concentration.



(a) Results for SRT of 2, 6 and 10 days, and OLR of 21 $kg_{COD}/m^3 - d$

(b) Results for OLR of 18, 24 and 30 $kg_{COD}/m^3 - d$, and SRT of 6 days

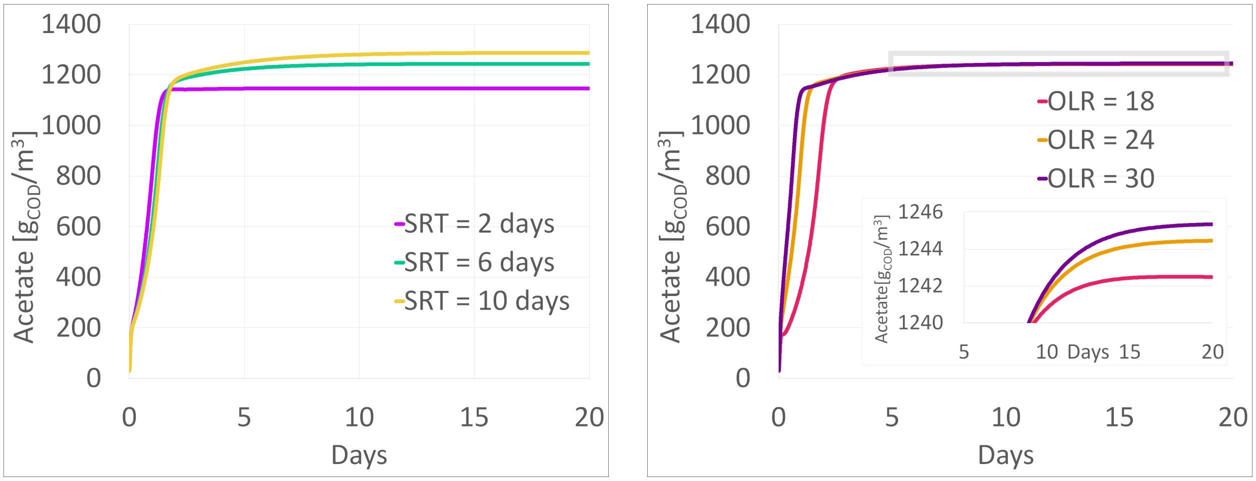
Figure 3.11: Results for long-chain fatty acids as a function of SRT and OLR

Table 3.3 presents a resume for sugar, amino acids and fatty acids as concentration. As mentioned, these concentrations were measured immediately after the digester. The results corroborate the analysis realized previously. The effluent COD is directly proportional to the SRT, and the OLR or reactor volume variations do not generate significant changes.

Table 3.3: Results for COD (sugars, amino acids, and fatty acids) for SRT of 2, 6 and 10 days (OLR of 21 $kg_{COD}/m^3 - d$), and for OLR of 18, 24 and 30 $kg_{COD}/m^3 - d$ (SRT of 6 days)

SRT [d]	COD [g/m^3]	OLR [$kg_{COD}/m^3 - d$]	COD [g/m^3]
2	2937	18	3280
6	3275	24	3270
10	3433	30	3261

The inverse relationship between the reactor pH and the solids retention time is related to acetate production. Figure 3.12 presents the results for acetate as a function of time. The profile shows that as the SRT increases, there is more production of acetate, which accumulation decreases the buffer capacity and lowers the pH [Siegrist et al., 2002]. On the contrary, variations in the OLR or reactor volume do not generate significant changes in the acetate concentration.



(a) Results at SRT of 2, 6 and 10 days, and OLR of 21 $kg_{COD}/m^3 - d$

(b) Results at OLR of 18, 24 and 30 $kg_{COD}/m^3 - d$, and SRT of 6 days

Figure 3.12: Results for acetate as a function of SRT and OLR

As was previously mentioned, amino acids and sugars are fermented to produce propionate, acetate and hydrogen. The relationship between hydrogen and SRT and OLR is similar to the one discussed for acetate (Figure 3.12). As the SRT increases, there is more fermentation of amino acids and sugars (Figure 3.10), which produces more hydrogen. However, the difference in the concentration between SRT of 2 days and 6 days is higher than between 6 and 10 days, which indicates that the increment rate decreases as the SRT increases. The OLR does not generate significant changes in the fermentation process.

In summary, the relationship between permeate COD and SRT is principally related to the hydrolysis of lipids, which increases with the SRT. Besides, the reactor pH variation is related to acetate, which concentration increases with SRT, and its accumulation lowers the pH. The MLVSS increment with SRT and OLR is related to the biomass concentration (fermenters). A higher SRT contributes to a higher bacterial concentration in the reactor, and higher OLR contributes to more carbon sources for the biomass to grow. Finally, hydrogen production increases with SRT because more sugar and amino acid fermentation occur.

Operating the AnMBR at a high solid retention time (SRT) allows higher hydrogen productions and smaller sludge volumes. Therefore, it is advisable to operate at higher SRT. However, there is less COD removal, the reactor pH decreases and increases the MLVSS. The OLR increment promotes the inhibitory mechanism of the methanogenic activity. Therefore, it is advisable to operate at a higher OLR. However, it does not influence the removal of COD and hydrogen production, and higher OLR increase the MLVSS and slightly increase the reactor pH. It is highlighted that higher OLR also means small reactor volumes and HRTs, which some authors prefer for hydrogen production [Banu et al., 2020].

3.3. Selection of the operational conditions for the AnMBR

The effect of changes in OLR and SRT on permeate COD was analyzed first. As discussed, there was consumption of the majority of the organic matter at some operational conditions. These conditions do not allow the CBMem implementation because the permeate COD was not higher than 2000 mg/L. Because of that, the researcher identified the minimum OLR for each SRT that fulfilled the requirement as illustrated in figure 3.13.

