



Treball Final de Grau

**Volatile fatty acids up-concentration in fermentation liquids
using Forward Osmosis**

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SUMMARY

In the face of the challenge posed by the current unsustainable situation, where large quantities of non-renewable resources, particularly petroleum, are being consumed to produce compounds of interest, there is a need to explore new production pathways based on biological processes.

In this field, Volatile Fatty Acids (VFA) are of particular interest. These products have an increasingly high demand due to their wide range of applications, including their use as a molecular platform in biorefineries or as direct chemical products. Currently, 90 % of the demand is met by petrochemical processes, but they can also be produced through anaerobic digestion of biodegradable matter. One of the most attractive substrates is the Organic Fraction of Municipal Solid Waste (OFMSW) due to its abundance and high degradability, although the maximum achievable concentration is limited by product inhibition.

This work focuses on obtaining a fermentation liquid from OFMSW and its subsequent treatment to broaden its field of application, specifically the recovery of ammoniacal nitrogen using a gas-permeable membrane and the up-concentration of VFA through direct osmosis.

To conduct this research, several experiments were conducted using synthetic liquid with known concentrations of TAN (Total Ammoniacal Nitrogen) and acetic acid to study the permeability and selectivity of these compounds at a specific temperature (35°C) and different pH levels (5, 7, 9). Subsequently, two experiments were performed using fermentation liquid, first recovering nitrogen through Gas-Permeable Membrane (GPM), and then concentrating the VFA in the resulting solution using a direct osmosis module.

The experiments with synthetic liquid showed very low rejection rates for TAN, regardless of the pH of the working solution. In contrast, acetic acid exhibited high rejection rates at pH levels above 7.

Regarding the experiments with fermentation liquid, the nitrogen recovery stage resulted in high percentages of nitrogen removal from the feed solution. In the subsequent treatment using a direct osmosis module, concentrations were obtained that were much higher than the limit observed in the acidogenic fermentation stage.

Therefore, from a technical standpoint, it is feasible to implement the following stages: fermenter, gas-permeable membrane, and direct osmosis. This approach yields a solution with a high concentration of $(\text{NH}_4)_2\text{SO}_4$ and another solution with a very high concentration of VFA, exceeding 70 g COD/L.

Keywords: Acidogenic fermentation, Bio-based, biorefinery, forward osmosis, nitrogen recovery, Organic Fraction of Municipal Solid Waste (OFMSW), up-concentration Volatile Fatty Acids (VFA)

RESUMEN

Ante el desafío que plantea la situación insostenible actual en la que se consumen grandes cantidades de recursos no renovables, con especial énfasis en el petróleo, para producir compuestos de interés, surge la necesidad de investigar nuevas rutas de producción basadas en procesos biológicos.

En este ámbito cobran especial interés los Ácidos Grasos Volátiles (AGV). Estos productos tienen una demanda cada vez más elevada debido a su amplio rango de aplicaciones, entre las que destacan el uso como plataforma molecular en biorrefinerías o como productos químicos directos. Actualmente, el 90 % de la demanda está cubierta por procesos petroquímicos, sin embargo, también son producto de la digestión anaerobia de materia biodegradable. Uno de los sustratos que más resulta más atractivo es la Fracción Orgánica de Residuos Sólidos Municipales (FORM) debido a su abundancia y a su alta degradabilidad, aunque la concentración máxima que puede alcanzarse está limitada por inhibición por producto.

Este trabajo se centra la obtención de un líquido de fermentación de OFMSW y su posterior tratamiento para ampliar su campo de aplicación, más concisamente la recuperación de nitrógeno amoniacal mediante el uso de una membrana permeable al gas y la concentración de AGV mediante ósmosis directa.

Para llevar a cabo esta investigación se han hecho varios experimentos con líquido sintético con concentraciones conocidas de TAN y de ácido acético para estudiar la permeabilidad y selectividad de estos compuestos a una temperatura determinada (35 °C) y a diferentes pH (5,7, 9). Posteriormente, se han realizado dos experimentos con líquido de fermentación, recuperando primero el nitrógeno mediante GPM y después concentrado los AGV en la solución resultante con un módulo de ósmosis directa.

Los experimentos con sintético tasas de rechazo muy bajas para el TAN, independientemente del pH de la solución de trabajo. Por el contrario, el ácido acético mostró altas tasas de rechazo a pH superiores a 7.

En cuanto a los experimentos con líquido de fermentación, la etapa de recuperación de nitrógeno condujo a altos porcentajes de eliminación de este de la solución de alimento y en su posterior tratamiento con un módulo de ósmosis directa, se obtuvieron concentraciones muy superiores al límite observado en la fermentación acidogénica.

Por lo tanto, desde un punto de vista técnico, es posible implementar las etapas: fermentador, membrana permeable a los gases y ósmosis directa. De esta manera se obtiene una solución con una elevada concentración de $(\text{NH}_4)_2\text{SO}_4$ y otra muy concentrada de AGV, por encima de 70 g DQO/L.

Palabras clave: Ácidos Grasos Volátiles (AGV), biorrefinería, concentración, fermentación acidogénica, Fracción Orgánica de Residuos Sólidos Municipales (FORM), ósmosis directa, recuperación de nitrógeno, vía biológica

SUSTAINABLE DEVELOPMENT GOALS

Este estudio está relacionado con algunos de los 17 objetivos de desarrollo sostenible propuestos por la Asamblea General de las Naciones Unidas, ya que es un proceso sostenible dentro del concepto de economía circular. A continuación, se nombran los que tienen una mayor repercusión en este Trabajo de Final de Grado:

- ODS 2: Hambre cero. Favorecer la agricultura sostenible mediante el uso de fertilizantes que no consuman grandes cantidades de recursos o generen subproductos. Se trata de limitar el proceso Haber-Bosch porque es altamente contaminante.
- ODS 7: Energía asequible y no contaminante. La demanda de energía debe ser cubierta mediante recursos renovables, de manera que se pueda garantizar el acceso a una energía asequible, segura, sostenible y moderna para todos
- ODS 11: Ciudades y comunidades sostenibles. Este objetivo incide especialmente en este trabajo, ya que propone un modelo para hacer un mejor uso de los residuos generados por la actividad humana.
- ODS 13: Acción por el clima. Combatir el cambio climático haciendo un mejor uso de las fuentes de recursos, así como la reducción de emisiones de gases de efecto invernadero.



1. INTRODUCTION

Currently, the trend in the treatment of resources is directed towards the recovery of resources from organic wastes within the framework of the circular economy in order to transform existing biowaste treatment plants into biorefineries. Volatile Fatty Acids (VFA) are key bioproducts within biorefineries, as a wide variety of other products could be further synthesized in downstream processes. This chapter focuses on VFA, their production from OFMSW, and the recovery of fermentation broth.

1.1. VOLATILE FATTY ACIDS (VFA)

Nowadays, a high percentage of chemical compounds are fossil-fuel derived and produced in the petrochemical industry. This fact contrasts with the need to reduce the dependence on non-renewable resources to achieve carbon neutrality. Several Biotechnological processes could be used to obtain some of these key chemical products using mixed microbial cultures while treating organic wastes. One of the products that could be obtained through biotechnological pathways are Volatile Fatty Acids (VFA).

VFA are saturated aliphatic monocarboxylic acids containing two to six carbon atoms (C_2 to C_6): acetic (C_2 /HAc), propionic (C_3 /HPr), iso-butyric (iC_4 /iHBu), n-butyric (C_4 /HBu), iso-valeric (iC_5 /iHVa), n-valeric (C_5 /HVa), iso-caproic (iC_6 /HCa) and n-caproic (C_6 /HCa) acids. As carboxylic acids, VFA's are weak acids, which means that they partially dissociate in neutral aqueous solvents such as water. Table 1.1 shows the main characteristics of VFA, including its Chemical Oxygen Demand (COD) equivalent, which is higher as the chain length increases.

VFA could be used in biorefineries as platform molecules to produce a multitude of valuable products, such as biochemicals, biofuels and biomaterials through catalytic reactions. VFA could also be used like drop-in chemicals in fiber and textile, food, leather, pharmaceuticals, polymers and pesticide industries or carbon source in a wastewater treatment denitrification process.

Particularly, acetic acid is the best alternative for petrochemical counterpart, propionic acid is used as food preservatives, in textiles, rubber auxiliaries and cosmetics, butyric acid is used as a biodiesel source and animal feeding sector and caproic acid is used in cosmetic industry. Therefore, the VFA platform is an emerging technology that needs to improve its yield and productivity and to develop cost-effective separation methods (Giduthuri and Ahring, 2023).

Table 1.1. Main characteristics of Volatile Fatty Acids (Adapted from Raposo et al., 2014)

Common name	IUPAC name	Acronyms	Formula	MW (g/mol)	COD _{equivalent} (g COD/ g)	Boiling point (°C)
Acetic	Ethanoic	C ₂ /HAc	C ₂ H ₄ O ₂	60.05	1.07	118
Propionic	Propanoic	C ₃ /HPr	C ₃ H ₆ O ₂	74.08	1.51	141
Iso-butyric	2-methyl propanoic	iC ₄ /iHBU	C ₄ H ₈ O ₂	88.11	1.82	154
n-butyric	Butanoic	C ₄ /HBU	C ₄ H ₈ O ₂	88.11	1.82	162
Iso-valeric	3-methyl butanoic	iC ₅ /iHVa	C ₅ H ₁₀ O ₂	102.13	2.04	176
n-valeric	Pentanoic	C ₅ /HVa	C ₅ H ₁₀ O ₂	102.13	2.04	185
Iso-caproic	4-methyl pentanoic	iC ₆ /iHCa	C ₆ H ₁₂ O ₂	116.16	2.21	200
n-caproic	Hexanoic	C ₆ /HCa	C ₆ H ₁₂ O ₂	116.16	2.21	204

Due to wide range of applications, VFA market demand is increasing: acetic acid is estimated to grow from USD 19.2 billion in 2022 to USD 28 billion by 2030 with a Compound annual growth rate (CAGR) of 4.8 % (Expert Market Research), propionic acid market is projected to grow from USD 1.3 billion in 2022 to USD 2.2 billion by 2030 with a CAGR of 6.5 % (Expert Market Research), butyric acid market is expected to increase from USD 497.2 million in 2022 to USD 1400 million by 2030 with a CAGR of 14.1 % (Expert Market Research), valeric acid market is estimated to rise from 2023 to 2030 with a 7.8% CAGR (MarketWatch) and caproic acid growth forecast from USD 191.8 million in 2022 to 358.8 million in 2030 with a CAGR of 8.1 % (Expert Market Research).

Traditionally, VFA have been produced from crude oil through processes like oxidation or carboxylation that need an immoderate use of energy and produce by-products (Agnihotri et al., 2021). Reported greenhouse gas (GHG) emissions from acetic acid production in the petrochemical industry are 3.3 t CO_{2eq}/t for cradle-to-grave (by incineration without energy recovery) (Atasoy et al., 2018).

Despite these limitations, 90 % of the market demand of VFA is covered by petrochemical-based production methods and the rest biologically through fermentation processes. VFA bio-based production methods cannot compete economically with petroleum-based methods due to the lower manufacturing cost of petro-based production and lower efficiency of bio-based production methods (Agnihotri et al., 2021). Nevertheless, adverse effects on the environment (depletion of petroleum resources, GHG emissions, high energy demand, huge generation of waste and wastewater during and after the production process, among others) urges the necessity to implement the transition from petroleum-based to bio-based production methods (Atasoy et al., 2018).

1.2. BIO-BASED VFA PRODUCTION FROM ORGANIC WASTES

Presently, Anaerobic Digestion (AD) is a widely used technology for organic waste management with the aim to produce bioenergy and digestate or compost with fertilizing value (Duraismy and Ananthasubramanian, 2021). However, biogas and compost produced from organic wastes from urban origin (i.e., sewage sludge or the organic fraction of municipal solid waste, OFMSW) have a relatively low market value compared to other bioproducts that could be produced, such as VFA that have market values between €450 and €2800 per tonne (depending on the molecular structure) while that of biogas is only €110 per tonne (Calt, 2015). Additionally, the production of VFA in AD have other advantages like the reduction of the retention times (lowering the capital cost of the process) and the savings derived from not adding growth supplements (Giduthuri and Ahring, 2023).

AD process of biodegradable organic matter consists of four biochemical reactions, namely: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Figure 1.1 shows a representation of these reactions, where it is observed that VFA are intermediary degradation products generated in the fermentative stages (acidogenesis and acetogenesis). Therefore, the accumulation of VFA in the fermentation broth is promoted by the inhibition of the methanogenesis stage, a practice that is recognized with the names of Arrested Anaerobic Digestion (AAD), acidogenic fermentation and arrested methanogenesis. With the aim of inhibit the last reaction of

the AD process without limiting the previous stages, it is necessary to deeply understand each step of the whole process.

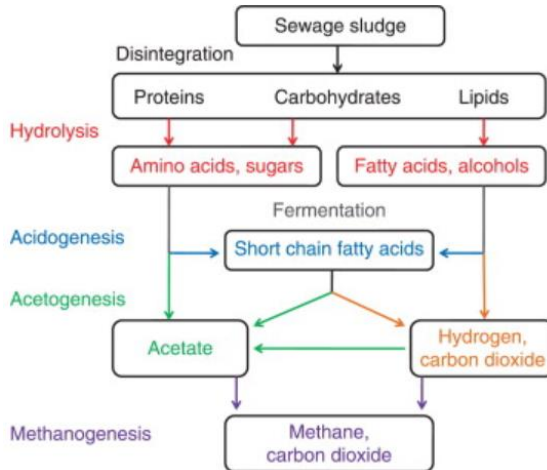


Figure 1.1. Scheme of the four biochemical reactions of Anaerobic Digestion (Tezel et al., 2011).

