COMBINING FORWARD OSMOSIS AND ANAEROBIC MEMBRANE BIOREACTOR TECHNOLOGIES FOR RAW MUNICIPAL WASTEWATER TREATMENT

Federico Ferrari

Doctoral Thesis

Combining forward osmosis and anaerobic membrane bioreactor technologies for raw municipal wastewater treatment

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DECLAREM:

Que el treball titulat Combining forward osmosis and anaerobic membrane bioreactor technologies for raw municipal wastewater treatment, que presenta Federico Ferrari per a l’obtenció del títol de doctor, ha estat realitzat sota la nuestra dirección.

I, perquè així consti i tingui els efectes oportuns, signo aquest document.

Girona, setembre 2020

Universitat de Girona

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DECLARATION OF AUTHORSHIP

I, Federico Ferrari, declare that this thesis titled, "Combining forward osmosis and anaerobic membrane bioreactor technologies for raw municipal wastewater treatment" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.

Federico Ferrari

Girona, september 2020

There’s only so much fortune a man really needs… and the rest is just for showing off.

-Forrest

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Contents

List of publications

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Federico Ferrari, Maite Pijuan, Ignasi Rodriguez-Roda, and Gaetan Blandin. 2019. “Exploring Submerged Forward Osmosis for Water Recovery and Pre-Concentration of Wastewater before Anaerobic Digestion: A Pilot-Scale Study.” Membranes 9 (8).

Soraya Zahedi, **Federico Ferrari**, Gaetan Blandin, Jose Luís Balcazar, Ignasi Rodriguez-Roda, Maite Pijuan. 2020. “Exploring the performance of anaerobic treatment for municipal concentrated wastewater through forward osmosis.” (in preparation)

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List of acronyms:

AD	Anaerobic digestion
AeMBR	Aerobic membrane bioreactor
AFMBR	Anaerobic fluidized membrane bioreactor
AnDMBR	Anaerobic dynamic membrane bioreactor
AnMBR	Anaerobic membrane bioreactor
AnOMBR	Anaerobic osmotic membrane bioreactor
BMP	Biochemical methane potential
Ca^{2+}	Calcium
CAS	Conventional activated sludge
CH_4	Methane
Cl^-	Chloride
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CTA	Cellulose triacetate
DNA	Deoxyribonucleic acid
DS	Draw solution
ECP	External concentration polarization
EGSB	Expanded granular sludge bed
FO	Forward osmosis
G-AnMBR	Granular anaerobic membrane bioreactor
Gl-AnMBR	Gas lift anaerobic membrane bioreactor
H_2S	Hydrogen sulfide
HRT	Hydraulic retention time
IA	Intermediate alkalinity
IAFMBR	Integrated anaerobic fluidized membrane bioreactor
Jw	Water flux
K^+	Potassium
MBR	Membrane bioreactor
MF	Microfiltration

Mg^{2+}	Magnesium
Na^+	Sodium
NH_3	Ammonia
NH_4^+	Ammonium
OBW	Osmotic backwash
OLR	Organic loading rate
OMBR	Osmotic membrane bioreactor
OTUs	Operational taxonomic units
PA	Partial alkalinity
PhACs	Pharmaceutical active compounds
PO_4^{3-}	Phosphate
PRO	Pressure related osmosis
RO	Reverse osmosis
rRNA	Ribosomal ribonucleic acid
RSF	Reverse solute flux
SCOD	Soluble chemical oxygen demand
SMP	Specific methane production
SO_4^{2-}	Sulfate
SRB	Sulfate-reducing bacterias
SRT	Solid retention time
T	Temperature
TA	Total alkalinity
TCOD	Total chemical oxygen demand
TFC	Thin-film composite
TKN	Total kjeldahl nitrogen
TOC	Total organic carbon
TS	Total solids
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
VFA	Volatile fatty acid
VS	Volatile solids
VSS	Volatile suspended solids