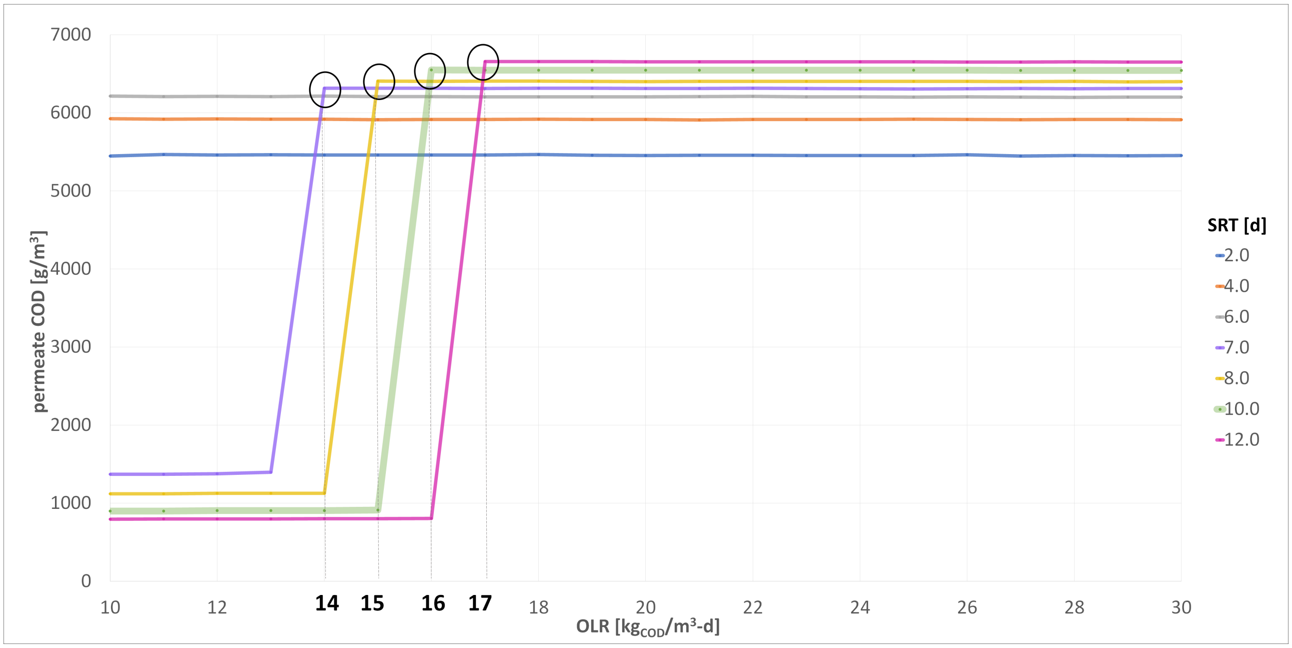


Figure 3.13: Permeate COD as function of OLR and SRT

The results for SRT between 2 and 6 days showed that at OLR in the range of 10 to 30 $kg_{COD}/m^3 - d$, the permeate COD was higher than 2000 mg/L. On the contrary, for higher SRT, the requirement was fulfilled at higher OLR. Table 3.4 presents the operational conditions that ensured a permeate COD greater than 2000 mg/L.

Table 3.4: Selected operational conditions that ensured a permeate COD greater than 2000 [mg/L]

SRT [d]	OLR $[kg_{COD}/m^3 - d]$
2-6	10-30
7	14-30
8	15-30
9-11	16-30
12-15	17-30

The effect on reactor pH was analyzed secondly. The reactor pH results ranged between 4.96 and 5.13. Considering that the literature recommends a pH higher than 5.0 for hydrogen production, the researcher identified the minimum OLR for each SRT that ensures that condition, as illustrated in figure 3.14.

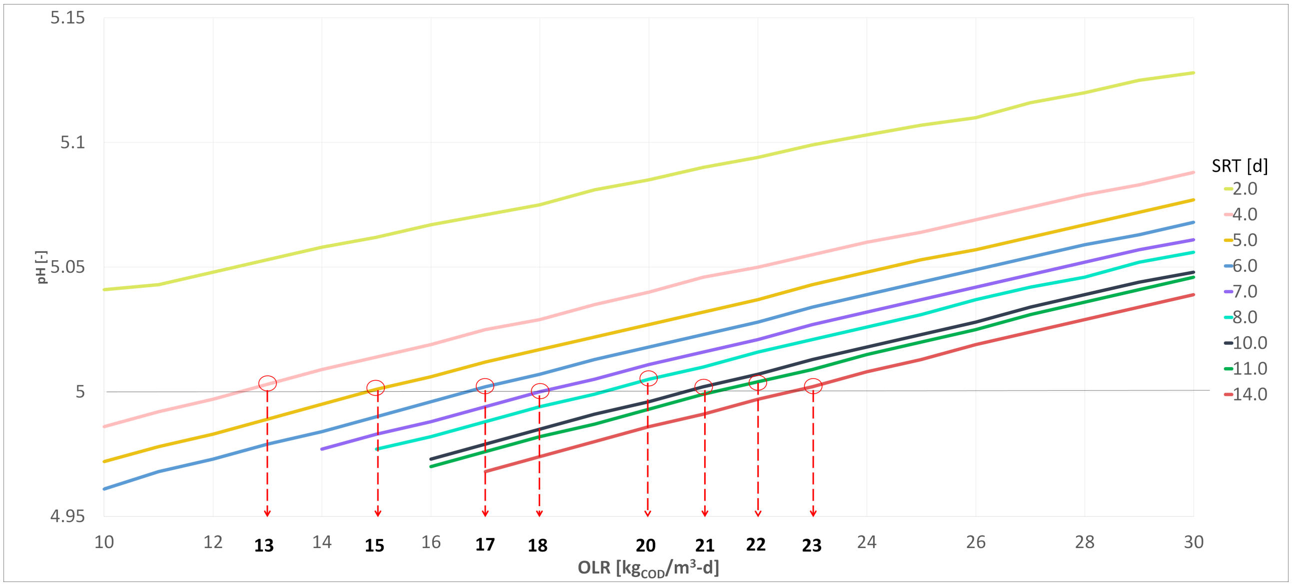


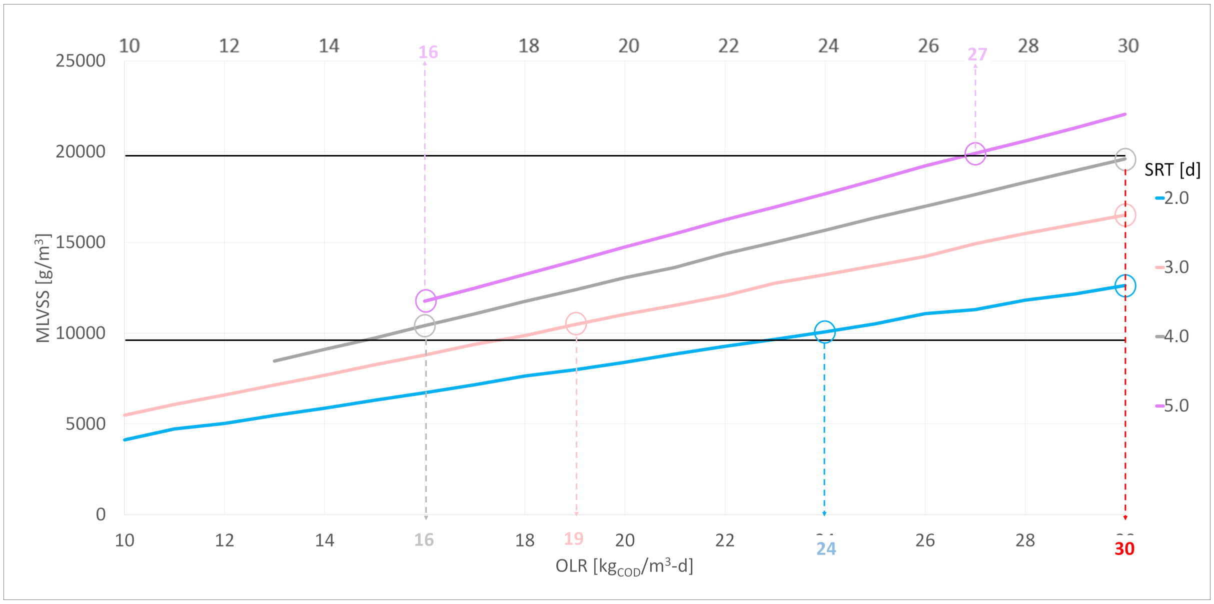
Figure 3.14: Reactor pH as function of OLR and SRT

The results for SRT of 2 and 3 days showed that at OLR in the range of 10 to 30 kg_{COD}/m^3d, the reactor pH was higher than 5.0. On the contrary, for higher SRT, the requirement was fulfilled at higher OLR. Table 3.5 presents the operation conditions selected that ensured a reactor pH higher than 5.0.