The 4 stages of traditional AD are briefly explained below:

Hydrolysis. Anaerobic digesters commonly encounter organic matter characterized by intricate polymers that are not readily accessible to microorganisms unless they undergo hydrolysis or pretreatment processes for further degradation (Meegoda et al., 2018). As a result of hydrolysis, carbohydrates, lipids and proteins are converted into sugars, long chain fatty acids (LCFAs) and amino acids, respectively, by the action of the bacteria's extracellular hydrolytic enzymes (e.g., lipases, proteases and glucosidases). After the conversion into monomers, the hydrolysed organic matter can diffuse through the cell membranes of acidogenic microorganisms.

Nevertheless, hard-to-digest substrates such as lignin, cellulose and hemicellulose could be inaccessible to microbes due to their complex structures. As a result, enzymes are frequently incorporated to augment the hydrolysis of these carbohydrates (Lin et al., 2018). For this reason, this stage could become a bottleneck of all the AD process (Millati et al., 2022).

In general, hydrolysis exhibits an optimal temperature range of 30-50°C and an optimal pH range of 5-7. However, there is no evidence indicating enhanced hydrolytic activity below a pH of 7 (Azman, 2016).

Acidogenesis. In the second stage of AD, acidogenic bacteria produce VFA, alcohols, lactate, aldehydes and gases such as hydrogen (H_2), CO_2 and ammonia by absorption of the products of hydrolysis through their cell membranes. Unlike other stages, acidogenesis is typically characterized by a notably accelerated rate compared to all other phases of anaerobic digestion. Acidogenic bacteria demonstrate a rapid regeneration time of less than 36 hours (Deublein and Steinhauser, 2011).

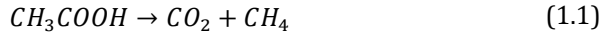
One drawback associated with anaerobic digestion, particularly during the rapid evolution of the acidogenic stage, is the occurrence of over-acidification in the digester. This phenomenon arises from the excessive accumulation of volatile fatty acids (VFA) due to an imbalance in the kinetics between acid production and consumption by acidogenic and acetogenic bacteria. Over-acidification typically leads to a significant decrease in pH and a reduction in the reactor's buffering capacity. The decline in pH below the optimal level not only hampers biogas production due to the heightened sensitivity of methane-forming bacteria to pH changes, but also disrupts the hydrolysis and acidogenesis stages (Alavi-Borazjani et al., 2020).

Acetogenesis. The third stage of the AD process, known as acetogenesis, has the function of converting VFA into a methanogenic substrate, such as acetate, H_2 and CO_2 . This is carried out by the conversion of VFA with carbon chains longer than one unit are oxidized into H_2 and acetate. The production of hydrogen is due to the use of protons as the final electron acceptor. Additionally, the acetogenic bacteria can use carbon dioxide, methanol, hydrogen or glucose to generate acetate. In the acetogenesis stage there are two mechanisms to produce acetate: Acetogenesis by hydrogenation (CO_2+H^+ , homoacetogenic bacteria, acetyl-CoA pathway) and dehydrogenation acetogenesis (anaerobic oxidation of long chain fatty acids).

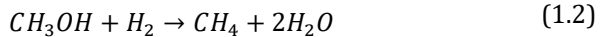
Methanogenesis. It is the final stage of AD, where the products of acetogenesis are consumed by methanogenic archaea to produce methane. Methanogenic microorganisms represent a group of obligate anaerobic archaea. In a demonstration of the pronounced sensitivity of methanogenic microorganisms to oxygen, it was observed that 99 % of *Methanococcus voltae* and *Methanococcus vannielii* cells were eliminated within ten hours of being exposed to oxygen (Meegoda et al., 2018).

More concisely, methanogenesis is carried out for three distinct pathways:

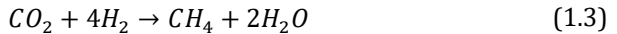
- *Acetoclastic methanogenesis* (carried out by Acetotrophic methanogens according to reaction 1.1):



- *Methylotrophic methanogenesis* (in which methanol or methylamines serve as substrates according to reaction 1.2)



- *Hydrogenotrophic methanogenesis* (uses H_2 as electron donor for the reduction of CO_2 , CO or formate according to reaction 1.3)



Typically, the acetoclastic methanogenesis represents approximately 2/3 of the methane production, and the hydrogenotrophic methanogenesis the remaining 1/3 (Meegoda et al., 2018). Methylotrophic methanogenesis is important in some marine sediments and other anoxic systems where methylated substrates occur (Fenchel et al., 2018).

The optimal conditions for methanogenesis are a pH more elevated than the previous stages in addition to a lower redox potential. The methanogens have a regeneration time between 5-16 d, that is significantly more elevated than other types of microorganisms involved in the Anaerobic Digestion process (Millati et al., 2022). Nevertheless, it has been documented that certain hydrogenotrophic species, such as *Methanococcus maripaludis*, exhibit an incredibly short doubling time of just two hours (Richards et al., 2016).

Considering the abovementioned pH, temperature, redox potential and/or retention time conditions, among other factors, VFA could be accumulated by promoting the occurrence of the three first stages of AD while inhibiting the final methanogenesis step. Moreover, the characteristics of the feedstock could also influence the viability of producing VFA or a certain VFA distribution over biomethane generation.

1.2.1. Feedstocks for VFA production in AD

The production of VFA is very influenced by the substrate used. Ideal raw materials for anaerobic digestion are easily degradable materials such as animal manure, food waste, sewage sludge, industrial waste, municipal solid waste, wastewater sludge and slaughterhouse waste (Millati et al., 2022). The amount of VFA produced from a given feedstock depends on the degree of acidification. This parameter is a key factor that is defined as the percentage of initial COD converted into organic acids and other fermentation products (Atasoy et al., 2018). Other determining factors for the economics of the process are the VFA yield (g VFA/g substrate) and productivity (g VFA/(L·day)). Figure 1.2 summarizes the acidification and net VFA production of several biodegradable organic wastes, where it is observed that OFMSW is one of the feedstocks that could lead to a high degree of acidification with an associated net VFA production enriched in acetic, propionic and butyric acids.

The typology of substrate not only has an impact on the quantity of VFA produced, but it also affects its quality (VFA distribution). The composition of VFA in the fermentation broth reflects the prevailing metabolic pathways. Acetic acid often accounts for 30–80 % of VFA produced from waste streams. Valeric acid and other kinds of VFA are usually produced in relatively low quantities. The variation in VFA composition derived from waste streams can be attributed to the organic matter characteristics present in the waste stream (Atasoy et al., 2018).

The present study is focused on the use of OFMSW as raw material for the acidogenic fermentation due to the following reasons:

- OFMSW is an ideal feedstock because it is composed by a high content of carbohydrates, proteins and lipids that could be converted into VFA without difficulty.
- This feedstock is generated constantly by anthropic action in large quantities, especially in urban areas. The implementation of acidogenic fermentation coupled to a subsequent anaerobic digestion unit for the treatment of OFMSW could help to boost the circular economy, recovering energy, materials and reducing disposal treatments (e.g., landfill or incineration).

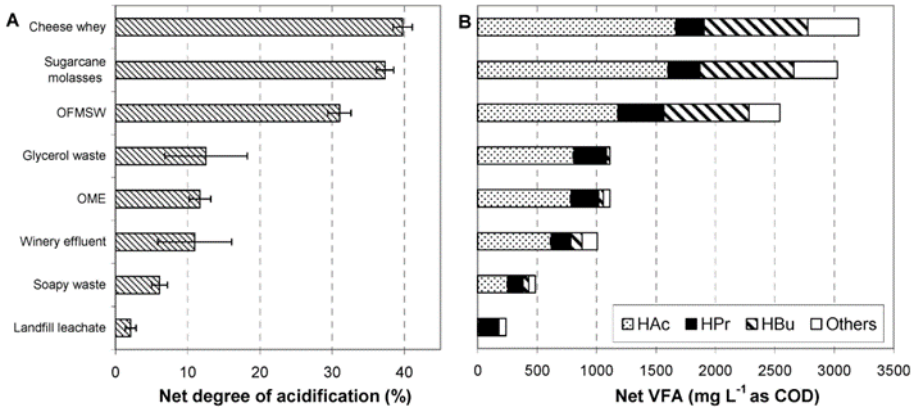


Figure 1.2. (A) Waste streams impact acidification levels. (B) Waste streams affect VFA production and composition (Silva et al., 2013).

1.2.2. Influencing factors in biobased VFA production

Apart from the feedstock used to produce bio-based VFA, there are several operational parameters such as pH, temperature, the hydraulic retention time (HRT), the organic loading rate (OLR) and the Oxidation-Reduction Potential (ORP or redox) that could affect both the VFA production and distribution.

To curb the methanogenesis stage to maximize VFA production, the methanogenesis archaea must be inhibited, which could be done through the addition of an inhibitor like 2-Bromoethanesulfonic acid (BES) and/or regulating the fermentation variables explained below.

pH: Is one of the determining factors that affects the VFA concentration and composition since it influences both acidogenic process and hydrolysis rate. Methanogens consortium normally grow at pH 6-8.5, hence operation at low (acidic) or high (alkali) pH will inhibit methanogens action (Giduthuri and Ahring, 2023). Traditionally, AD has been carried out as acidic conditions (pH < 6.5) have been maintained using alkali additions for pH control. While these acidic conditions inhibit methanogenesis, they have a negative effect on volatile fatty acid (VFA) production due to the stress they impose on microbes. At low pH, weak acids such as lactic acid and acetic acid remain in their protonated form, disrupting the functionality of bacterial cells by affecting the lipid

bilayer. Extreme pH levels (above 10 or below 5) are detrimental to acidogens, leading to reduced reduction of volatile solids and lower VFA concentrations.

Temperature: Temperature is another key parameter that can affect the enzymatic activity, microorganisms' growth, hydrolysis rate and metabolic pathways. Mesophilic temperate is considered the most optimum and economically favorable for VFA bio-based production, since the VFA's yields are quite similar at thermophilic and mesophilic conditions (Sukphun et al., 2021). Temperature also affects the VFA distribution but slightly lesser than pH.

HRT: For Giduthuri and Ahring, (2023) and other authors HRT is, together with pH, one of the most important to inhibit methane production. HRT is the average time that the feed remains inside the reactor. Methanogens have generation times of 5-16 d while acidogenesis and acetogenesis bacteria have no more than 90 h. This difference causes that at low HRT the slowest-growing bacteria could be washed out from bioreactor. However, the optimal HRT depends on digestibility of substrate and other operational conditions, so it should be tuned based on these other factors. Moreover, VFA distribution is also affected by HRT, being acetic acid the main product at low HRTs while propionic is predominant at high values (Sukphun et al., 2021)

OLR: This parameter expresses the amount of substrate fed into the reactor per unit of reactor's volume and time and it is usually expressed on COD or Volatile Solids (VS) basis. According to Sukphun et al. (2021), the recommended OLR for acidogenic fermentation ranges from 2 to 8 g VS/(L·day).

An elevation in the VS content of the feed, along with a subsequent increase in OLR up to a certain threshold, can result in a greater conversion of organic matter into VFA, thereby enhancing the acidogenic fermentation process. However, excessively high VS content in the feed can reach inhibitory levels, leading to reduced yield. Additionally, an increase in OLR can contribute to elevated viscosity, thereby impeding mass and heat transfer and diminishing the conversion of substrate into VFA.

1.3. VFA UP-CONCENTRATION AND RECOVERY

VFA up-concentration and recovery is one of the major challenges in bio-based VFA production, which can represent approximately 30-40 % of the total production cost. Mixture complexity of fermentation broth and low concentration of VFA in fermented stream contributes to increased costs. Recovery processes of individual VFA are more difficult instead of mixed VFA.

VFA separation usually involves more than one stage: (1) A primary stage to remove VFA from the fermentation broth and (2) a secondary stage to purify the VFA and concentrate them for potential sale in market or for upgrading (Giduthuri and Ahring, 2023). VFA needs to be up-concentrated and recovered without incurring excessive cost that would make bio-based VFA production non-viable. VFA recovery processes can be generally classified into non-membrane-based, such as liquid-liquid extraction, distillation, adsorption and gas stripping, and membrane-based.

1.3.1. Non-membrane-based technologies

Several non-membrane-based techniques have been reported in literature for bio-based VFA recovery:

Liquid-liquid extraction (LLE): This separation method, also called solvent extraction, is based on the different solubility of targeted species (VFA) in two immiscible solvents. This process requires using a solvent and sometimes a co-solvent. The efficiency of this process depends on the kind and composition of VFA in digestate, the working pH and the extractant type.

The use of hydrophobic deep eutectic solvents (HDES), a new generation of water-immiscible solvents, is being investigated to recover VFA from fermentation broths. These solvents present a green way due to their low cost, non-toxic nature, and sustainable manufacturing (Brouwer et al., 2021).

Other type of solvents under investigation way are ionic liquids (IL) used in reactive extraction. These custom-made solvents with enhanced distribution coefficient for carboxylic acids require low solvent to feed ratio (Duraisamy and Ananthasubramanian, 2021). Key parameters that need to be controlled in LLE with ionic liquids are nature and selectivity of diluent, distribution coefficient, viscosity, boiling point of solvent and hydrophobicity of VFA streams.

Gas stripping: It is a process for VFA separation from fermentation liquid broths through a gas stream. This process is controlled by Henry's law, which establishes a relationship between the concentration of a compound in the aqueous phase and its concentration in the gas phase.

Nitrogen gas is usually used as a stripping agent in VFA recovery. For an efficient gas stripping, VFA must be in undissociated form, which depends on their respective pKa. The nitrogen gas with VFA stripped from fermentation liquid (at acidic values) could be passed through a recovery system that contains absorbents (e.g. calcium carbonate). Consequently, salts of VFA are formed and these VFA could be recovered after evaporation.

Adsorption: In this physicochemical process, the solute compound (such as VFA) adheres to a surface. The method can be carried out by passing a VFA-rich digestate stream through a column of adsorbent material.

Generally, the extraction of VFA is conducted using ion-exchange resins where the unprotonated carboxylic group allows ionic bonding with the resin charged positively. Rebecchi et al. (2016) investigated the VFA recovery efficiency of four different amino resins and concluded that the tertiary amino resin was the best due to its high ion exchange performances in the presence of acetic acid and its low price.