WR	Water recovery
WW	Wastewater
WWTP	Wastewater treatment plant
$\Delta\pi$	Osmotic pressure differential

List of figures:

List of tables:

Summary:

In the last decades, the scarce availability of freshwater in many locations has triggered the need for wastewater (WW) reclamation and reuse. Indeed, the increasing demand for water and a decrease in water quality due to the combined effects of the increasing urbanization and climate change are forcing many countries to consider significant policy changes and expensive measures for water reclamation and WW treatment. Two of the solutions being considered to tackle this challenge are lowering potable water consumption and reusing WW from various sources, mainly municipal WW. WW has also a high content of other valuable products besides water like nutrients such as phosphorus and nitrogen and chemical energy contained in the organic matter. These are highly diluted in the WW stream making their recovery often not profitable and hard to achieve. However, the introduction of new technologies for water and WW treatment along with water scarcity has changed the classical concept of WW treatment and pollution removal towards treatment lines and processes that promote the recovery of water, energy, and chemical compounds. Among others, forward osmosis (FO) and anaerobic digestion (AD) are WW treatment technologies that result in high-quality water appropriate for reuse and energy recovery in the form of methane-rich biogas, respectively.

In this thesis, different studies were performed to investigate the combination of FO for the pre-concentration of municipal WW with an anaerobic membrane bioreactor (AnMBR) for the production of biogas.

In the first chapter, a lab-scale AnMBR was operated for 11 months treating synthetic WW that mimicked the concentrate from a FO process treating municipal WW with 80% water recovery. The effect of temperature on reactor performance was assessed at 34°C to acclimate the biomass to the new substrate at the same temperature of the anaerobic digester where it was taken, for then lowering it to 23°C, 17°C and 15°C mimicking the typical temperature seasonal variations of the sewage. Average chemical oxygen demand (COD) removal and methane production decreased with lower temperatures. Dissolved methane in the permeate was low and did not significantly change with temperature probably due to the high mixing efficiency. After 2 months operating at 15°C, temperature was progressively increased, resulting in an immediate increase in methane production and COD removal efficiencies. Microbial analysis showed important changes

in the archaeal community when temperature was changed from 34 to 23°C but the mesophilic archaeal population was always highly present permitting a fast system recovery once temperature was brought back to higher temperatures.

The second chapter of this thesis investigated for the first time at a pilot scale, the feasibility of concentrating real raw municipal WW using a submerged plate and frame FO module to reach 70% water recovery. Membrane performance, fouling behavior, and effective concentration of WW compounds were examined, as well as the use of two different draw solutes (NaCl and $MgCl_2$) operating either with constant draw concentration or in batch with draw dilution over time. The impact of gas sparging on fouling and external concentration polarization was also assessed. When using real WW, submerged FO proved to be resilient to clogging, demonstrating its suitability for application on municipal WW. High water fluxes were obtained and were in line with previous results obtained with lab-scale membranes. Positively, total and soluble COD concentration factor increased, making the concentrated WW more suitable for anaerobic treatment.

FO and AD technologies were finally coupled as showed in the third chapter of this thesis, to compare the anaerobic treatment of municipal WW and that of concentrated WW at 25ºC. First, biochemical methane production (BMP) tests were conducted with municipal WW and with two concentrated WW. Concentrated WW through FO proved to have higher methane production and higher specific methane production (SMP) but presented a longer lag phase probably due to the higher salinity present in the concentrated WW causing inhibition. Secondly, a continuous AnMBR was operated and showed similar COD removal efficiencies when treating municipal WW (at 12 and 8 hours hydraulic retention time (HRT)) and concentrated WW (at 24 and 12 hours HRT). No methanogenic inhibition due to higher salinity was observed in the reactor when operating with concentrated WW as shown by the low concentration of volatile fatty acids (VFAs) in the permeate.

Overall, results obtained in this thesis demonstrate the feasibility of combining both technologies for more sustainable treatment of WW and set up the basis for further investigations at a larger scale.