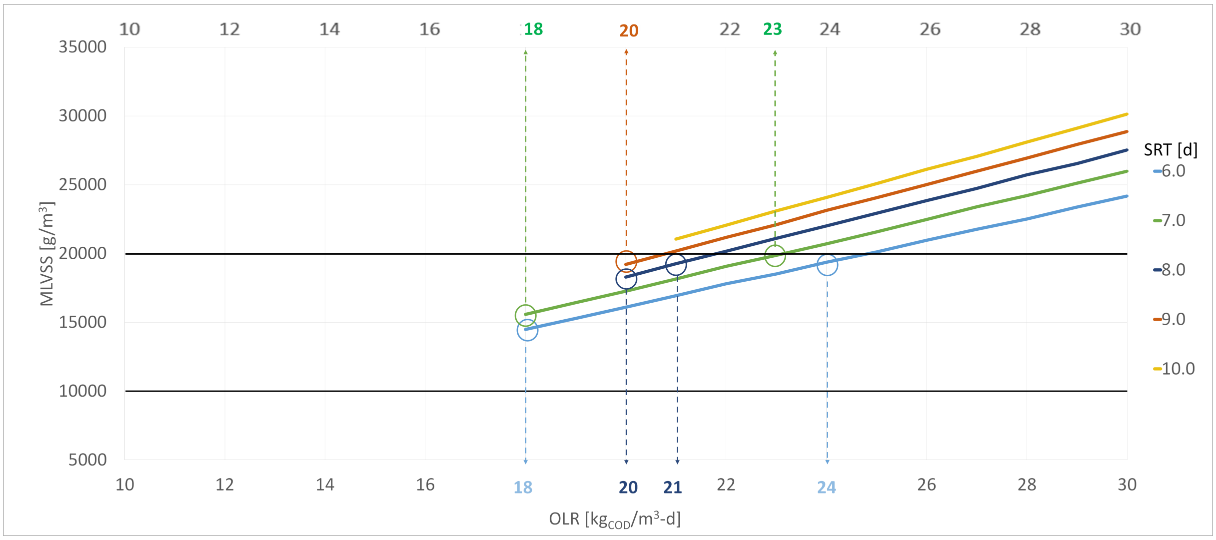
Table 3.5: Selected operational conditions that ensured a reactor pH higher than 5.0

SRT [d]	OLR $[kg_{COD}/m^3 - d]$
2-3	10-30
4	13-30
5	15-30
6	17-30
7	18-30
8-9	20-30
10	21-30
11-12	22-30
13-15	23-30

The effect on MLVSS was analyzed afterward. The MLVSS results ranged between 4000 and 35000 g/m^3. Considering that the literature recommends a MLVSS in the range of 10 to 20 g/L (membrane criteria), the researcher identified the minimum OLR for each SRT that ensures that condition, as illustrated in figure 3.15.



(a) Results for SRT of 2, 3, 4 and 5 days



(b) ResultsSRT of 6, 7, 8, 9 and 10 days

Figure 3.15: Results for mixed liquor volatile suspended solids as function of OLR and SRT

Table 3.6 presents the operation conditions selected that ensured the mixed liquor volatile suspended solids in the range of 10 to 20 g/L

Table 3.6: Selected operational conditions that ensured a MLVSS in the range of 10 to 20 g/L

SRT [d]	OLR [$kg_{COD}/m^3 - d$]
2	24-30
3	19-30
4	16-30
5	16-27
6	8-24
7	18-23
8	20-21
9	20
10-15	-

The effect on biogas and hydrogen production was analyzed at last. It was observed that as the SRT increased so did the biogas production, due to the diminution in the waste flow. Besides, a 56% of hydrogen in the biogas was obtained on average.

The hydrogen production is directly proportional to SRT and the increment rate decreases as the SRT increases, as illustrated in figure 3.16.

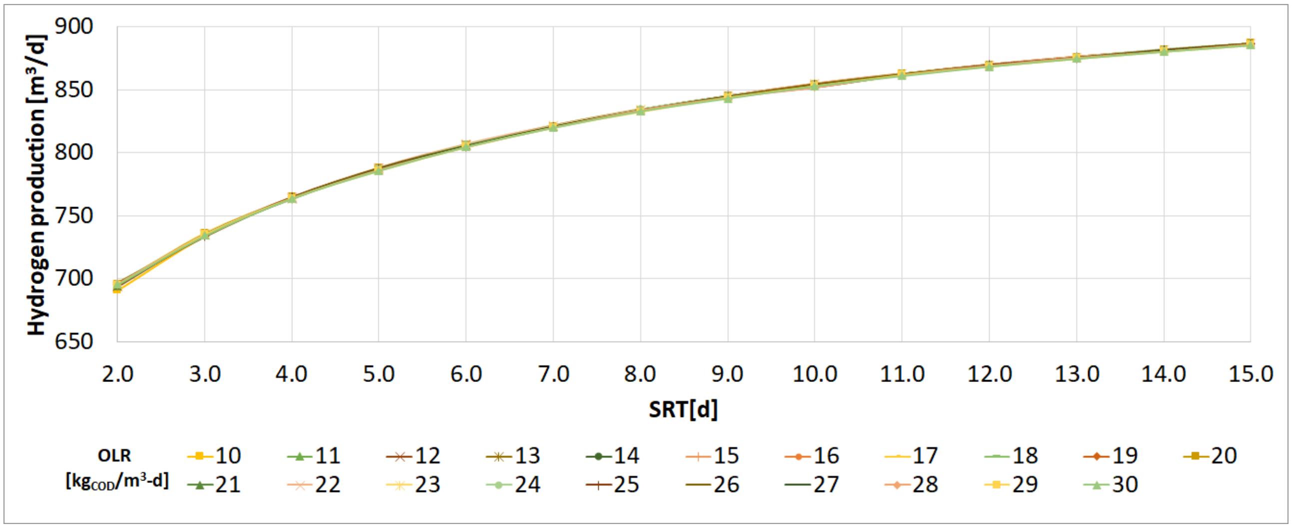


Figure 3.16: Hydrogen production as function of OLR and SRT

Table 3.7 presents the results obtained for hydrogen production as function of the SRT.

Table 3.7: Hydrogen production as function of SRT

SRT [d]	H_2 [m^3/d]	H_2 [kg/d]
2.0	695	58.3
3.0	735	61.7
4.0	764	64.1
5.0	788	66.1
6.0	806	67.6
7.0	821	68.8
8.0	834	69.9
9.0	845	70.9

In conclusion, for hydrogen generation is better to operate the AnMBR at higher SRT. Besides, as the SRT increases, the reactor volume should be low to ensure the fulfillment of the CBMem requirement, a reactor pH above 5.0, and a MLVSS in the range of 10 to 20 g/L.

Finally, the researcher selected the operational condition that obtained higher hydrogen production and maintained an MLVSS in the range of 15 to 18 g/L (design criteria). Table 3.8 presents the condition selected to implement the AnMBR as pre-treatment for the CBMem and for hydrogen production.

Table 3.8: Selected operational condition for AnMBR

SRT [d]	7.0	pH	5.02
HRT [hr]	9.4	H_2 [m^3/d]	821
Volume [m^3]	392	H_2 [kg/d]	68.8
OLR [$kg_{COD}/m^3 - d$]	21	COD_{rem}	23%
Permeate soluble COD [g/m^3]	6312	Q gas [m_3/d]	1372
Wasted sludge [kg/d]	1020	% H_2	55.8%