In any case, factors such as adsorbate medium, ionic strength, solubility, pH, temperature, hydrophobicity and acidity must be considered in designing a specific adsorbent. The nature of organic acids and pH of the solution plays an important role in anion-exchange resins, since the dissociation of organic acid (that occurs when $\text{pH} > \text{pKa}$) is significant for an effective interaction with the adsorbent.

Distillation: Distillation is a widely employed traditional technique for purifying streams containing VFA. This method relies on the varying boiling points of VFA (refer to Table 1.1). The efficiency of distillation in separating VFA is generally influenced by their concentration in the fermentation broth. Distillation proves effective when the VFA concentration is low. However, at high concentrations, particularly near the azeotropic point, distillation becomes significantly less efficient (Huang et al., 2007). Although this process yields highly pure products, it is associated with high capital costs and energy requirements (Aktij et al., 2019). Consequently, alternative methods such as vacuum distillation, reactive distillation, and extractive distillation are being investigated.

1.3.2. Membrane-based technologies, Forward Osmosis

An alternative to conventional methods for VFA recovery are membrane-based processes that could be divided into gradient-driven membrane separation such as pervaporation or pertraction and pressure-driven membrane separation, such as microfiltration (MF) or nanofiltration (NF). Membrane-based separation processes have become increasingly promising in recent years due to studies demonstrating their ability to achieve high VFA recovery yields and selectivity, with low energy requirements and reactor footprints (Zhu et al., 2020). One of the drawbacks associated with these processes is the issue of fouling, which includes problems like clogging, scaling, and biofouling.

Table 1.2 shown the comparative attributes and efficiencies of the main concentration processes based on membrane technology.

Table 1.2. Comparative properties and performances of concentration processes (Blandin et al., 2020)

	UF/MF	NF/RO	MD/OD	Evaporation	Cryo-Concentration	Forward Osmosis
Temperature	Ambient	Ambient	Moderate	High	Low	Ambient
Pressure	Moderate	High	No	No	No	No
Concentration capability		Limited	High	High	Medium	High
Organoleptic preservation	Good	Good	Good-moderate	Poor	Good	Good
Applications	WW, food, waste streams, desalination	WW, food, waste streams, desalination	Desalination (MD)/food (OD)	Food, Desalination	Food	WW, food, waste streams, desalination
Energy	Moderate	High	Low-high	Very high	High	Low-high
Technology readiness level	Established technology	Established technology	Pilot scale	Established technology	Established technology	Reaching market

In Forward Osmosis, the osmotic pressure differential acts as a driving force between two solutions separated by a selectively permeable membrane. The permeation of water is carried out through the membrane from the lowest concentration solution called feed solution to the highest solute concentration solutions known as draw solution. Suspended solids, consisting mostly of dissolved molecules or ions, are unable to permeate through the membrane and instead become concentrated in the feed solution.

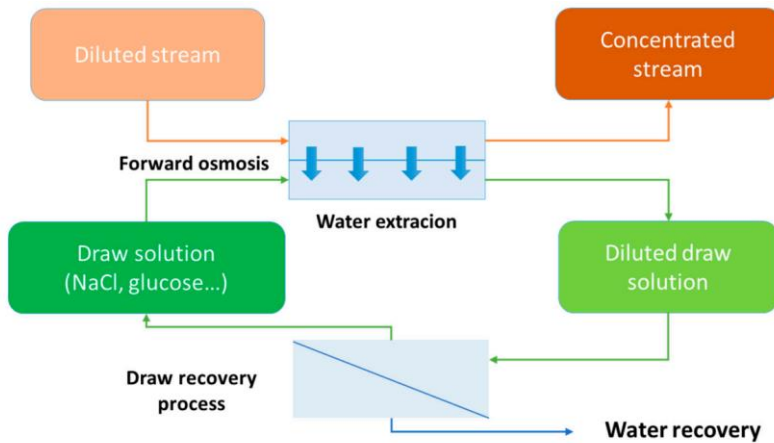


Figure 1.3. Fundamental tenets governing forward osmosis as a concentration process (Blandin et al., 2020)

The characteristics of Forward Osmosis (FO) can be summarized as follows:

1. Use of dense membrane with high selectivity and rejection of most compounds.
2. The osmotically-driven force enables simplified operation without the need for pressure vessels or costly high-pressure pumps.
3. The absence of a temperature gradient requirement eliminates the risk of feed compound degradation and substantially reduces energy costs.
4. Operating the process at low flux results in a reduced fouling rate, and cleaning is made easier due to the non-compaction of fouling layers on the membrane, unlike in pressurized processes.

The parameters used in FO process are:

- Water flux (J_w): It is the amount of water, either in volume or in mass, that crosses the membrane per unit of area and time from the feedstock to the draw solution. This can be calculated using the following equation:

$$J_w = K \cdot \Delta\pi \quad (1.4)$$

Where K is the permeability of water and $\Delta\pi$ is the osmotic pressure difference between FS and DS. This equation is an approximation as the membrane experiences concentration polarization,

and the effective concentrations at the membrane surface are not equal to those in the FS and DS.

- Reverse salt flux (J_s): Is used to describe the phenomenon where salt ions migrate in the opposite direction to the water flow, specifically from the draw solution to the feed. This results in a reduction in water flux and an increase in the cost associated with replenishing the draw solute. Camilleri-Rumbau et al. (2019) proposed the following equation:

$$J_{s,i} = \frac{C_{F,i} \cdot [V_{F,i} - J_{w,i} \cdot A_{FO} \cdot (t_i - t_0)] - C_{F,0} \cdot V_{F,0}}{A_{FO} \cdot (t_i - t_0)} \quad (1.5)$$

Where $C_{F,i}$ is the concentration of solute in the feed, A_{FO} is the membrane active area, V_F is the volume of FS and t_i is the time elapsed.

- Rejection rate: Refers to the efficiency with which a membrane can retain or reject specific solutes or contaminants present in a solution. The equation to calculate the membrane rejection rate is:

$$R_j = \left(1 - \frac{C_{j,permeate}}{C_{j,feed}} \right) \cdot 100 \quad (1.6)$$

Where $C_{j,permeate}$ is the concentration of solute (j) present in the solution that passes through the membrane from the feedstock and $C_{j,feed}$ is the concentration of solute in the feed.

- Water concentration factor (WCF): It refers to the change in the volume of water in the feed solution between the initial state and a specific time.

$$WCF = \frac{V_{F,0}}{V_F(t)} \quad (1.7)$$

The semipermeable membranes tailor-made for forward osmosis developed in the early 2000s make this operation a process with a wide range of applications, such as the up-concentration of VFA. For feed solutions that have a lower osmotic potential and require dewatering, FO offers a cost-effective and eco-friendly solution with a low carbon footprint (Bona et al., 2020).

VFA up-concentration through FO is highly influenced by the presence of anions in the digestate, pH of the feed, concentration of VFA and the membrane surface charge (Duraismy and Ananthasubramanian, 2021). Different draw solutions such as NaCl, CaCl₂, MgCl₂, KCl and (NH₄)HCO₃ can be employed.

1.4. CASE STUDY

Biowaste treatment facilities process various organic waste materials such as animal manure, agricultural waste, food waste, and sewage sludge. In Mechanical-biological treatment (MBT) plants, OFMSW is treated through anaerobic digestion and/or composting. Recently, acidogenic fermentation has been studied as an option to enhance the production of VFA in MBT plants, supporting innovative biotechnologies and diversifying the plant's economy. The technologies enabling value addition to VFA are currently at a Technology Readiness Level (TRL) between 4 and 6, indicating they are still under development. It is expected that future renovations in MBT facilities will integrate VFA production (Fernández-Domínguez et al., 2020)

To obtain a stream of OFMSW rich in VFA, the MBT facilities must incorporate (i) an acidogenic fermenter to produce VFA, and (ii) separation units to up-concentrate and/or recover the produced VFA as depicted in Figure 1.4. This scheme illustrates the placement of the proposed new equipment within the existing layout of an MBT plant. As can be seen, the acidogenic fermenter should be located after hydrocyclones due to:

- Inert materials (e.g. glass, debris, metals) separated in hydrocyclones can damage acidogenic fermenter hence the costs associated with maintaining the plant are rising, and sediment is gathering at the bottom of the fermenter, which is decreasing the overall capacity of the fermenter
- Voluminous and non-biodegradable materials have been separated in the preceding processes, such as sieve, trommel and ballistic conveyor.
- A lower fermenter volume is required since half of the fermentation process has already occurred during OFMSW pre-treatment.

2. OBJECTIVES

Given that the production of bio-based VFA is an alternative to producing these compounds through petrochemical processes, the main limitation of biological production must be addressed: low concentration due to product inhibition. The overall objective is to assess the technical feasibility to the production of VFA from OFMSW, along with subsequent stages of nitrogen recovery and VFA up-concentration.

To reach this general objective, the following goals were planned:

- To evaluate the VFA production in lab-scale fermenters operated in batch and semi-continuous mode treating OFMSW.
- To study the rejection of VFA and TAN at pH values in the range of 5 and 9 of a biomimetic forward osmosis membrane to concentrate fermentation liquids.
- To analyse the performance of Gas Permeable Membrane to recover nitrogen from OFMSW fermentation liquids as a previous step for VFA up-concentration using a FO membrane.
- To study the technical feasibility of using FO for VFA up-concentration in OFMSW fermentation liquids.

3. MATERIALS AND METHODS

This chapter provides a detailed explanation of the synthetic wastewater characteristics and substrate used, the experimental set-up employed and the methodology followed, as well as the analytical methods utilized to carry out this study.

3.1. SUBSTRATE

This study was performed using synthetic wastewater and a residual stream rich in biodegradable organic matter, namely Organic Fraction of Municipal Solid Waste (OFMSW).

The synthetic wastewater was initially used to evaluate the performance of the FO module before treating fermentation liquids from an urban organic waste. The synthetic wastewater contained up to 10.7 g COD/L of acetic acid (equivalent to 10 g HAc/L), and up to 5 g NH_4^+ -N/L of NH_4Cl , since these values have been found in previous fermentation assays (Serra-Toro et al., 2022). Depending on the working pH of each test, NaOH 10 M was added to the synthetic wastewater to reach the desired working pH (5-9).

OFMSW collected from a mechanical-biological Treatment (MBT) Plant (Ecoparc) of the Barcelona Metropolitan Area. More concisely, the substrate was collected just before its feeding to the Anaerobic Digesters of the MBT plant, and it was kept at 5 °C before its use. Table 3.1 shown the main initial characteristics of OFMSW collected for batch unit (OFMSW 1) and semi-continuous (OFMSW 2) where it is observed that the collected substrate already had a high content of VFA that could be further increased in acidogenic fermentation units.

Table 3.1 Characteristics of OFMSW collected at MBT Plant of the Barcelona Metropolitan Area

	Initial characteristics	
	OFMSW 1	OFMSW 2
VFA [g/L]	13.82	13.88
VFA [g COD/L]	19.66	18.53
HAc [% COD]	31.43	43.01
HPr [% COD]	31.14	32.23
HBut [% COD]	34.00	21.51
HVal [% COD]	1.68	1.61
HCap [% COD]	1.74	1.61
TAN [g/L]	3.59	3.45
pH [-]	6.73	7.00

3.2. EXPERIMENTAL SET-UP

In this work, several experimental devices have been used: (i) a fermentation unit used to produce VFA from OFMSW, (ii) A gas-permeable membrane contactor to recover TAN from the fermentation liquid generated and (iii) a Forward Osmosis membrane unit to up-concentrate VFA. In the following sections, these three experimental devices are detailed.

3.2.1. Acidogenic fermentation units

In this study, two different types of acidogenic fermentation units were used to produce VFA from OFMSW.

Firstly, a batch unit was used, consisting of 40-L fermenter at 35 °C. 30 L of OFMSW were fed to the reactor without addition of inoculum. The fermenter was equipped with a pH probe system (Crison pH 28), a heating system (AS, Electric Heating Jacket), a mechanical stirrer and an

alleviation valve located in the upper part to avoid possible overpressures due to the generated gases.

On the other hand, the second fermentation unit consisted of a lab-scale semi-continuous fermenter (2 L capacity) operated at mesophilic conditions, an HRT of 4 days and fed once per day (Peña-Picola et al., 2023).

3.2.2. Gas-permeable membrane (GPM) contactor

Figure 3.1 shows a scheme of the lab-scale gas-permeable membrane contactor unit used in this study to recover TAN from the VFA-rich liquid generated in the previous acidogenic fermentation step.

This unit consisted in two tanks (one for the feed stream and the other for an acidic solution) connected by a membrane unit. A 5-L jacketed glass tank equipped with a thermostatic bath (Haake B5-DC30) to control the working temperature at 35 °C was used as chamber for the feed solution (fermentation liquid). The acidic trapping solution (initial solution of 0.4 M H₂SO₄) was deposited in a 2-L glass tank without temperature control. The feed and trapping solutions were circulated through a closed loop using two peristaltic pumps (Masterplex 7518-10 and Masterplex 7518-12) and directed towards a microporous hollow-fiber polypropylene membrane contactor (3 M, 1.7 x 5.5 MiniModule) with an active surface area of 0.50 m². For maintenance reasons, the feed solution circulated in the shell side of the membrane while trapping solution did by the lumen side of the contactor. The feed glass tank was sealed to minimise NH₃ and VFA volatilisation and to minimize the entrance of air to this tank, since volatile fatty acids could be aerobically degraded by microorganisms present in the fermentation liquid. Both tanks were equipped with a magnetic stirrer (IKA, C-MAG HS 7) and a pH meter (WTW ProfiLine pH 3210 Portable pH Meter).

Due to the nature of the gas-permeable membrane, charged species are not able to diffuse through the membrane, hence the trapping solution must be maintained in acidic condition to retain the NH₃ diffused from the feed solution as NH₄⁺. On the other hand, the pH of the feed solution needs to be alkaline to shift the TAN equilibrium towards the formation of NH₃ (see equation 3.8). Therefore, the acidic solution was maintained at a pH below 1.5 by dosing a well-known volume of acid solution (95-98 % H₂SO₄) while the feed solution was controlled at a

pH set-point of 9 by the addition of an alkali solution (NaOH 10 M). Each hour, 2 mL of the feed and trapping solution were extracted for its analysis.