Resumen:

La escasa disponibilidad de agua dulce en muchos lugares ha provocado en las últimas décadas la necesidad de recuperación y reutilización de aguas residuales (WW). De hecho, la creciente demanda de agua, y una progresiva disminución en su calidad debido a los efectos combinados de una urbanización creciente y el cambio climático, están obligando a muchos países a plantear cambios significativos en sus políticas y medidas costosas para la recuperación de agua y el tratamiento de WW. Dos de las soluciones consideradas para hacer frente a este desafío son reducir el consumo de agua potable y reutilizar agua residual de varias fuentes, destacándose el agua residual municipal. El agua residual municipal también tiene un alto contenido en otros productos valiosos, como son los nutrientes (fósforo y nitrógeno) o la energía contenida en la materia orgánica. Éstos están muy diluidos en las aguas residuales, lo que hace que su recuperación sea difícil y no siempre rentable. Sin embargo, la introducción de nuevas tecnologías combinado con la escasez de agua ha cambiado el concepto clásico de tratamiento hacia líneas y procesos que promueven la recuperación de agua, energía y compuestos químicos. Entre otros, la ósmosis directa (en inglés forward osmosis, FO) y la digestión anaeróbica (anaerobic digestion, AD) son tecnologías de tratamiento de aguas residuales que obtienen respectivamente, agua de alta calidad apropiada para reutilización y recuperación de energía en forma de biogás rico en metano (CH_4). En esta tesis se realizaron diferentes estudios de investigación sobre la combinación de FO, para la preconcentración de agua residual municipal, con un biorreactor de membrana anaerobia (en inglés anaerobic membrane biorreactor, AnMBR) para la producción de biogás. En el primer capítulo, se operó un AnMBR a escala de laboratorio durante 11 meses tratando aguas residuales sintéticas que imitaban el concentrado de un proceso de FO con un 80% de recuperación de agua. En este estudio se evaluó el efecto de la variación estacional de la temperatura en el funcionamiento del AnMBR. Como el inóculo se obtuvo de un mesofílico anaerobio (34ºC), la primera temperatura evaluada fue 34ºC. Posteriormente la temperatura fue decrecida a 23°C, 17°C y 15°C reproduciendo así la variación estacional típica de la temperatura en las aguas residuales. La disminución de la temperatura supuso tanto una disminución de la eliminación de demanda química de oxígeno (DQO), como de la producción de CH_4. El CH_4 disuelto en el permeado fue bajo y no cambió con la temperatura, probablemente debido a la alta eficiencia de la agitación. Después de 2 meses de funcionamiento a 15 °C, la temperatura se incrementó