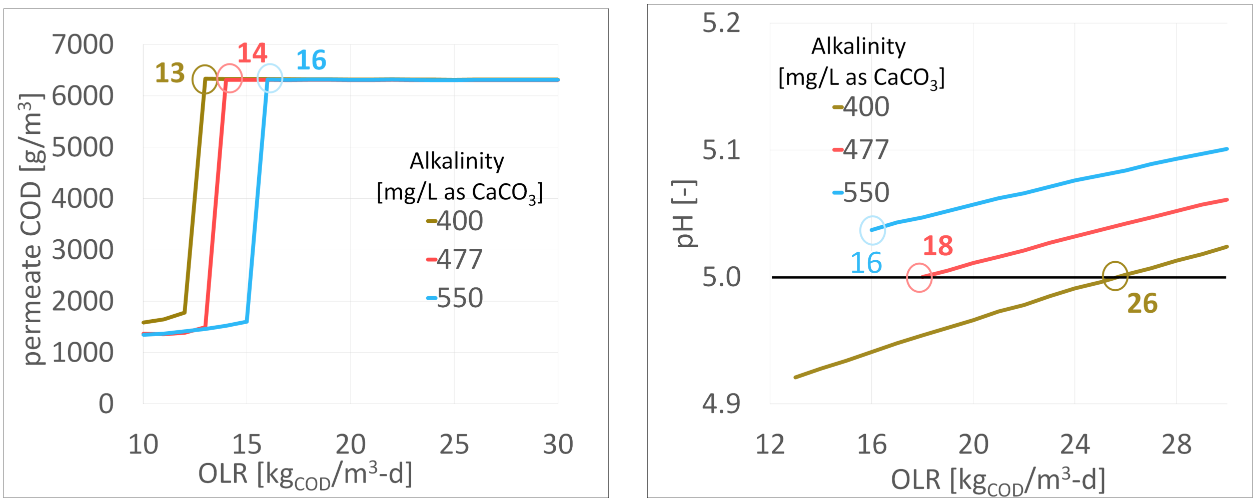
It is essential to highlight that the results obtained were for a particular wastewater. Therefore, it is not advisable to directly use these results. It is imperative to ensure that the influent characteristics and the fractions are comparable to apply this study to another wastewater.

3.4. Overall operation of AnMBR under alkalinity changes at selected operating conditions

The effect of changes on the alkalinity on permeate COD, reactor pH, MLVSS and hydrogen production was analyzed. The values adopted were 400, 477 and 550 mg/L as $CaCO_3$.

The effect of changes in the alkalinity on permeate COD was analyzed first, as presented in figure 3.17 (a). The curves show that as the wastewater has more alkalinity, it is more probable that occurs the four stages of anaerobic digestion at low OLRs. On the contrary, at lower acid neutralization capacity, the inhibition of the methanogenesis process occurs at smaller OLR (higher volumes).

The effect on reactor pH was analyzed secondly. Figure 3.17 (b) presents the results for reactor pH as a function of OLR and alkalinity for SRT of 7 days. The curves show that as the acid neutralization capacity of the wastewater is lower, the AnMBR should operate at lower HRT and volume (higher OLR) to ensure a reactor pH above 5.0. On the contrary, the AnMBR could operate at higher volumes when the wastewater has higher alkalinity.



(a) Permeate COD as function of OLR and alkalinity (b) Reactor pH as function of OLR and alkalinity

Figure 3.17: Results for permeate COD and reactor pH as a function of OLR and alkalinity for SRT of 7 days

The effect on MLVSS was analyzed afterward. Figure 3.18 presents the results for MLVSS as a function of OLR and alkalinity for SRT of 7 days. The curves show that as the wastewater has low alkalinity, no operation condition ensures the MLVSS is in the range of 10 to 20 g/L. This outcome is due to the high OLR required to fulfill the pH requirement, which respective small volume generates a high concentration in the reactor. On the contrary, when the acid neutralization capacity is higher, the AnMBR could operate at higher HRTs or volumes.

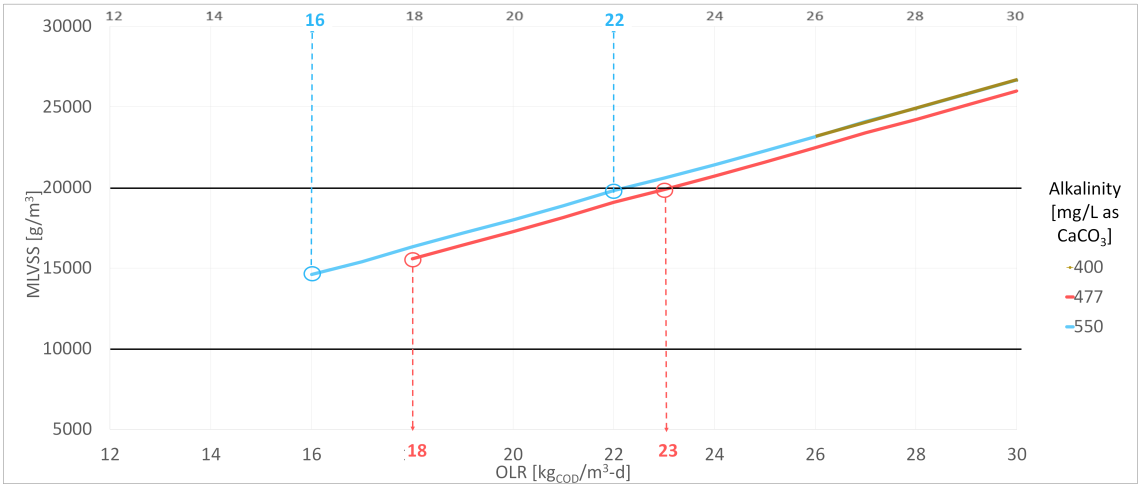


Figure 3.18: Mixed liquor volatile suspended solids as function of OLR and alkalinity for SRT of 7 days

Finally, the effect of the alkalinity on hydrogen production was analyzed. Table 3.9 presents the results for H_2 production as a function of alkalinity for SRT of 7 days. The results show that as the alkalinity increased, the biogas production increased as well, hence, the hydrogen production.

Table 3.9: Hydrogen production as function of alkalinity for SRT of 7 days

Alkalinity [mg/L as $CaCO_3$]	H_2 [m^3/d]	H_2 [kg/d]
400	818	68.6
477	821	68.8
550	825	69.2

To analyze this outcome, figure 3.19 presents the results for amino acids fermenters as a function of alkalinity. The curves show that the fermenters concentration increases with the alkalinity, mainly due to less inhibition by pH.

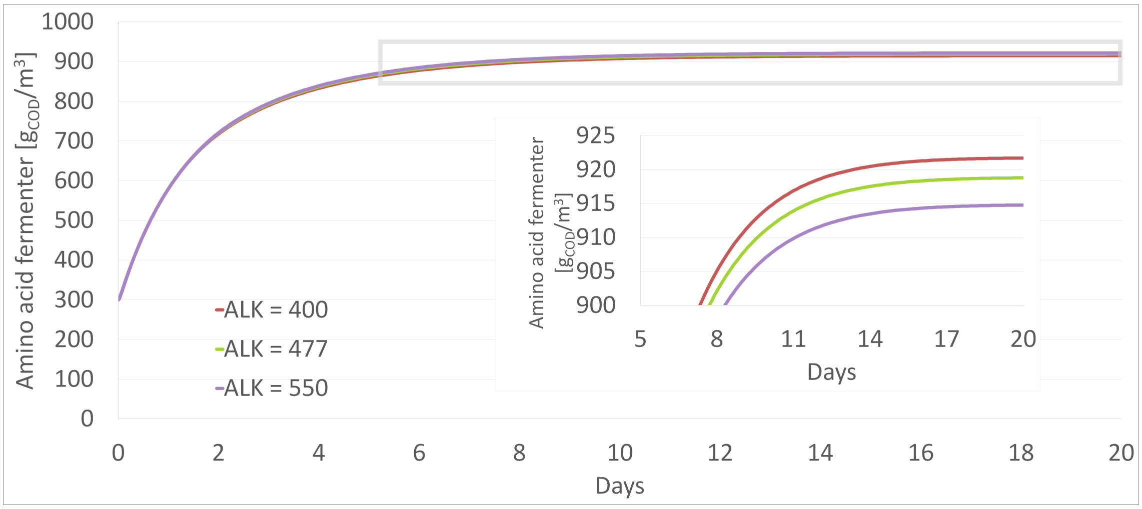
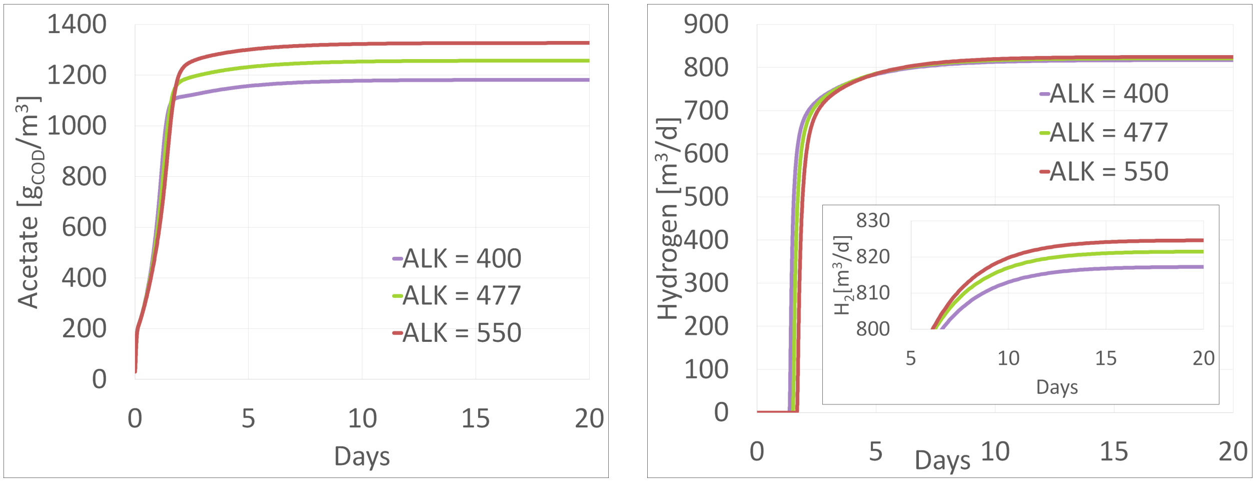