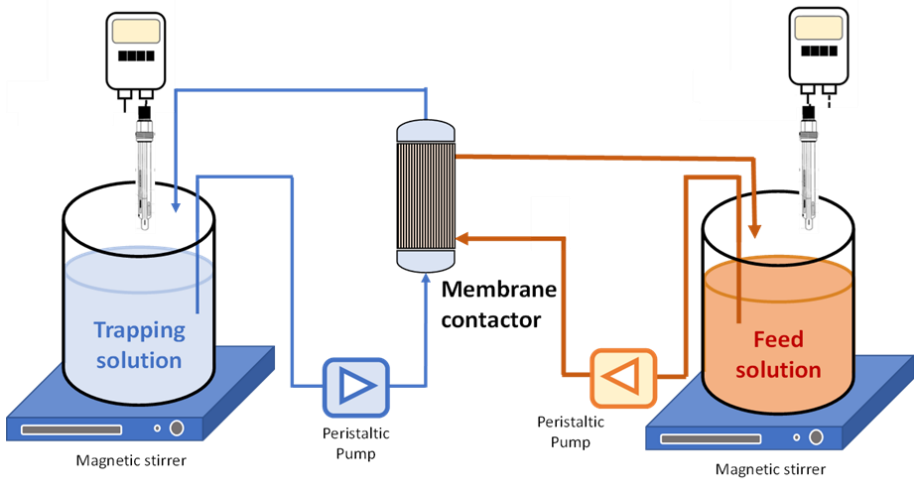


Figure 3.1. Scheme of the experimental set up used in this study to assess the performance of a Gas-Permeable Membrane (GPM) contactor for the treatment of fermentation liquids

3.2.3. Forward Osmosis membrane

Fig. 3.3 shows the Forward Osmosis membrane experimental set-up employed to up concentrate the VFA present in the feed solution. Two 5-L jacketed glass tanks were employed for the feed and draw solution (initial solution of 1.25 M $MgCl_2$). The feed solution temperature was controlled at 35 °C by means of a thermostatic bath. Two peristaltic pumps (LongerPump, WT600-3J and Watson-Marlow, 323) were utilized to circulate the feed and draw solutions within closed loops, guiding them towards a hollow fiber forward osmosis module (Aquaporin, HFFO2 module) with a membrane area of 2.3 m². The feed glass tank was sealed to minimise NH_3 and VFA volatilisation. The draw solution and the feed solution tanks were equipped with a mechanical stirrer (Heidolph, Hei-TORQUE Expert 100) and a magnetic stirrer (IKA, C-MAG HS 7), respectively. Moreover, both tanks were equipped with a pH meter (WTW ProfiLine pH 3210 Portable pH Meter). On the one hand, in tests where synthetic wastewater was used, samples (2 mL) of the draw and feed solution were taken as follows: 1 sampling event every 4 minutes during the first 12 minutes

of the assay, 1 sampling event in minute 20 and afterwards, one sampling event every 10 minutes until the end of the experiment. On the other hand, when the pre-treated OFMSW fermentation liquid was used, samples (2 mL) were taken every 2 minutes until the experiment concludes.

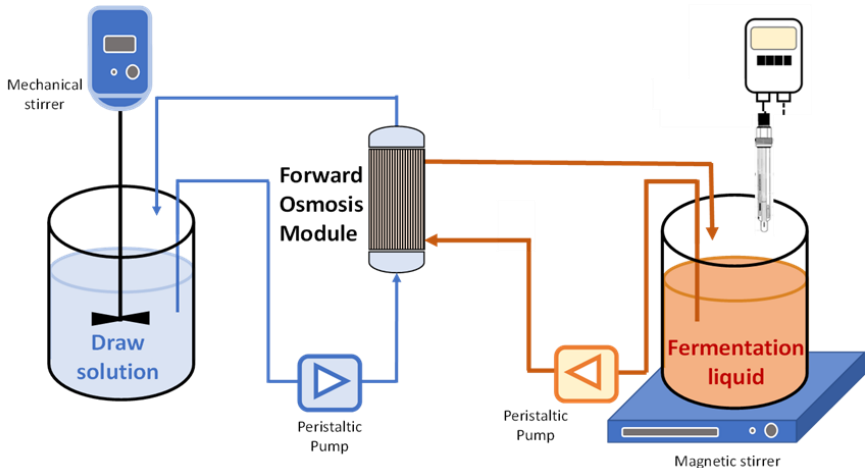


Figure 3.2. Scheme of the experimental set up used in this study to assess the performance of a FO membrane for the treatment of fermentation liquids

3.3. METHODOLOGY

This section describes in detail the methodology used in this study to investigate the nitrogen recovery coupled with VFA up concentration from fermentation liquids, including both the experimental design and the measured and manipulated variables. This methodology is organized in three phases according to the three stages of the proposed process.

Phase 1 – Batch and semi-continuous fermentation of OFMSW.

Two acidogenic fermentation experiments were conducted to produce TAN and VFA with the objective of carrying out the stages of nitrogen recovery and VFA up-concentration.

Table 3.2. Tests performed to TAN and VFA production from OFMSW collected from a MBT Plant of the Barcelona Metropolitan Area

Test	Number of replicates	Type	Feed	Product	T [°C]	HRT [days]
FU-1	1	Batch	OFMSW 1	OFMSW FL 1	35	6
FU-2	1	Continuous	OFMSW 2	OFMSW FL 2	35	4

Then, 4 experiments were carried out to determine the total suspended solids generated when the pH of the fermentation liquid was adjusted to pH values of 8, 9, 10 and 11 in order to define the most appropriate pH to implement the subsequent recovery of TAN using gas-permeable membranes. For these tests, TSS measurements of the Fermentation liquid were carried out in triplicate to determine the average value and the experimental error.

Phase 2 – Nitrogen recovery from fermentation liquids.

Table 3.4 shown the experimental conditions to carry out the nitrogen recovery as a previous stage of VFA up-concentration for two fermentation liquids.

Table 3.4. Tests performed to evaluate the nitrogen recovery from fermentation effluents using a gas permeable membrane contactor with a working temperature of 35 °C in the feed tank

Test	Number of replicates	Feed	Initial Feed volume [L]	pH set-point (feed)	Initial Trapping solution volume [L]	pH set-point (trapping)
NR-1	1	OFMSW FL 1	4.00	9.00	0.37	1.00
NR-2	1	OFMSW FL 2	4.00	9.00	0.37	1.00

Phase 3 – VFA up-concentration from fermentation liquids.

In this phase, the VFA and TAN selectivity and permeability of the forward osmosis module were studied. Table 3.5 summarizes the experiments carried out with both synthetic wastewater and pretreated OFMSW fermentation liquids. In this Table, there are three types of experiments: The first set (Aq-1, A-2, and Aq-3) with 10.7 g COD/L at different pH values, studying the permeability and selectivity of the FO module for acetic acid due to it is smallest of the VFA and therefore the one that would have the easiest to diffuse through the membrane. The second set (Aq-4, Aq-5, and Aq-6) investigates these same parameters for TAN at the same pH values and the consequences of not carrying out a prior nitrogen recovery stage. The last group, except for the other two, is performed using the fermentation liquids from the acidogenic fermentation stage at a pH of 9. All experiments excluding Aq-7 are conducted in duplicate to obtain the average value and experimental error.

Table 3.5. Tests performed to evaluate the Forward Osmosis process using Aquaporin to up-concentrate the VFA content of fermentation liquids using 1.25M MgCl₂ as draw solution and a working temperature of 35 °C for the feed tank

Test (replicates)	Initial Feed volume [L]	Feed characteristics				Initial draw solution volume [L]
		Synthetic/ OFMSW-FL	VFA [g COD/L]	TAN [g N/L]	pH	
Aq-1 (a,b)	1.90	Synthetic	10.70	-	5.00	1.90
Aq-2 (a,b)	1.90	Synthetic	10.70	-	7.00	1.90
Aq-3 (a,b)	1.90	Synthetic	10.70	-	9.00	1.90
Aq-4 (a,b)	1.90	Synthetic	-	5.00	5.00	1.90
Aq-5 (a,b)	1.90	Synthetic	-	5.00	7.00	1.90
Aq-6 (a,b)	1.90	Synthetic	-	5.00	9.00	1.90
Aq-7 (a)	1.90	OFMSW-FL 1	32.25	0.30	8.34	1.90
Aq-8 (a,b)	1.90	OFMSW-FL 2	37.32	0.27	8.87	1.90

3.4. ANALYTICAL METHODS

The analytical methods used in this work are briefly discussed below. All these analyses were performed according to Standards Methods for the examination of Water and Wastewater (APHA, 2017).

3.4.1. Solids content

Total Solids (TS) and Volatile Solids (VS). TS and VS concentration were determined using the standard methods 2540B and 2540E, respectively (APHA, 2017). A known volume (V) of sample was added in a porcelain capsule previously weighed (W_1) and it was maintained at 105 °C for 24 hours in a laboratory oven (JP Selecta) to evaporate the water. Then, the porcelain capsule was introduced in a desiccator until reaching ambient temperature, after it was weighed (W_2) once again. The Total Solids content can be determined through equation 3.1. Thereafter, the porcelain capsule was deposited in a muffle (HD-230, Hobersal) at 550 °C for 2 hours. Then, the porcelain capsule was introduced in a desiccator until it reached ambient temperature, a moment when it was weighed (W_3) for the last time. The Volatile Solids content can be determined through equation 3.2.

$$TS \left(\frac{g}{L} \right) = \frac{W_2(g) - W_1(g)}{V(L)} \quad (3.1)$$

$$VS \left(\frac{g}{L} \right) = \frac{W_2(g) - W_3(g)}{V(L)} \quad (3.2)$$

Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS). TSS and VSS were determined using the standard methods 2540D and 2540E, respectively (APHA, 2017).

To start with, a Millipore standard filter of 1.2 μm was introduced in a muffle (HD-230, Hobersal) for 10 minutes to ensure the removal of possible impurities deposited in the filter. Afterwards, this filter was weight (W_4) and a known volume (V) of sample was filtered through it using a filtration system with vacuum pump (Dinko, D-95). After sample filtration, deionized water was passed to remove all possible soluble traces retained in the filter. Then, the filter was introduced in a laboratory oven (JP Selecta) at 105 °C for 24 hours. After that, the filter was put in a desiccator for 10 minutes, and it was weighed (W_5). TSS can be calculated through equation 3.3. Finally, the

filter was deposited in a muffle (HD-230, Hobersal) at 550 °C for 15 minutes. Afterwards, the filter was put in a desiccator for 10 minutes and, it was weighed (W_6). VSS can be calculated through equation 3.4.

$$TSS \left(\frac{g}{L} \right) = \frac{W_5(g) - W_4(g)}{V(L)} \quad (3.3)$$

$$VSS \left(\frac{g}{L} \right) = \frac{W_5(g) - W_6(g)}{V(L)} \quad (3.4)$$

3.4.2. Volatile Fatty Acids (VFA)

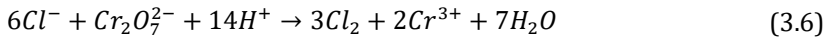
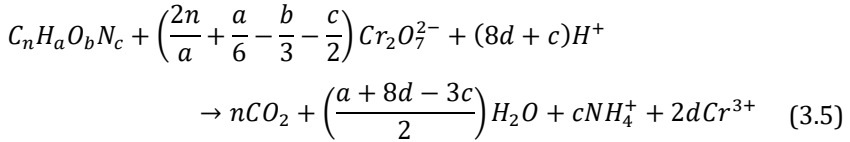
The VFA concentration and distribution were analysed employing a gas chromatograph (Shimadzu GC 2010 plus) equipped with a capillarity column (Nukol™, 15 m x 0.53 mm x 0.5 µm) and a flame ionization detector (FID) following the 5560D Standard Method procedure from the Standards Methods for the examination of Water and Wastewater (APHA, 2017). The chromatograph used helium as carrier gas, hydrogen as fuel gas and synthetic air as the oxidizing gas. The chromatograph used was able to detect acetic, propionic, iso-butyric, butyric, isovaleric, valeric, iso-caproic, caproic and heptanoic acids. The concentrations were obtained in ppm VFA and the detection limit were between 0 and 500 mg VFA/L.

Samples were centrifuged and filtered using a syringe-filter (Simsi Syringe Filter with a pore size of 0.45 µm and a diameter of 25 mm). 1 mL of the sample (diluted or not) was added to the vial together with 100 µL of a solution of acid phosphoric at 80% with a known concentration of 2-ethylbutyric acid (internal standard).

3.4.3. Chemical oxygen demand (COD)

Chemical oxygen demand analysis indicates the quantity of matter in the sample that can be chemically oxidized. This parameter is expressed in terms of mg COD/L, that represents the oxygen-equivalents needed to oxidise the matter present in the sample. COD was determined using the standard method 5220D from the Standards Methods for the examination of Water and Wastewater (APHA, 2017). This colorimetric method is based on the complete oxidation of the

matter in the sample (see equation 3.5), by addition of strong oxidising reagent (potassium dichromate) under acidic conditions (accomplished by introducing sulfuric acid). Furthermore, silver sulphate was used as a catalyst of the reaction and mercury (II) sulphate was added to avoid chloride interference in COD analysis (see equation 3.6).



For total COD analysis, 2.5 mL of sample were mixed in one vial with 4.5 mL of silver sulphate solution 10 g/L in sulphuric acid and 1.5 mL of potassium dichromate 0.04 mol/L (with 80 g/L of mercury (II) sulphate). Moreover, 5 patrons of 0, 50, 250, 500 and 1000 mg COD/L (potassium biphthalate) were prepared. COD vials were introduced in a COD digester (ECO 25 thermoreactor, VELP Scientifica) at 150 °C for 2 hours to guarantee the occurrence of the full reaction. Following the digestion process, the samples were kept at room temperature until the following day to allow for the settling of any formed solids (i.e. HgCl₂). To conclude the analysis, the absorbance (ABS) of the samples and patrons was analysed in a spectrophotometer (J.P Selecta, V-1100D Spectrophotometer) at λ=620 nm. A calibration curve was obtained with the absorbance of the patrons (see equation 3.7).