Figure 3.19: Amino acids fermenters as function of alkalinity for SRT of 7 days and OLR 21 $kg_{COD}/m^3 - d$

Figure 3.20 presents the results for acetate and hydrogen produced as a function of alkalinity. The profiles show that there is more fermentation of amino acids and sugars. Therefore, there is more production of acetate and hydrogen, as discussed before.



(a) Results for acetate

(b) Results for hydrogen

Figure 3.20: Results for acetate and hydrogen produced as function of alkalinity for SRT of 7 days and OLR 21 $kg_{COD}/m^3 - d$

In summary, it is better that the wastewater has more alkalinity because there is more fermentation of amino acids and sugars. Besides, the AnMBR could operate at higher HRTs or volumes, and it still will be ensured the inhibition of the methanogenesis process, a reactor pH above 5.0, and higher hydrogen production. However, adding alkalinity to the wastewater entails an economical cost. Therefore, the designer of the treatment plant should analyze if the increase in hydrogen production is economically favorable.

3.5. Advantages and disadvantages of the implementation of the AnMBR in the wine production industry.

The main disadvantages of anaerobic processes are the requirement of a long time to stabilize the microbial culture within the reactor and constant monitoring of the process parameters. The AnMBR has a high investment cost primarily because of the membrane. Besides, fouling is a perennial issue [Pramodbabu et al., 2021; Náthia-Neves et al., 2018].

Anaerobic bacteria have a slower metabolism than aerobic. They require a longer time to stabilize the microbial culture within the reactor. The behavior of the microorganisms responsible for biogas production is affected by the process parameters, such as temperature, pH, HRT, and OLR. For example, acetogenic bacteria are more difficult to adapt to pH changes than other microorganisms. Thus, it is crucial to a real-time control for the success of the anaerobic digestion process [Wu et al., 2019]. This problem is challenging to overcome, primarily because most treatment plants focus on guaranteeing the fulfillment of the legislation without the need for comprehensive process monitoring. Besides, most anaerobic reactors operation is as *black boxes* [Wu et al., 2019; Madsen et al., 2011].

Regarding membrane fouling, it is a perennial issue that has impeded greater acceptance of the system. It depends on the membrane material, operating conditions, influent, and sludge characteristics. Researchers have developed control strategies to slow the rate of fouling. These strategies may be physical, chemical, or biological. Biogas sparging and crossflow velocity (CFV) are the most commonly used to generate high shear force at membrane surfaces during AnMBR operation. These control strategies have proven effective in scouring the membrane surface and mitigating the AnMBR fouling rate. However, they have a specific gas demand per unit membrane area (the produced biogas is recycled) or a specific crossflow velocity demand [Bokhary et al., 2020; Ng et al., 2020].

Moreover, the process allows the formation of a sludge that could go through another anaerobic digestion to obtain methane and a co-product called digestate [Srisowmeya et al., 2020; INN, 2015]. The digestate has positively affected grains, vegetables, and fruit yields compared to other fertilizers and soil amendments. However, most research has been conducted using palm oil mill effluent and food and dairy processing wastes [Marti et al., 2021; Groot & Bogdanski, 2013]. Therefore, the sludge produced from winery wastewater is a by-product that requires more research and defining a strategy for its disposal in the meantime.

The principal advantages of implementing the AnMBR in the wine production industry are energy recovery, COD removal, and that it could be a compact system. Due to shorter HRT, the AnMBRs are suitable for applications in urban areas, which minimizes conveyance costs and allows decentralized treatment [Pramodbabu et al., 2021]. The AnMBR achieved a 23% of COD removal, which could reduce the posterior treatment costs.

Regarding energy recovery, the researcher evaluated the potential of the selected operational condition (SRT of 7 days and OLR of 21 kg_{COD}/m^3-d), for which hydrogen production was 68.6 kg_{H_2}/d. Besides, the conversion efficiency considered was the minimum for H_2-air fuel cell (75.7%) [Haseli, 2018]. Table 3.10 presents the energy recovery potential of the AnMBR that treated winery wastewater at an influent flow of 1000 m^3/d.

Table 3.10: Energy potential of the hydrogen produced in the AnMBR for a plant of 1000 m^3/d

Conversion Hydrogen energy potential [kWH/kg]	33.33
Conversion efficiency	75.7%
H_2 [kg/d]	68.6
Energy Production [MWH per annum] (261 working days in the 2021)	451.5

Regarding the energy demand, the total requirement of the winery was 3819 MWh in 2021, and for the AnMBR the researcher considered a requirement of 1.3 kWh/$m^3_{treated}$ contemplating a crossflow velocity strategy to mitigate the fouling [Viña Concha y Toro, 2022; Zhen et al., 2019]. Besides, an average discharge flow of 476 m^3/d in 2021 was considered [SEIA, 2017]. Table 3.11 presents the results for the energy recovery potential. The result shows that the available energy amount the 1.4% of the demand.

Table 3.11: Energy potential of the hydrogen produced

Energy production [MWH per annum]	215
AnMBR energy demand [MWh per annum]	162
Available energy [MWh per annum]	53.4

In summary, this type of initiative helps reduce the emission of contaminant gases, move forward in decarbonization and climate change mitigation, and foster research, generating knowledge and innovation on bioenergy and production of new products [Náthia-Neves et al., 2018]. However, it requires more research to diminish its costs and ensure that the process is well monitored and understood [Bokhary et al., 2020; Wu et al., 2019]. Regarding the results, the AnMBR could remove 23% of COD. Thus, it must be implemented with another technology to fulfill the legislation. The hydrogen produced could be transformed to energy by implementing a H_2-air fuel cell, and the available energy could cover up to 1.4% of the demand.

Chapter 4

Conclusion

Among different anaerobic bioreactors, the researcher concluded that the anaerobic membrane bioreactor (AnMBR) was the more promising to treat winery wastewater and fulfill the CBMem restrictions. The author built the AnMBR model using the software SIMBA, and it was analyzed the suitability of using it as pretreatment of a CBMem system and for the production and recovery of biohydrogen from winery wastewater.

The researcher analyzed the performance of the anaerobic digestion model included in SIMBA and the effect of the hydraulic retention time (HRT) and solids retention time (SRT) on the quality of the permeate, reactor pH, MLVSS, and hydrogen production.

In summary, pH and hydrogen inhibited the anaerobic oxidation processes entirely, and pH partially inhibited the fermentation. These results allowed the researcher to conclude that the anaerobic digestion model described the critical processes for the CBMem implementation (hydrolysis and fermentation). Regarding the operation, a high SRT allows higher hydrogen productions; however, there is less COD removal, the reactor pH decreases and increases the MLVSS. The OLR increment promotes the inhibitory mechanism of the methanogenic activity; therefore, it is advisable to operate at a higher OLR.

The researcher selected an SRT of 7 days, HRT of 9.4 hours, and OLR of 21 $kg_{COD}m^3 - d$ as the operational condition that ensured the fulfillment of the CBMem requirement, a reactor pH above 5.0, maintained an MLVSS in the range of 15 to 18 g/L and obtained a hydrogen production of 821 m^3/d. The author selected the operational conditions for a particular wastewater, and it is not advisable to directly use these results. It is imperative to correctly characterize the wastewater and the fractionation of the COD because those condition the performance of the AnMBR.

The effect of the alkalinity in the system response at the selected operating condition was analyzed. The results allowed the researcher to conclude it is better that the wastewater has more alkalinity because there is more fermentation of amino acids and sugars, therefore, more hydrogen production. However, adding alkalinity to the wastewater entails an economical cost; so it is required to analyze if the increase in hydrogen production is economically favorable.

The main disadvantages of anaerobic processes are the requirement of a long time to stabilize the microbial culture within the reactor and constant monitoring of the process parameters. Besides, even though the cost associated with the membrane has decreased over the years and it has been developed strategies to slow the rate of fouling, the associated costs are a perennial issue. Therefore, some challenges must be overcome to achieve the widespread of this technology.

The principal advantages of implementing the AnMBR in the wine production industry are energy recovery, COD removal, and that it could be a compact system [Pramodbabu et al., 2021]. The AnMBR achieved a 23% of COD removal, which could reduce the posterior treatment costs. However, it must be implemented with another technology to fulfill the legislation. The hydrogen produced could be transformed to energy by implementing a H_2-air fuel cell, and the available energy could cover up to 1.4% of the demand. Although the energy produced was a small fraction of the total demand in the winery, this technology could help with the decarbonization and mitigation of climate change by the reduction of green gases emissions.

Finally, forward work could be focused on optimizing the selection of the operational conditions and analyze the AnMBR-CBMem system.

Annexed A

Anaerobic digestion model - *admsieg02*

The five essential processes included in the model with the corresponding process rates (ρ_j), kinetic expressions, and inhibition functions ($I_{i,j}$) are as follows [Siegriest et al., 2002]:

- Process 2: Hydrolysis of particulate organic matter and dead biomass (X_s), containing carbohydrates, proteins, and lipids, into amino acids, sugars, and long-chain fatty acids.

$$\rho_2 = k_H \cdot X_s \tag{A.1}$$

- Processes 3 and 4: Fermentation of amino acids and sugars.

$$\rho_3 = \mu_{max,3} \cdot \frac{S_{aa}}{K_{s,aa} + S_{aa}} \cdot I_{pH,3} \cdot X_{aa} \tag{A.2}$$

$$\rho_4 = \mu_{max,4} \cdot \frac{S_{su}}{K_{s,su} + S_{su}} \cdot I_{pH,4} \cdot X_{su} \tag{A.3}$$

- Process 5: Anaerobic oxidation of long-chain fatty acids (LCFA).

$$\rho_5 = \mu_{max,5} \cdot \frac{S_{fa}}{K_{s,fa} + S_{fa}} \cdot I_{pH,5} \cdot I_{ac,5} \cdot I_{H_2,5} \cdot X_{fa} \tag{A.4}$$

- Process 6: Anaerobic oxidation of intermediary products (only propionate).

$$\rho_6 = \mu_{max,6} \cdot \frac{S_{pro}}{K_{s,pro} + S_{pro}} \cdot I_{pH,6} \cdot I_{ac,6} \cdot I_{H_2,6} \cdot X_{pro} \tag{A.5}$$

Besides, the inhibition models for pH inhibition, acetate, H_2 and free ammonia are:

- pH inhibition:

$$I_{pH,j} = \frac{(K_{I,H,j})^2}{(K_{I,H,j})^2 + (S_H)^2} \tag{A.6}$$

- Acetate inhibition:

$$I_{ac,j} = \frac{K_{I,ac,j}}{K_{I,ac,j} + S_{ac}} \tag{A.7}$$

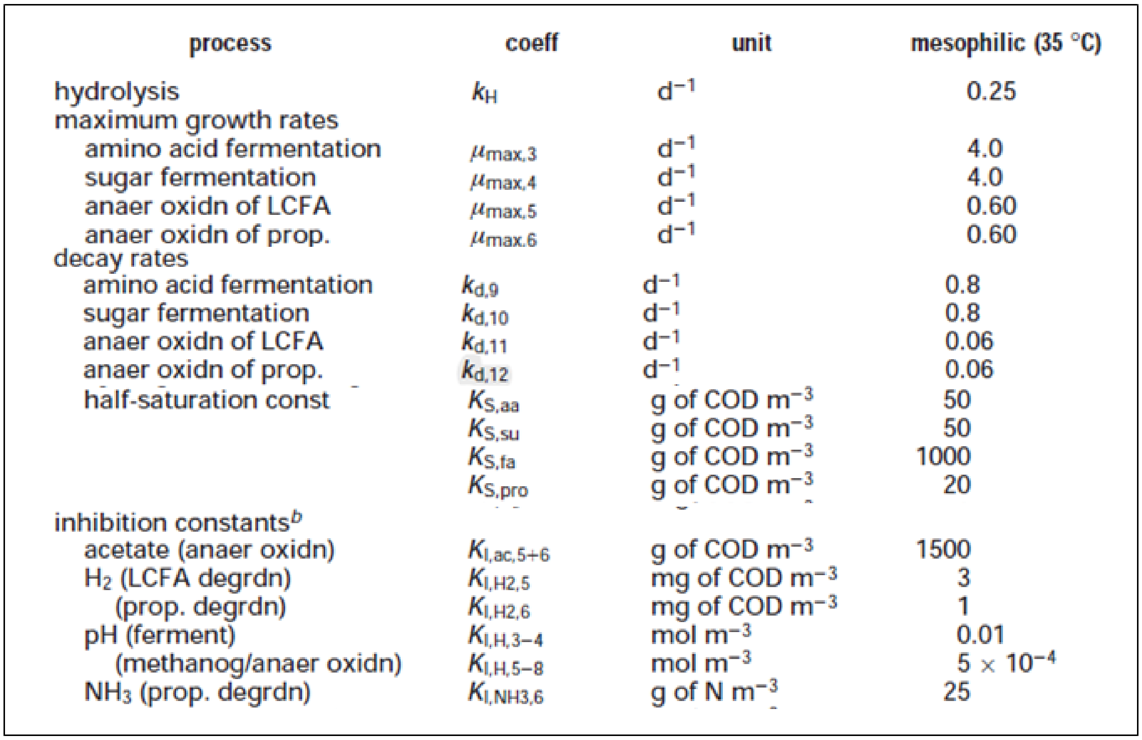
- Hydrogen inhibition:

$$I_{H_2,j} = \frac{K_{I,H_2,j}}{K_{I,H_2,j} + S_{H_2}} \tag{A.8}$$

- Free ammonia inhibition:

$$I_{NH_3,j} = \frac{(K_{I,NH_3,j})^2}{(K_{I,NH_3,j})^2 + (S_{NH_3})^2} \tag{A.9}$$