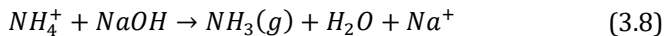
$$ABS = a \cdot C \quad (3.7)$$

For the analysis of Soluble COD (sCOD), the procedure was the same as for total COD, but samples were previously filtered using a syringe-filter (Simsi Syringe Filter with a pore size of 0.45 µm and a diameter of 25 mm).

3.4.4. Total Ammonium Nitrogen (TAN)

Total Ammonium Nitrogen (TAN or $\text{NH}_4^+\text{-N}$) concentration was determined with a specific high performance ammonia electrode (Orion 9512HPBNWP, Thermo Scientific) connected to a voltmeter (Orion DualStar pH/ISE Benchtop, Thermo Scientific) following the standard method 4500-NH3D from the Standards Methods for the examination of Water and Wastewater (APHA, 2017).

This method is based on the addition of few drops of strong base (10 M NaOH) for the samples to the complete conversion of N-NH_4^+ into free ammonia nitrogen (see equation 3.8). Hence, there is a subsequent diffusion of $\text{NH}_3(\text{g})$ through the hydrophobic gas-permeable membrane of the electrode. When the pH of the sample is increased, the electrode is submerged to detect the potential variation (ΔV) in mV. The correlation between $\text{NH}_4^+\text{-N}$ concentration and potential variation is obtained by means of a semilogarithmic expression (see equation 3.9). For the calibration of the electrode, six samples of 10, 25, 50, 100 and 150 mg $\text{NH}_4^+\text{-N/L}$ were prepared and analysed every time.



$$\ln(\text{NH}_4^+ - \text{N}) = a \cdot \Delta V + b \quad (3.9)$$

4. EXPERIMENTAL RESULTS AND DISCUSSION

In this section 4 types of experiments will be presented and discussed: the production of VFA by means two lab-scale acidogenic fermentation units, the effect of pH in VFA and TAN up-concentration, the effect of pH on TSS concentration, GPM test using fermentation liquid and VFA up-concentration in a fermentation broth.

4.1. FERMENTATION LIQUIDS PRODUCTION

During the experimentation, two lab-scale digesters with the operational conditions fixed at Materials and Methods were operated. Table 4.1 throw information about VFA concentration and distribution, pH and TAN concentration for the start and end of the fermentation.

As stated in Table 4.1, the fermentation liquids of both fermentation units were characterised by a high VFA content (35-37 g CODVFA/L) dominated by acetic, propionic and butyric acids. Moreover, the TAN content was very high in the range of 5.0-5.4 g N/L. As observed in this Table, the pH of the fermentation liquids was set in slightly acidic or neutral values, regardless of the high VFA production, which is related to the high buffer capacity of the collected OFMSW samples.

A special mention should be made to the VFAs concentration evolution in the batch fermentation test. As shown in Figure 4.1 (a), the VFA concentration in day 6 suffered a small decrease, which suggests that in this point the maximum VFA concentration was reached due to the fermentation inhibition by product. This reinforces the idea that a method of VFA concentration is needed to obtain higher concentrations than those achieved in the acidogenic fermentation units.

Table 4.1. Initial and final characteristics for batch (OFMSW 1) and continuous (OFMSW 2) fermentation

	Initial characteristics		Final characteristics	
	OFMSW 1	OFMSW 2	OFMSW 1	OFMSW 2
VFA [g/L]	13.82	13.88	24.62	26.12
VFA [g COD/L]	19.66	18.53	35.16	37.32
HAc [% COD]	31.43	43.01	33.93	32.45
HPr [% COD]	31.14	32.23	27.24	27.93
HBut [% COD]	34.00	21.51	24.46	31.31
HVal [% COD]	1.68	1.61	8.77	5.62
HCap [% COD]	1.74	1.61	5.60	2.70
TAN [g/L]	3.59	3.45	5.02	5.35
pH [-]	6.73	7.00	7.13	6.55

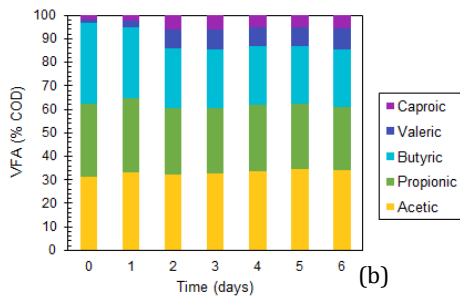
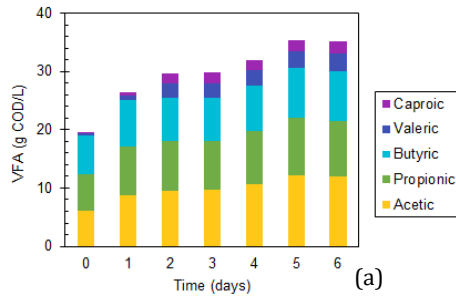


Figure 4.1. OFMSW batch fermentation test (a) evolution of VFA concentration, (b) proportion of the VFA

4.2. FORWARD OSMOSIS TEST USING SYNTHETIC WASTEWATER

This section contains the results of forward osmosis testing with synthetic wastewater. The experimental values of each pH have been analysed and compared with the others. This is carried out for TAN and acid acetic proofs.

4.2.1. Effect of pH in VFA up-concentration

Table 4.2 shown the initial and final volume, acetic acid concentration, conductivity and pH for the feed and the draw solution, while figure 4.1 illustrates the evolution of these parameters during the experiment.

Table 4.2. Initial and final characteristics for acetic acid experiments

	Initial characteristics		Final characteristics	
	Feed	Draw solution	Feed	Draw solution
Experiment at pH 5				
Volume [L]	1.90 ± 0.00	1.90 ± 0.00	0.75 ± 0.01	3.05 ± 0.01
HAc [g COD/L]	10.70 ± 0.00	0.00 ± 0.00	10,94 ± 0.11	3.70 ± 0.04
Conductivity [mS/cm]	66.65 ± 0.74	243.68 ± 1.10	150.85 ± 1.56	154.68 ± 0.60
pH [-]	5.01 ± 0.02	6.26 ± 0.06	4.96 ± 0.02	4.56 ± 0.03
Experiment at pH 7				
Volume [L]	1.90 ± 0.00	1.90 ± 0.00	0.76 ± 0.01	3.04 ± 0.01
HAc [g COD/L]	10.70 ± 0.00	0.00 ± 0.00	23.93 ± 1.33	0.31 ± 0.08
Conductivity [mS/cm]	68.60 ± 0.25	240.02 ± 5.92	141.00 ± 0.99	154.55 ± 2.76
pH [-]	7.19 ± 0.06	6.20 ± 0.00	7.57 ± 0.48	6.80 ± 0.07
Experiment at pH 9				
Volume [L]	1.90 ± 0.00	1.90 ± 0.00	0.78 ± 0.02	3.02 ± 0.02
HAc [g COD/L]	10.70 ± 0.00	0.00 ± 0.00	25.65 ± 0.80	0.21 ± 0.01
Conductivity [mS/cm]	69.48 ± 0.25	236.35 ± 12.80	138.30 ± 9.05	148.75 ± 4.74
pH [-]	9.25 ± 0.05	6.24 ± 0.08	8.96 ± 0.04	7.77 ± 0.11

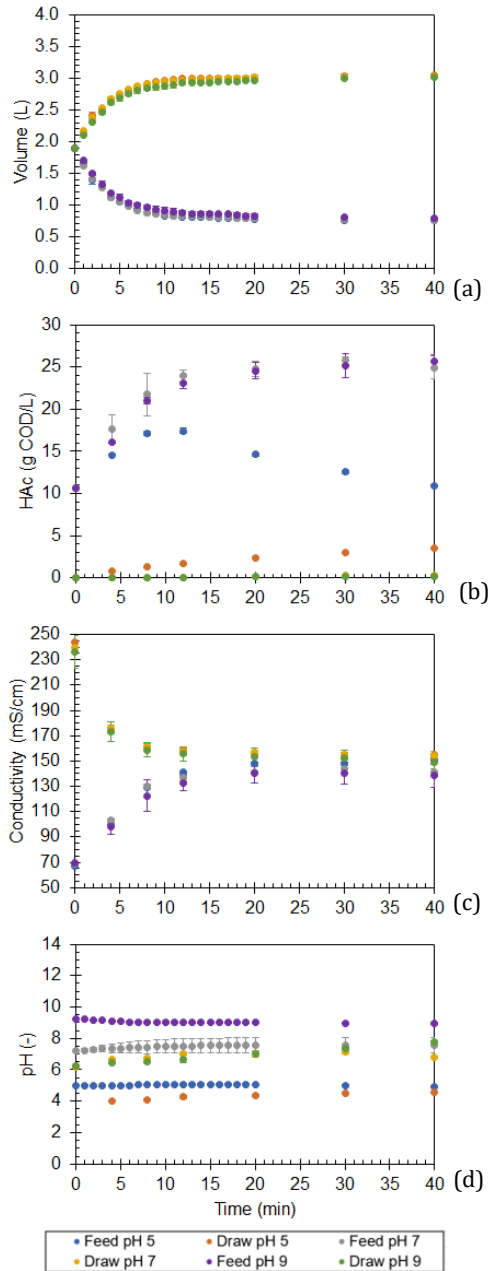


Figure 4.2. Monitoring acetic acid test. (a) volume, (b) acetic acid concentration (c) conductivity and (d) pH evolution

For pH 5 a great volume diminution was observed in figure 4.2 (a) in the feed between minute 0 and 6. Hence, a large difference in osmotic pressure causes an important water flux defined by the Equation 1.4. In terms of acetic acid concentration, in the first minutes the concentration in the feed increased as a consequence of the high-water flux towards the draw solution, however, when this decreased, a significant amount of acetic acid began to diffuse through the membrane to the draw solution, reaching a concentration of 3.70 ± 0.04 g COD /L at the end of the experiment. As for the conductivity, a great difference was measured at the start of the experiment between feed and draw solution, but this divergence was rapidly reduced with the passage of water. Regarding the pH of the two solutions, a high decrease (1.70 ± 0.09) was observed in the draw solution due to the permeation of the unionized acetic acid, reaching a final pH value of 4.56 ± 0.03 .

For pH 7 a volume decreases very similar to that observed in the experiment at pH 5 was reported. In contrast to the previously mentioned experiment, when the water flux decreases, no decline in the concentration of acetic acid is observed since at pH 7, the majority present form is acetate, and there is electrostatic repulsion with the membrane. The draw solution reaches a concentration of 0.31 ± 0.08 g COD/L (equivalent to 0.29 ± 0.07 g HAC/L), indicating that acetic acid permeation was not favoured at this pH but was not completely prevented. In terms of the pH of the feed, in one of the replicates the pH remained practically constant while in the other it increased, which is why the values of this parameter are associated with a higher standard deviation than in other experiments. It was decided not to eliminate any of the replicates since the other parameters such as conductivity, volume and acetic acid concentration were very similar.

For pH 9 a lower water flux compared to the experiments at pH 5 and 7 can be observed in Figure 4.2 (a). In terms of acetic acid concentration, the difference between this experiment and the previous one is very small, which suggests a low increase in the rejection rate for acetic acid once pH 7 has been exceeded.

As previously mentioned, the water flow observed in the experiments at pH 5 was higher than the other two, reaching a WCF of 2.53 ± 0.03 compared to pH 7, 2.50 ± 0.03 and 9, 2.44 ± 0.06 , this coincides with the expected results. This is because less amount of NaOH was required to adjust

the pH to 5 compared to 7 and 9, this smaller quantity in the same feed solution produces a small increase in osmotic pressure, hence, more water must pass through the membrane for the osmotic pressures of the two solutions to equalize.

In terms of acetic acid concentration, the highest value achieved in the feed, was at the experiment at pH 9 when the ratio of acetate to acetic acid concentration is higher. This matches the predicted outcomes, given the Forward Osmosis module used to allow the pass of water and similar molecules (both the charge and the size of the molecule) and acetate is a charged specie. It has been observed that the difference between working at pH 7 and 9 is not remarkable, but a significant difference was noticed at pH 5, when the final concentration of the feedstock was the lowest recorded although the WCF was the greatest of all experiments. In the draw solution, the acetic acid concentrations were always concordant with those obtained in the feed, being 3.70 ± 0.04 g COD/L, the highest value achieved when working at an initial pH of 5 in the feed. A minor difference between pH 7 and 9 was detected, when the highest concentrations recorded were 0.31 ± 0.08 and 0.21 ± 0.01 g COD/L, respectively.

The rejection rate for acetic acid (see equation 1.6) is another parameter that could be used to compare the process performance at different pH values.

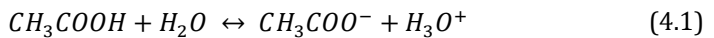
Table 4.3. Rejection rates for acetic acid obtained in this study with synthetic wastewater

pH [-]	R [%]
5	66.12 ± 0.73
7	98.74 ± 0.38
9	99.17 ± 0.07

The rejection rates shown in table 4.3 aligns with the values reported by Blandin et al., (2019) who informed around 90% rejection of all VFA was achieved at pH 7.5 and Zhu et al., (2022) who recorded a rejection rate for acetic acid higher than 90 % working at pH 7 and 20 % lower at pH 5. The discernible influence of pH on the rejection of acetic acid can be attributed to its relatively low pKa value, indicating that most of the acetic acid exists in ionized form at pH values above 4.76, while it predominantly exists in undissociated molecular form at pH values below this threshold.

Consequently, the rejection is augmented due to the electrostatic repulsion between the negatively charged surface of the FO membrane and the ionized form of acetic acid, leading to improved rejection efficiency.