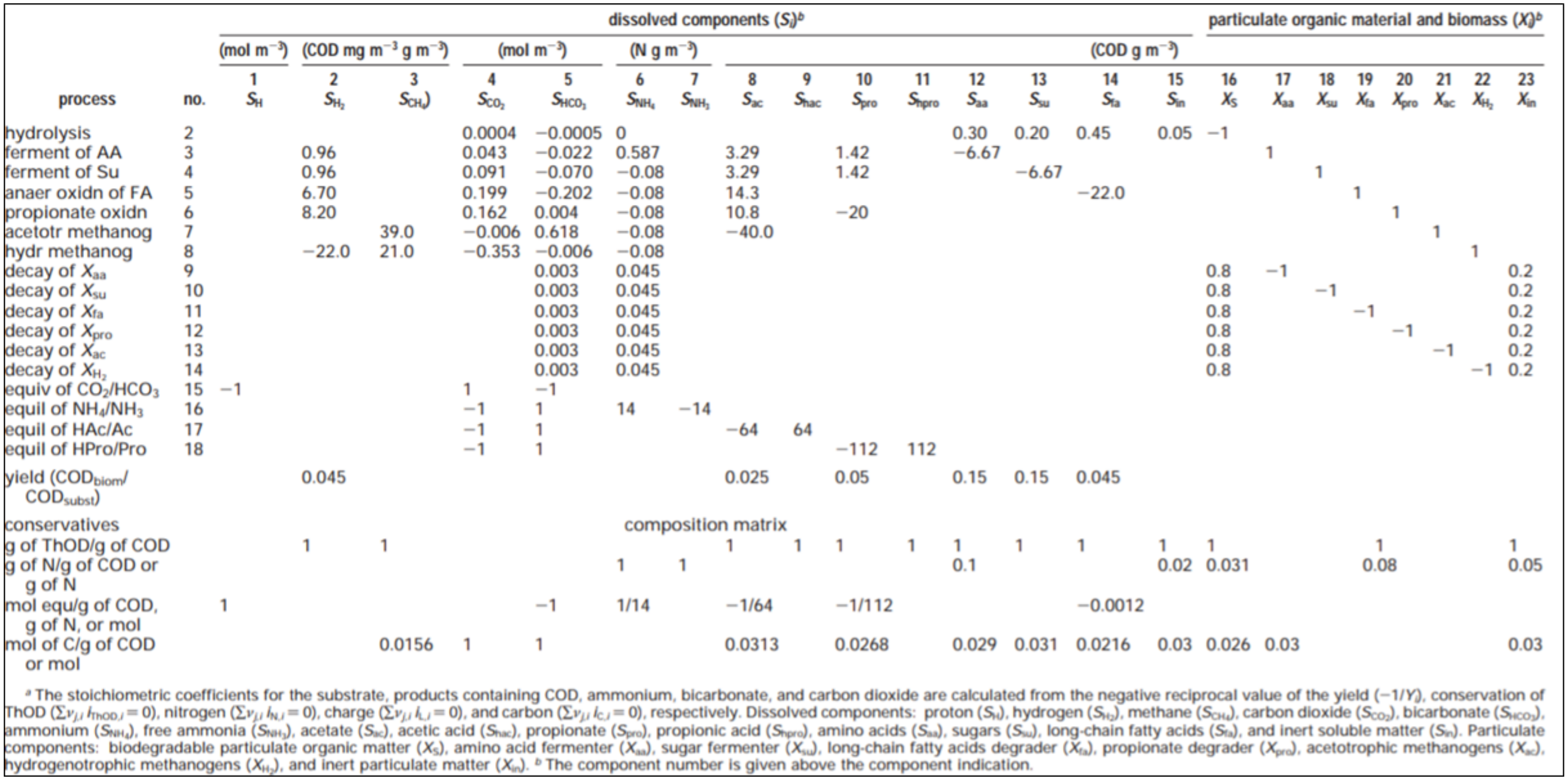
Figure A.1 presents the kinetic values at 35°C.



process	coeff	unit	mesophilic (35 °C)
hydrolysis	k_H	d^{-1}	0.25
maximum growth rates			
amino acid fermentation	$\mu_{max,3}$	d^{-1}	4.0
sugar fermentation	$\mu_{max,4}$	d^{-1}	4.0
anaer oxidn of LCFA	$\mu_{max,5}$	d^{-1}	0.60
anaer oxidn of prop.	$\mu_{max,6}$	d^{-1}	0.60
decay rates			
amino acid fermentation	$k_{d,9}$	d^{-1}	0.8
sugar fermentation	$k_{d,10}$	d^{-1}	0.8
anaer oxidn of LCFA	$k_{d,11}$	d^{-1}	0.06
anaer oxidn of prop.	$k_{d,12}$	d^{-1}	0.06
half-saturation const	$K_{S,aa}$	g of COD m^{-3}	50
	$K_{S,su}$	g of COD m^{-3}	50
	$K_{S,fa}$	g of COD m^{-3}	1000
	$K_{S,pro}$	g of COD m^{-3}	20
inhibition constants^b			
acetate (anaer oxidn)	$K_{I,ac,5+6}$	g of COD m^{-3}	1500
H_2 (LCFA degrdn)	$K_{I,H2,5}$	mg of COD m^{-3}	3
(prop. degrdn)	$K_{I,H2,6}$	mg of COD m^{-3}	1
pH (ferment)	$K_{I,H,3-4}$	mol m^{-3}	0.01
(methanog/anaer oxidn)	$K_{I,H,5-8}$	mol m^{-3}	5×10^{-4}
NH_3 (prop. degrdn)	$K_{I,NH3,6}$	g of N m^{-3}	25

Figure A.1: Kinetic Values of the Mesophilic (35°C) Temperature [Siegrist et al., 2002]

Figure A.2 presents the matrix of stoichiometric coefficients (îj,i), yields (Yi), and conservatives of the processes.



		dissolved components (S_i)[b]															particulate organic material and biomass (X_i)[b]							
		(mol m^{-3})	(COD mg m^{-3} g m^{-3})		(mol m^{-3})		(N g m^{-3})		(COD g m^{-3})															
process	no.	1 S_H	2 S_{H_2}	3 S_{CH_4}	4 S_{CO_2}	5 S_{HCO_3}	6 S_{NH_4}	7 S_{NH_3}	8 S_{ac}	9 S_{hac}	10 S_{pro}	11 S_{hpro}	12 S_{aa}	13 S_{su}	14 S_{fa}	15 S_{in}	16 X_S	17 X_{aa}	18 X_{su}	19 X_{fa}	20 X_{pro}	21 X_{ac}	22 X_{H_2}	23 X_{in}
hydrolysis	2				0.0004	−0.0005	0						0.30	0.20	0.45	0.05	−1							
ferment of AA	3		0.96		0.043	−0.022	0.587		3.29		1.42		−6.67					1						
ferment of Su	4		0.96		0.091	−0.070	−0.08		3.29		1.42			−6.67					1					
anaer oxidn of FA	5		6.70		0.199	−0.202	−0.08		14.3						−22.0					1				
propionate oxidn	6		8.20		0.162	0.004	−0.08		10.8		−20										1			
acetotr methanog	7			39.0	−0.006	0.618	−0.08		−40.0													1		
hydr methanog	8		−22.0	21.0	−0.353	−0.006	−0.08																1	
decay of X_{aa}	9					0.003	0.045										0.8	−1						0.2
decay of X_{su}	10					0.003	0.045										0.8		−1					0.2
decay of X_{fa}	11					0.003	0.045										0.8			−1				0.2
decay of X_{pro}	12					0.003	0.045										0.8				−1			0.2
decay of X_{ac}	13					0.003	0.045										0.8					−1		0.2
decay of X_{H_2}	14					0.003	0.045										0.8						−1	0.2
equiv of CO_2/HCO_3	15	−1			1	−1																		
equil of NH_4/NH_3	16				−1	1	14	−14																
equil of HAc/Ac	17				−1	1			−64	64														
equil of HPro/Pro	18				−1	1					−112	112												
yield (COD_{biom}/ COD_{subst})			0.045						0.025		0.05		0.15	0.15	0.045									
conservatives									composition matrix															
g of ThOD/g of COD			1	1					1	1	1	1	1	1	1	1	1			1				1
g of N/g of COD or g of N							1	1					0.1			0.02	0.031			0.08				0.05
mol equ/g of COD, g of N, or mol		1				−1	1/14		−1/64		−1/112				−0.0012									
mol of C/g of COD or mol				0.0156	1	1			0.0313		0.0268		0.029	0.031	0.0216	0.03	0.026	0.03						0.03

[a] The stoichiometric coefficients for the substrate, products containing COD, ammonium, bicarbonate, and carbon dioxide are calculated from the negative reciprocal value of the yield ($-1/Y_i$), conservation of ThOD ($\Sigma \nu_{j,i}\, i_{ThOD,i} = 0$), nitrogen ($\Sigma \nu_{j,i}\, i_{N,i} = 0$), charge ($\Sigma \nu_{j,i}\, i_{-,i} = 0$), and carbon ($\Sigma \nu_{j,i}\, i_{C,i} = 0$), respectively. Dissolved components: proton (S_H), hydrogen (S_{H_2}), methane (S_{CH_4}), carbon dioxide (S_{CO_2}), bicarbonate (S_{HCO_3}), ammonium (S_{NH_4}), free ammonia (S_{NH_3}), acetate (S_{ac}), acetic acid (S_{hac}), propionate (S_{pro}), propionic acid (S_{hpro}), amino acids (S_{aa}), sugars (S_{su}), long-chain fatty acids (S_{fa}), and inert soluble matter (S_{in}). Particulate components: biodegradable particulate organic matter (X_S), amino acid fermenter (X_{aa}), sugar fermenter (X_{su}), long-chain fatty acids degrader (X_{fa}), propionate degrader (X_{pro}), acetotrophic methanogens (X_{ac}), hydrogenotrophic methanogens (X_{H_2}), and inert particulate matter (X_{in}). [b] The component number is given above the component indication.

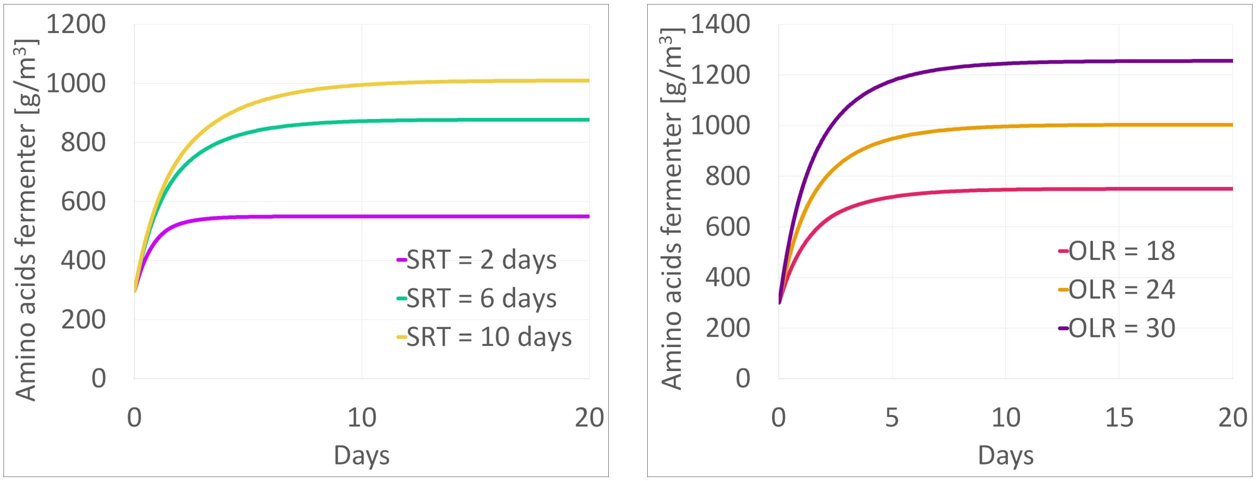
Figure A.2: Matrix of stoichiometric coefficients (îj,i), yields (Yi), and conservatives of the processes [Siegrist et al., 2002]

Annexed B

Results

B.1. Overall operation of AnMBR under OLR and SRT changes

Figure B.1 presents the results for sugars fermenters as a function of time.

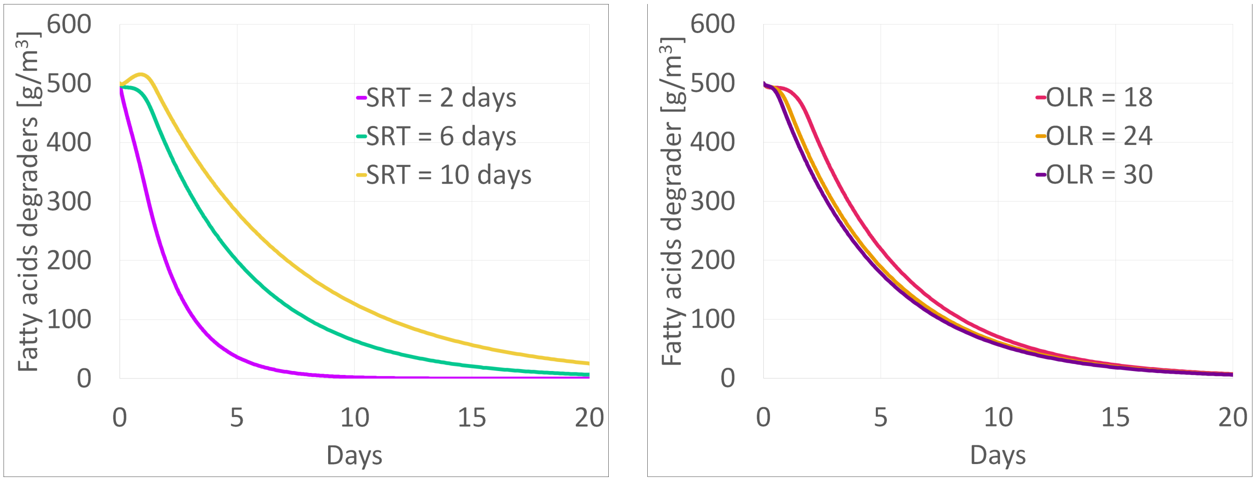


(a) Results for SRT of 2, 6 and 10 days, and OLR of 21 $kg_{COD}/m^3 - d$

(b) Results for OLR of 18, 24 and 30 $kg_{COD}/m^3 - d$, and SRT of 6 days

Figure B.1: Results for amino acids fermenters as a function of SRT and OLR

Figure B.2 presents the results for fatty acids degraders as a function of time.



(a) Results for SRT of 2, 6 and 10 days, and OLR of 21 $kg_{COD}/m^3 - d$

(b) Results for OLR of 18, 24 and 30 $kg_{COD}/m^3 - d$, and SRT of 6 days

Figure B.2: Results for long-chain fatty acids degrader as a function of SRT and OLR

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