As for evolution of pH of the draw solution, it depends on the majority form found in the feed (acetate or acetic acid) and therefore crosses the membrane in greater or lesser quantity and produces an increase or decrease in the pH of the draw solution. At pH 5 experiment, the final pH was 4.56 ± 0.03 , which entails a notable difference with the initial, this is due to diffusion of acetic acid across the membrane and consequently the acidification of the draw solution (see equation 4.1). In experiments at pH 7 and 9 an increase in pH of the draw solution is noticed that in absolute terms is less than that the observed at pH 5, this is because less acetate (majority form) crosses the membrane and the molecules that do so increase the pH (see equation 4.2).



To conclude, it is necessary to highlight that given the characteristics of the membrane used, the rejection rate of the rest of VFA will be higher than that of acetic acid, so the up-concentration of VFA is feasible at pH above 7.

4.2.2. Effect of pH in TAN up-concentration

Fig 4.3 illustrates the evolution of volume, TAN concentration, conductivity and pH of feed and draw solution of the experiment carried with synthetic wastewater with 5 g TAN/L at pH 5, 7 and 9 and Table 4.4 summarises these parameters at the beginning and the end of the experiment.

For pH 5, there was a substantial decrease in volume observed in Figure 4.3 (a) of the feed between minute 0 and 8. Like in acetic acid test, this is due to the high-water flux generated by difference in osmotic pressures (see equation 1.4). In terms of TAN concentration in feedstock, it reaches its maximum at minute 8 with a value of 7.02 ± 0.20 g/L, at which point the water flux has decreased compared to the beginning due to the decrease in osmotic pressure difference. From

minute 8 the concentration of TAN begins to decrease rapidly until reaching the minimum at the end of the experiment.

About conductivity, the significant difference between the feed and draw solution rapidly decreases until reaching minute 8, at which point they practically equalize. The pH of feedstock slightly, while the pH of the draw solution decreased more significantly.

Table 4.4. Initial and final characteristics for TAN experiments

	Initial characteristics		Final characteristics	
	Feed	Draw solution	Feed	Draw solution
Experiment at pH 5				
Volume [L]	1.90 ± 0.00	1.90 ± 0.00	0.72 ± 0.01	3.08 ± 0.01
TAN [g/L]	5.00 ± 0.00	0.00 ± 0.00	3.41 ± 0.10	2.06 ± 0.16
Conductivity [mS/cm]	100.45 ± 1.63	230.70 ± 2.69	158.55 ± 1.91	161.10 ± 1.27
pH [-]	5.09 ± 0.07	6.81 ± 0.22	5.30 ± 0.12	5.96 ± 0.08
Experiment at pH 7				
Volume [L]	1.90 ± 0.00	1.90 ± 0.00	0.74 ± 0.01	3.06 ± 0.01
TAN [g/L]	5.00 ± 0.00	0.00 ± 0.00	3.52 ± 0.02	2.16 ± 0.09
Conductivity [mS/cm]	102.40 ± 1.27	229.90 ± 2.97	158.30 ± 1.56	161.05 ± 0.21
pH [-]	6.98 ± 0.11	6.68 ± 0.09	6.74 ± 0.23	7.15 ± 0.35
Experiment at pH 9				
Volume [L]	1.90 ± 0.00	1.90 ± 0.00	0.79 ± 0.01	3.01 ± 0.01
TAN [g/L]	5.00 ± 0.00	0.00 ± 0.00	3.44 ± 0.18	2.10 ± 0.08
Conductivity [mS/cm]	98.55 ± 1.20	234.30 ± 0.99	163.70 ± 0.28	165.10 ± 2.83
pH [-]	8.92 ± 0.05	6.72 ± 0.04	8.46 ± 0.06	8.47 ± 0.04

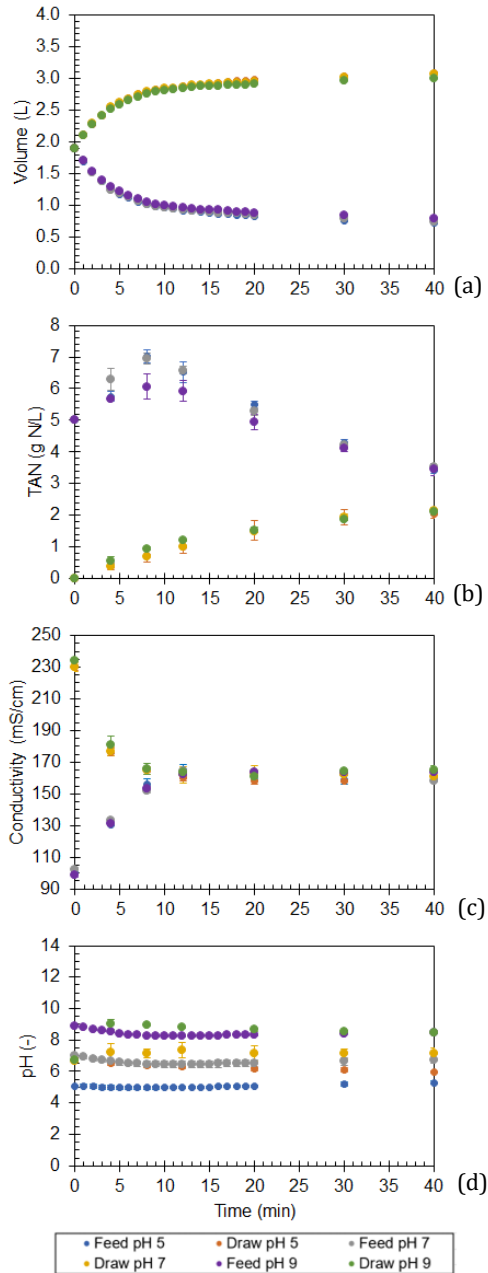


Figure 4.3. Monitoring acetic acid test. (a) volume, (b) TAN concentration (c) conductivity and (d) pH evolution

For pH 7, figure 4.3 (b) shows a trend in the evolution of volumes very similar to that of pH 5, so it can be explained by the same causes. No statistical difference in concentration values has been found between the feed and draw solution at both pH 5 and pH 7. In some points of Figure 4.3 (b), the experiment values at pH 7 are not distinguishable as they overlap with those at pH 5. For pH 9 in Figure 4.2 (a), a decrease in water flux can be observed for pH 9 in comparison to the experiments conducted at pH 5 and 7. Regarding the observed TAN concentration in the feedstock, the trend is the same as in the other experiments, reaching its maximum concentration at minute 8. There is complete agreement among the three experiments at minutes 30 and 40, while the pH 9 test differs from the other two experiments at the remaining points. These results raise whether this small difference is due to experimental error or if there is a possibility that the greater diffusion towards the draw solution is due to the proximity of the pH to the pKa (8.94 at 35 °C). The latter hypothesis gains credibility when observing Figure 4.3 (b) and (d); at points where there is a greater difference in TAN concentration compared to the rest of the experiments, the feedstock pH was very close to the pKa, whereas towards the end, when all three points overlap, the pH was 8.46 ± 0.06 .

In terms of WCF, the maximum value was achieved at pH 5 of 2.64 ± 0.04 , since no addition of alkali is required to adjust the pH at 5 and, hence, a higher water flow is required for the equalization of osmotic pressures between the two solutions.

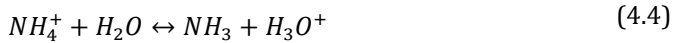
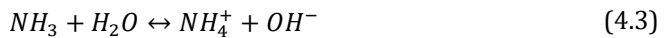
TAN concentrations evolve in a very similar way for the three pHs, with special emphasis on 5 and 7. Both water and TAN diffuse through the membrane into the draw solution. In the feed, there is the loss of water and TAN, which are two contributions at different speeds, as can be seen in Figure 4.3 (a) and (b).

Table 4.5. Rejection rates for TAN obtained in this study with synthetic wastewater

pH [-]	R [%]
5	39.76 ± 6.31
7	38.48 ± 2.92
9	38.98 ± 5.57

Based on available literature with Thin Film Composite (TFC) forward osmosis membranes, this results contrast with the reported by and Zhu et al., (2022) who recorded a higher TAN rejection for acidic conditions and extreme sensitivity to pH variations.

The results are attributed to the fact that the used Forward Osmosis module is composed by an active layer of polyamide thin film composite (TFC) and a biomimetic part comprised of integrated aquaporin proteins that enhances water permeability and selectivity flux (Engelhardt et al., (2019) In terms of pH of the draw solution, a decrease is observed in the experiment with the feed at pH 5, due to the acidification (see equation 4.4) of the draw solution. When the pH in feed solution was 7 and 9, the pH of draw solution increased, being the highest pH increase when the feed was more alkaline. This change of pH is justified by the diffusion of NH_3 through the membrane, and the consequent increase in pH of the draw solution (see equation 4.3). The increase in the pH of the draw solution when the feedstock has a pH of 7 is not expected, given that at this pH the main species is the ammonium ion, which could suggest the diffusion of OH^- through the membrane.



Due to the low rejection rate of the membrane towards TAN regardless of pH, it is necessary to have fermentation liquids with low levels of ammonia nitrogen. Therefore, the implementation of a nitrogen recovery stage through GPM will be studied, positioned between the acidogenic fermentation and the FO module.

4.3. FERMENTATION LIQUIDS TESTS

This section contains the results of the effect of pH in TSS concentration, the recovery of TAN using GPM and the up concentration of VFA.

4.3.1. Effect of pH in TSS concentrations

With the aim of determining the optimum pH of the feedstock to be able to carry out the recovery of TAN and the up concentration of VFA, the total suspended solids of the prefiltered OFMSW FL-2 at 1.2 μm and with a pH of 6.55 were determined at four different pHs, 8,9,10 and 11.

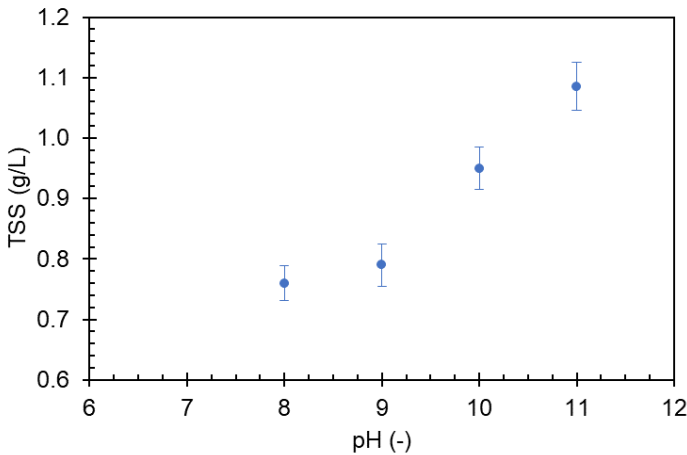


Figure 4. 4. Effect of pH in TSS content for OFMSW FL-2

It is important to highlight that these values are overestimated due to the higher salinity of the feedstock compared to seawater and although the steps found in the "Materials and methods" for TSS analysis have been followed, a small amount of salt could have been still present on the filter.

Nevertheless, TSS at pH 8 and 9 were remarkably similar while when this pH was increased, the TSS content began to grow exponentially ($R^2 = 0.99$), reaching a value of (1.09 ± 0.04) g/L when feedstock is at pH 11.

In TAN recovery, the better performance of the Gas Permeable Membrane is at pH values higher than the pKa (8,95 at 35 °C) when a percentage of NH_3 is more than 50 %. For the treatment of

2 L of wastewater with 2 g N/L and a gas-permeable membrane module with 0.5m², Serra-Toro et al. (2022) reported that in 8 hours a 65 % TAN recovery was achieved at pH 8, 91 % at pH 9, and 100 % at pH 10 and 11. Lee et al. (2021) also conducted a recent study proposing that using moderate alkaline pH values, specifically 9, could offer advantages in mitigating inorganic fouling on the membrane and moreover a diminution of alkali consumption.

For the up-concentration of VFA, pH 9 is a suitable value, as has been shown in experiments of synthetic wastewater with 10 g/L of acetic acid, furthermore, the membrane manufacturer does not recommend operating the forward osmosis module at pH values higher than 10. For these reasons and aiming to prevent fouling of the membrane due to a high TSS content in the fermentation liquid at high pH values, the selected pH to carry out the two stages was 9.

4.3.2. Nitrogen recovery using a membrane contactor

This section includes the results of the nitrogen recovery using GPM for the two fermentation liquids as well as their comparison and discussion.

Table 4.6. GPM performance for the Nitrogen recovery for each OFMSW fermentation liquid

Parameter	Units	Value	
		OFMSW-FL 1	OFMSW-FL 2
<i>Fermentation liquor (feed)</i>			
Experiment	-	1	2
Initial feed volume	L	4.00	4.00
Final pH	-	9.04	9.03
Initial VFA concentration	g COD _{VFA} /L	32.10	37.32
Final VFA concentration	g COD _{VFA} /L	31.81	37.50
Initial TAN concentration	g N/L	4.86	5.35 ± 0.66
Final TAN concentration	g N/L	0.30	0.22 ± 0.00
NaOH consumption	mol NaOH/mol N recovered	1.17	1.07
N removal	%	94.02	96.09
<i>Trapping solution</i>			
Initial trapping solution volume	L	0.37	0.37
Final pH	-	1.80	1.43
Final VFA concentration	g COD _{VFA} /L	0.00	0.00
Final TAN concentration	g N/L	34.81	32.07
H ₂ SO ₄ consumption	mol H ₂ SO ₄ /mol N recovered	0.55	0.77
N recovery	%	93.38	95.98

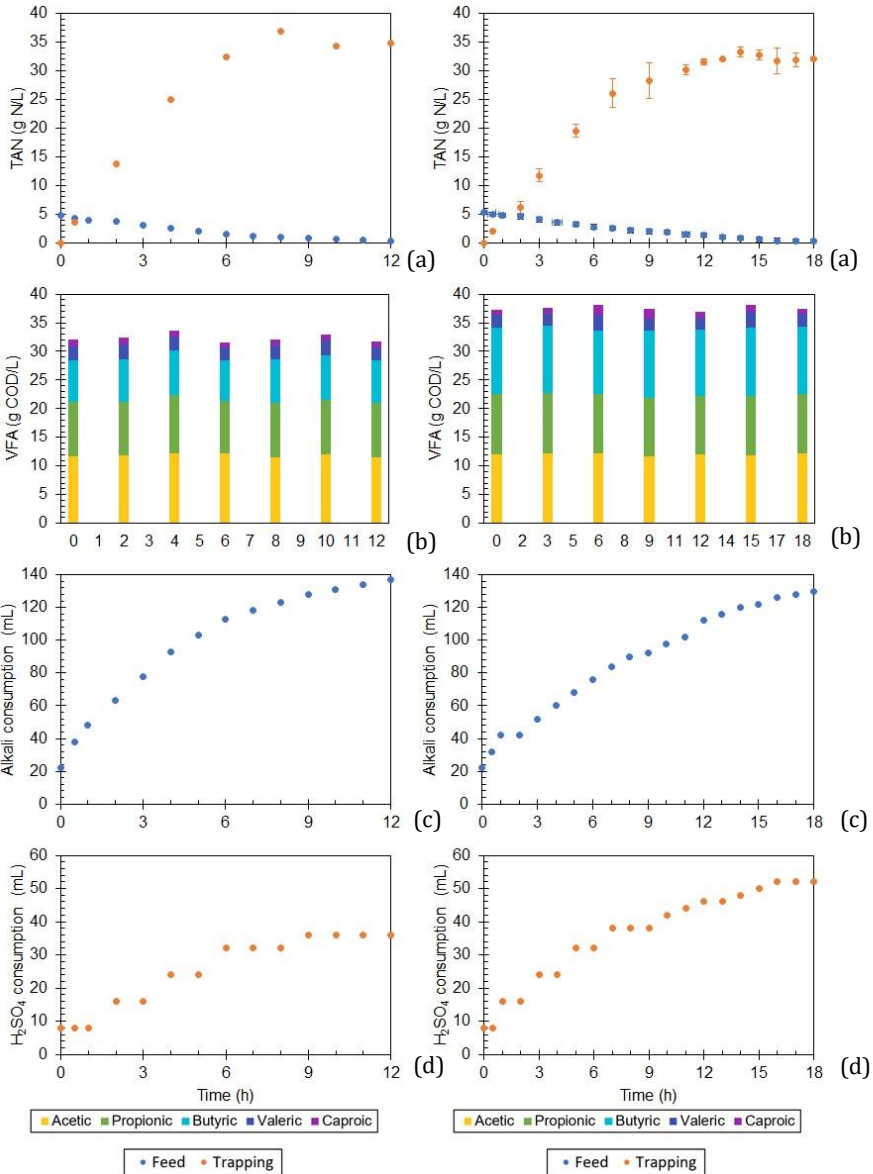


Figure 4.5. Monitoring of nitrogen recovery from OFMSW FL-1. (a) TAN and (b) VFA concentration, (c) alkali and (d) sulfuric acid consumption

Figure 4.6. Monitoring of nitrogen recovery from OFMSW FL-2. (a) TAN and (b) VFA concentration, (c) alkali and (d) sulfuric acid consumption

NR-1 Test: For the experiment with the first fermentation liquid (OFMSW FL-1) generated from batch fermentation, the VFA initial concentration was 22.96 ± 0.88 g VFA/L (equivalent to 32.25 g COD_{VFA}/L), and the TAN content was 4.86 g N/L. Moreover, 22 mL of NaOH 10 M were required to adjust the initial pH at 9. The trapping solution had an initial volume of 0.368 mL, with a pH of 0.11, and did not contain VFA nor TAN.

During the first 8 hours, the TAN concentration in the feed decreases following the equation:

$$\frac{C_{\text{TAN},f}(t)}{C_{\text{TAN},f}(t=0)} = \exp\left(\frac{-K_m A}{V_f} t\right) \quad (4.5)$$

Where $C_{\text{TAN},f}(t)$ is the concentration of TAN in the feed at time t , A is the area of the membrane and V_f is the volume of the feed.

This equation considers a constant working pH, an instantaneous ammonium/ammonia acid-base equilibrium and no water diffusion from one side to the other side of the membrane (Reig et al., 2021). Therefore, after the first 8 hours, this equation could not be longer applied since water permeation was detected from the fermentation liquid to the acidic trapping solution due to the high salts content of the trapping solution (>30 g N/L). Further work is needed in order to propose a model capable of predicting water passage through the membrane when high ammonium sulphate concentration is obtained in the trapping solution. Then, the nitrogen uptake rate slowed down until reaching a final concentration of 0.30 g TAN/L after 12 hours of the experiment.

For TAN concentrations obtained in the laboratory, the K_m value was $4.48 \cdot 10^{-7}$ m/s.

The TAN concentration in the trapping solution reached a maximum value of 36.94 g TAN/L. From this point, the concentration started to decrease. At this time, an increase in the volume of the trapping solution and a decrease in the feed were observed in the laboratory, along with a change in colour from transparent to yellowish. It is believed that the substance passing through is water, but the exact causes are currently unknown, and it is being further studied in the Environmental Biotechnology research group of the University of Barcelona. The values for N removal and N recovery were 94.02% and 93.38%, respectively, which indicates that no ammonia losses by volatilization were detected.

As can be observed in figure 4.5. (b), the concentration of VFA in the feed remained practically constant. The small deviations may be attributed to the chromatograph's associated error or a slight degradation of the VFA throughout the experiment. This hypothesis is reinforced by the fact that no VFA have been detected in the trapping solution in any of the samples. Therefore, it can be concluded that the rejection of VFA in the GPM is 100 %.

During the experiment, the total consumption of NaOH 10 M was 115 mL without considering the initial volume for pH adjustment to 9. As observed in figure 4.5. (c) the addition of NaOH during the first 6 hours was (13 ± 3) mL/h, which corresponds to the period of highest diffusion rate through the membrane. From hour 6 until the end of the experiment, (4 ± 1) mL of NaOH were added per hour. The alkali consumption throughout the experiment was 1.17 mol NaOH/mol N recovered.

The total consumption of H₂SO₄ (98 % w/w) during the experiment was 36 mL. In figure 4.5. (d) the evolution throughout the entire experiment can be observed. During the first 6 hours, 8 mL were added every 2 hours, and in hour 9, the final addition of 4 mL was made. The sulfuric acid consumption throughout the experiment was 0.55 mol H₂SO₄/mol N recovered.

The initial conductivity of the feed was 49.78 ± 1.73 mS/cm, and the final conductivity was 43.45 ± 2.90 mS/cm. On the other hand, the final conductivity of the trapping solution was 321.88 ± 23.51 mS/cm. The total solids (TS) content at the beginning was 35.59 ± 3.23 g TS/L, with volatile solids (VS) of 19.91 ± 3.24 g VS/L. At the end of the experiment, the TS content was 51.11 ± 0.20 g TS/L, and the VS content was 22.86 ± 0.59 g VS/L, respectively. Currently, other complementary analyses such as particle size distribution, metals, or total organic carbon (TOC) are being carried out to gain more information about the GPM process.

NR-2 test: The OFMSW FL-2 used in this experiment, apart from being produced differently than OFMSW FL-1, also came from a different collection period of the Ecoparc. Since its composition, including the TAN content, was different, it was expected that the nitrogen recovery process performance using a GPM would not be the same as when working with OFMSW FL-2. In any case, the variability of OFMSW fermentation liquids is something inherent to this substrate, and the treatment processes should be flexible enough to cope with this variability.

In the experiment with OFMSW FL-2, the initial concentration was 5.35 ± 0.66 g TAN/L and 26.12 ± 2.79 g VFA/L (37.32 ± 4.10 g COD_{VFA}/L), 22 mL of NaOH 10 M were required to adjust the initial pH to 9. The trapping solution had an initial volume of 0.368 mL, with a pH of 0.60, and did not contain VFA or TAN.

During the initial 10 hours of the experiments, no water passage phenomenon occurred, and the evolution of TAN concentration in the feed was represented by the equation 4.5 with a K_m value of $1.33 \cdot 10^{-7}$ m/s. From this point onwards, the TAN concentration in the trapping solution continued to increase until reaching a maximum value of 33.27 ± 0.83 g/L at 14 hours. From this moment until the end of the experiment, the concentration of the trapping solution decreased due to the reduction in NH₃ flow and water passage. The values for N removal and N recovery were 96.09 % and 95.98 %, respectively, which indicates that no ammonia losses were detected in this study.

Figure 4.6 (b) shows the evolution of VFA over the 18-hour experiment, where it is observed that VFA concentration was nearly kept constant during the nitrogen recovery process. Similarly to the experiment with OFMSW FL-2, deviations in VFA concentration and profile are attributed to the error associated with the chromatograph and the possible degradation of a small amount of VFA. No VFA was detected in the trapping solution samples.

Throughout the experiment, 130 mL of NaOH 10 M were required in the feed solution for pH control. During the first 12 hours, 7.5 ± 2.50 mL/h of NaOH was added, while from that point until the end, this alkali was added at a rate of 3.0 ± 1.0 mL of NaOH/h. The alkali consumption throughout the experiment was 1.07 ± 0.01 mol NaOH/mol N recovered. On the other hand, the total consumption of H₂SO₄ was 0.77 ± 0.01 mol H₂SO₄/mol N recovered.

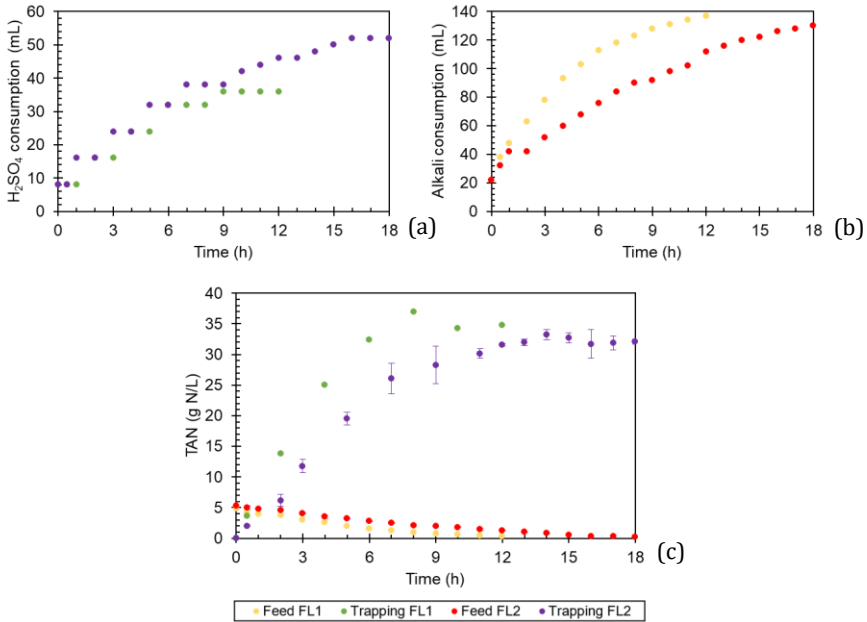


Figure 4.7. (a) acid sulfuric and (b) alkali consumption and (c) TAN evolution for NR-1 and NR-2 test

Considering that only NH₃ is capable of diffusing through the membrane, both the alkali and acid consumption in both experiments was near the maximum theoretical consumption, obtained by stoichiometry, which is 1 mol NaOH/mol N recovered and 0.5 mol H₂SO₄/mol N recovered, respectively. However, the alkali consumption was slightly higher due to the necessity of raising the pH from the fermentation liquid up to 9. In the experiment working with OFMSW FL-1, the alkali consumption was slightly higher than with OFMSW FL-2, due to the different buffer capacity of the fermentation liquids.

In terms of sulfuric acid consumption, both experiments exceeded the maximum theoretical value, and the consumption was higher in the second experiment. It is important to note that the high consumption of H₂SO₄ could be attributed to the excess acid added between hours 9 and 15 of the second experiment.

Regarding the TAN uptake rate, comparing specific values can be complex due to the different origin and treatment of the liquids, as well as their different initial concentrations. Therefore, the discussion will focus on the trends observed throughout the experiment.

The first experiment showed a faster decrease in TAN concentration compared to the second experiment, resulting in a more pronounced increase in the concentration of the trapping solution. In the first experiment, there is a significant drop in TAN concentration due to the passage of water, while this drop is not as noticeable when the same phenomenon occurs in the second experiment. The final concentration of the trapping solution in the first experiment was higher than that obtained in the second experiment, despite the higher available amount of TAN in the feed of the second experiment. This is because in the second experiment, a greater amount of water passed through the membrane, causing the concentration to decrease. The differences in TAN transfer rate through the membrane are attributed to the different composition of the fermentation liquid, either due to different treatments or belonging to different batches. The first fermentation liquid reaches a concentration below 0.30 g TAN/L more quickly.

More specifically, the K_m values obtained were $5.17 \cdot 10^{-7}$ m/s for the first experiment and for the second $3.94 \cdot 10^{-7}$ m/s for the second experiment. These results align with those reported by Serratoro et al. (2022), who found a K_m of $(2.8 \pm 6.0) \cdot 10^{-7}$ m/s while working with the same membrane at 35 °C, pH 9, and a similar OFMSW fermentation broth.

4.3.3. VFA up-concentration using FO module

Aq-7 test: After the GPM treatment for nitrogen recovery, The VFA concentration of OFMSW FL-1 was up-concentrated using a draw solution of the same volume and an initial concentration of 1.25 mol $MgCl_2/L$. This experiment was conducted without prior pH adjustment in the fermentation liquid, as it was originated from the nitrogen recovery unit where pH was controlled at 9.

Figure 4.8 (a) shows the evolution of the feedstock and draw solution volumes over time, wherein a rapid change could be observed within the first 8 minutes, followed by a nearly constant state, due to the decrease in the difference between the osmotic pressures. The fermentation liquid achieved a WCF of 2.23, and the draw solution's dilution factor is 1.55.

The evolution of VFA is shown in Figure 4.8 (c), in the feedstock, the highest content was observed until 11 minutes, and from this to the end of the experiment, it remained relatively constant, reaching an VFA concentration of 78.93 ± 2.86 g COD/L. The VFA concentration factor

was 2.45 ± 0.20 . In the draw solution, VFA concentration increased linearly, reaching a maximum value of 0.24 g COD/L at the end of the experiment.

Figure 4.9 shows the evolution of the VFA composition (on COD basis) for both the feed and the draw solution during the 15-minute experiment. In the feed, small changes in the composition could be observed due to the diffusion of acetic, propionic, and butyric acids into the draw solution, as well as the inevitable experimental error. In the draw solution, it could be observed that only acetic, propionic, and butyric acids passed through, while valeric and caproic acids were not detected. Acetic, propionic and butyric acids permeated through the membrane in the same proportion from the beginning of the experiment.

The evolution of TAN (Total Ammonia Nitrogen) that has not been removed in the first stage was also monitored. The concentration in the feedstock sharply increased during the first 8 minutes, when the greatest volume reduction occurred. Once this time was surpassed, the concentration remained practically constant. TAN concentration in the draw solution, it evolved linearly over time, reached a maximum concentration of 0.050 g TAN/L.

Finally, it is important to highlight that TS after the nitrogen recovery was 51.11 ± 0.20 g TS /L while after the VFA up-concentration 119.55 ± 4.37 g TS /L was obtained.

Aq-8 test: 3.8 L of OFMSW FL-2 from the TAN recovery stage are divided into two for the execution of two replicas of the acid concentration stage. The Figures 4.8 and 4.10 represent the average values and standard deviations of the two replicas. The initial concentration used for the draw solution was the same as that for the first fermentation liquid.

Figure 4.8 (a) illustrates the evolution of the feed and the draw solution volumes during the experiment. A significant development is observed within the first 10 minutes, followed by a constant state. The feedstock achieves a WCF of 2.44 ± 0.01 , while the draw solution has a dilution factor of 1.59 ± 0.02 .

The figure 4.8 (b) depicts the evolution of the VFA concentration over time. During the first 10 minutes, which correspond to the largest volume change, the concentration increases significantly in the feed. Once this time is surpassed, the composition continues to increase at a slower rate due to the gradual decrease in the total feed volume. A final concentration of (75.90 ± 3.50) g COD/L is achieved, with a concentration factor of (2.03 ± 0.32) . The VFA concentration in the draw solution grows linearly, and at the end of the experiment, it is (0.22 ± 0.01) g COD/L

The figure 4.10 displays the composition of VFA in both the feed and draw solution throughout the experiment. In the feed, the composition remains practically constant, and there is no clear decrease in the acids that diffuse through the membrane (acetic, propionic, and butyric acid) as they do so in very small quantities that may not be observable in this graph. The composition of the draw solution also remains constant, but special attention should be paid to the significant deviation in the acetic acid composition, resulting from the difference in absolute values between the two replicas.

Despite being different fermentation liquids, the change in volumes over time were very similar. In the experiment with OFMSW FL-2, a higher concentration factor was achieved in the feed, resulting in a higher dilution factor in the draw solution. This may indicate that this liquid had a greater osmotic pressure difference with the draw solution compared to OFMSW FL-1.

Although the initial VFA concentration were different between OFMSW FL-1 and FL-2, the change in concentrations was very similar in both experiments (see figure 4.8 (b)). Additionally, the difference between the concentrations achieved after 15 minutes in both cases was quite small, suggesting that this may be the maximum concentration that can be attained with the initial concentration of MgCl_2 being used.

Just like in the feed, the evolution of the individual VFA concentration in the draw solution was very similar for both fermentation liquids. As discussed previously, only acetic, propionic and butyric acids were detected, suggesting that under the working conditions, the rejection rate of valeric and caproic acid in the employed direct osmosis module is almost 100 %.

In terms of TAN concentration, the performance followed the same trends in both cases, considering that the starting concentration was somewhat lower for the OFMSW FL-2. In the draw solution, in which there was initially no nitrogen, the growth trend was the same in both experiments and the final concentrations were practically the same.

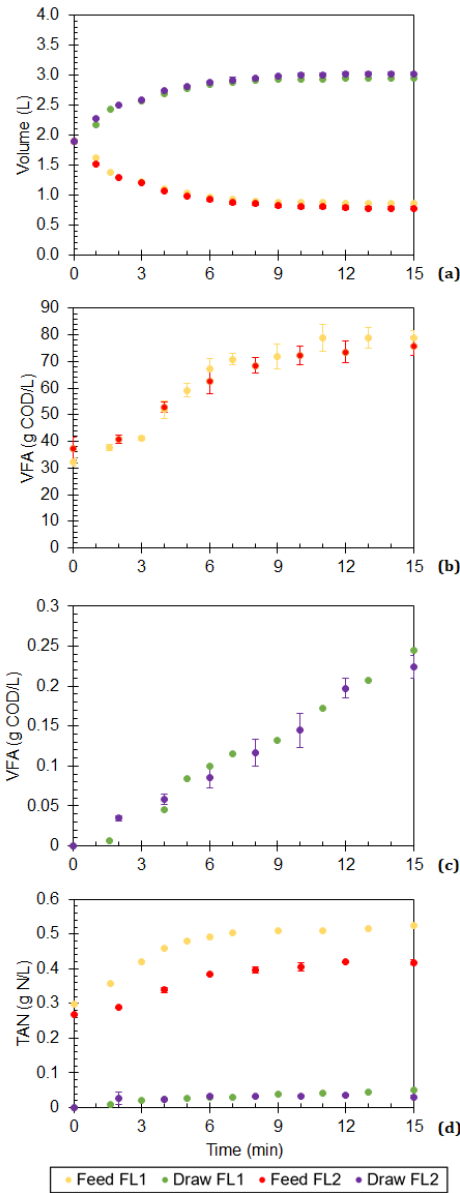


Figure 4.8. Evolution of (a) volume, (b) and (c) VFA concentration in feedstock and draw solution and (d) TAN

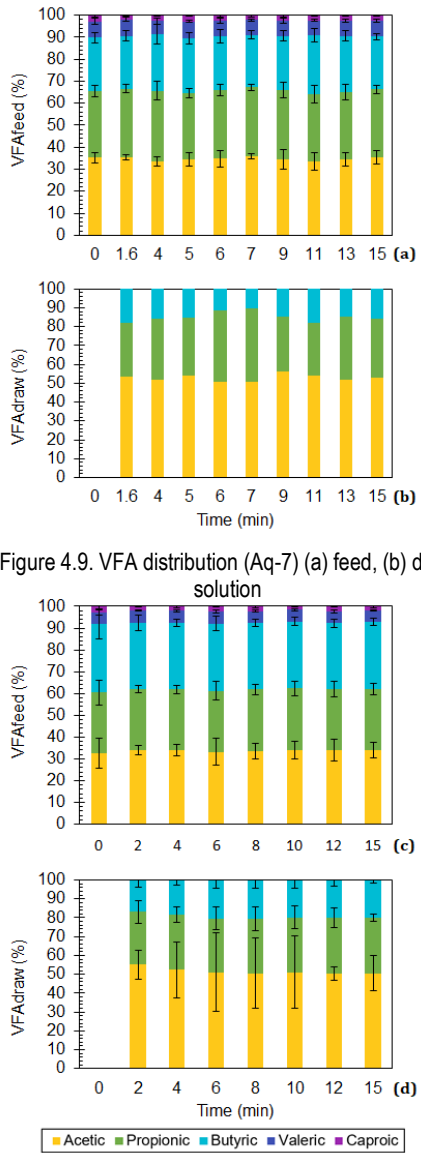


Figure 4.9. VFA distribution (Aq-7) (a) feed, (b) draw solution

Figure 4.10. VFA distribution (Aq-8) (a) feed, (b) draw solution

Table 4.7. Main characteristics of feed and draw solution for FO process

	Initial characteristics		Final characteristics	
	Feed	Draw solution	Concentrate	Draw solution
OFMSW-FL 1				
Volume [L]	1.90	1.90	0.85	2.95
VFAs [g/L]	22.96 ± 0.88	0.00	56.32 ± 2.13	0.19
VFAs [g COD/L]	32.25 ± 1.50	0.00	78.93 ± 2.86	0.24
HAc [% COD]	35.19 ± 2.13	0.00	35.32 ± 3.11	52.88
HPr [% COD]	30.30 ± 2.42	0.00	30.89 ± 1.70	31.40
HBut [% COD]	24.27 ± 2.42	0.00	24.01 ± 1.32	15.72
HVal [% COD]	7.43 ± 1.28	0.00	7.09 ± 0.64	0.00
HCap [% COD]	2.81 ± 1.06	0.00	2.68 ± 0.47	0.00
sCOD [g/L]	48.10 ± 2.37	not measured	99.56 ± 1.59	not measured
TAN [g/L]	0.30	0.00	0.52	0.05
Conductivity [mS/cm]	43.45 ± 2.90	231.77 ± 1.93	91.93 ± 3.87	172.50 ± 15.56
pH [-]	8.34	not measured	7.91	not measured
OFMSW-FL 2				
Volume [L]	1.90	1.90	0.78 ± 0.03	3.02 ± 0.03
VFAs [g/L]	26.12 ± 2.79	0.00	53.62 ± 2.56	0.17 ± 0.01
VFAs [g COD/L]	37.32 ± 4.10	0.00	75.90 ± 3.50	0.22 ± 0.01
HAc [% COD]	32.45 ± 6.94	0.00	33.85 ± 3.58	50.56 ± 9.27
HPr [% COD]	27.93 ± 5.70	0.00	28.05 ± 2.59	29.43 ± 2.01
HBut [% COD]	31.31 ± 6.59	0.00	30.83 ± 1.72	20.01 ± 1.58
HVal [% COD]	5.62 ± 1.47	0.00	5.34 ± 0.73	0.00
HCap [% COD]	2.70 ± 1.28	0.00	1.93 ± 0.88	0.00
sCOD [g/L]	59.46 ± 0.94	not measured	110.81 ± 0.35	not measured
TAN [g/L]	0.27 ± 0.00	0.00	0.42 ± 0.01	0.03 ± 0.00
Conductivity [mS/cm]	52.65 ± 0.55	232.18 ± 0.74	95.68 ± 4.04	151.10 ± 0.99
pH [-]	8.87 ± 0.11	7.17 ± 0.18	7.94 ± 0.01	9.30 ± 0.09

5. CONCLUSIONS AND RECOMMENDATIONS

In the present work, the possibility of concentrating the VFA generated in the fermentation of organic waste has been successfully explored while recovering nitrogen in the form of a fertilizing agent. The conclusions obtained for each of the stages of this process are detailed below.

- OFMSW fermentation allows the generation of a fermentation liquid with a concentration between 30-40 g COD_{VFA}/L where the proportion of HAc, Hprop and HBut represents more than 85 % on a COD basis and a high concentration of TAN around 4.5-5.5 g N/L.
- For certain downstream applications where a low N/VFA ratio is required, the application of GPM technology is highly beneficial: on the one hand, a fermentation liquid is obtained that maintains the content and distribution of VFA, and on the other, more than 94 % of TAN is recovered in the form of (NH₄)₂SO₄ solution with interest as fertilizer.
 - In GPM, it is necessary to work at a pH not exceeding 9 to prevent an increase in the concentration of suspended solids.
 - A trapping solution without the presence of VFA and a TAN concentration between 30-40 g/L has been reached, but it has not been possible to overcome it due to the passage of water.
- In forward osmosis experiments with Aquaporin membranes, a high rate of rejection of VFA has been observed (>98 %) at pH values higher than 7 but a high diffusion rate for acidic pH (~5). On the other hand, the rejection of the membrane to TAN was less than 40 %, which makes a prior nitrogen recovery stage necessary to avoid a high concentration in the draw solution.
- When working with OFMSW fermentation liquid and an initial concentration in the draw solution of 1.25 M MgCl₂, a FC of 2.0-2.50 has been achieved, reaching a VFA concentration of 75.93 and 78.93 g COD_{VFA}/L in the concentrate.

- When applying FO with Aquaporin at a slightly alkaline pH, a minimal loss (<2 %) of VFA is observed, with acetic acid exhibiting higher permeability compared to propionic acid, and propionic acid showing higher permeability compared to butyric acid. HVal and HCapr were not detected in draw solution.

Recommendations and future studies:

- Given that the possibility of concentrating VFA using a FO module has been demonstrated, a potential continuation of the work would be to conduct a comprehensive economic study of this process to analyze the profitability of its implementation in current facilities. Another possible continuation of the work is the study of how particle size affects the direct osmosis module and, therefore, the concentration of VFA. Additionally, different concentrations of $MgCl_2$ in the draw solution can be explored to investigate their impact on the VFA concentration factor obtained.
- For future work, the inertization of the feed tank with an inert gas such as nitrogen should be considered to minimize VFA losses.
- The acquisition of an osmometer is recommended to improve the control of parameters associated with VFA concentration.
- In line with the figure 1.4 it is recommended to use KOH instead of NaOH to increase the pH of the solution before nitrogen recovery, since sodium hydroxide would inhibit the anaerobic digestion process after acidogenic fermentation and VFA concentration.

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ACRONYMS

AD, Anaerobic Digestion; **BES**, 2-Bromoethanesulfonic acid; **COD**, Chemical Oxygen Demand; **DS**, Draw Solution; **FL**, Fermentation Liquid; **FO**, Forward Osmosis; **FS**, Feedstock; **HRT**, Hydraulic Retention Time; **MBT**, Mechanical-Biological Treatment; **OFMSW**, Organic Fraction Municipal Solid Waste; **ORP**, Oxidation-Reduction Potential; **TAN**, Total Ammonia Nitrogen; **TRL**, Technology Readiness Level; **TS**, Total Solids; **TSS**, Total Suspended Solids; **VFA**, Volatile Fatty Acids; **VS**, Volatile Solids; **VSS**, Volatile Suspended Solids; **WCF**, Water Concentration Factor