progresivamente, lo que resultó en un aumento inmediato de la producción de CH_4 y en la eficiencia de eliminación de DQO. El análisis microbiano mostró cambios importantes en la comunidad de arqueas cuando la temperatura cambió de 34 a 23 °C, pero aún así la población de arqueas mesofílicas siempre se mantuvo presente, lo que permitió una recuperación rápida del sistema una vez que la temperatura volvió a incrementarse. El segundo capítulo investigó por primera vez a escala piloto, la viabilidad de concentrar las aguas residuales municipales reales (de entrada a la depuradora) utilizando un módulo de FO de placa y marco sumergido para alcanzar el 70% de recuperación de agua. Se examinó el rendimiento de la membrana, el comportamiento de la incrustación y la concentración efectiva de compuestos de aguas residuales, así como el uso de dos solutos de extracción (NaCl y $MgCl_2$) que funcionaron tanto con concentración de extracción constante como con dilución de extracción a lo largo del tiempo. También se evaluó el impacto de la inyección de gas en el ensuciamiento y la polarización de la concentración externa. Al utilizar aguas residuales reales, el sistema de FO sumergido mostró ser resistente a la colmatación, constatando su idoneidad para la aplicación en aguas residuales municipales. Se obtuvieron altos flujos de agua, en línea con los resultados anteriores obtenidos con membranas a escala de laboratorio. El factor de concentración de DQO total y soluble aumentó, haciendo que las aguas residuales concentradas fueran más adecuadas para el tratamiento anaeróbico. Las tecnologías FO y AD finalmente se combinaron como se muestra en el tercer capítulo, para comparar el tratamiento anaeróbico de agua residual municipal y el de agua residual concentrada a 25ºC. En primer lugar, se realizaron pruebas de producción bioquímica de CH_4 (en inglés Biochemical Methane Production, BMP) con agua residual municipal y con aguas concentradas. El agua residual concentrada mostró tener una mayor producción de CH_4 y una mayor producción específica de CH_4 (SMP) aunque presentó una fase de latencia mayor, probablemente debido a la mayor salinidad presente en dicho concentrado que pudo causar una inhibición inicial. Posteriormente, se operó un AnMBR en continuo y se observaron eficiencias de eliminación de DQO similares al tratar agua residual municipal, a las 12 y 8 horas de tiempo de residencia hidráulico (en inglés, HRT) y, agua concentrada a las 24 y 12 horas HRT. No se observó inhibición metanogénica por el incremento de salinidad en el reactor cuando se operó con el agua concentrada, quedando demostrado por la baja concentración de ácidos grasos volátiles en el permeado. En general, los resultados obtenidos en esta tesis demuestran la viabilidad de combinar ambas

tecnologías para un tratamiento más sostenible del agua residual y establecen las bases para futuras investigaciones a mayor escala.

Resum:

A les darreres dècades, l'escassa disponibilitat d'aigua dolça en molts llocs ha provocat la necessitat de recuperació i reutilització d'aigües residuals. De fet, la creixent demanda d'aigua i una progressiva disminución de la qualitat de l'aigua a causa dels efectes combinats de la creixent urbanització i el canvi climàtic estan obligant a molts països a considerar canvis significatius en les polítiques i implementar mesures costoses per a la recuperació d'aigua i el tractament de les aigües residuals. Dues de les solucions que s'estan considerant per fer front a aquest desafiament són reduir el consum d'aigua potable i reutilitzar aigües residuals de diverses fonts, com les aigües residuals municipals. L’aigua residual també té un alt contingut en altres productes valuosos a més de l'aigua com són els nutrients (fòsfor i nitrogen) i l'energia continguda en la matèria orgànica. Aquests productes estan altament diluïts en les aigües residuals, la qual cosa fa que la seva recuperació no sigui difícil d’aconseguir i no sempre rendible. No obstant això, la introducció de noves tecnologies per al tractament d’aigües residuals ha canviat el concepte clàssic de tractament i eliminació cap a línies i processos de tractament que promouen la recuperació d'aigua, energia i compostos químics. Entre d'altres, l'osmosi directa (en inglés, FO) i la digestió anaeròbica (en inglés, AD) són tecnologies de tractament d’aigües que resulten, en aigua d'alta qualitat apropiada per a reutilització i recuperació d'energia en forma de biogàs ric en metà. En aquesta tesi es van realitzar diferents estudis per investigar la combinació de FO per a la preconcentració d’aigua residual municipal amb un bioreactor de membrana anaeròbia (en inglés, AnMBR) per a la producció de biogàs. En el primer capítol, es va fer funcionar un AnMBR a escala de laboratori durant 11 mesos tractant aigües residuals sintètiques que imitaven el concentrat d'un procés de FO que tracta les aigües residuals municipals amb un 80% de recuperació d'aigua. L'efecte de la temperatura sobre el rendiment del reactor es va avaluar a 34 ° C per aclimatar la biomassa a el nou substrat a la mateixa temperatura del digestor anaerobi on es va prendre, per després baixar-la a 23 ° C, 17 ° C i 15 ° C imitant la temperatura típica de les variacions estacionals de les aigües residuals. La mitjana de l'eliminació de la demanda química d'oxigen (DQO) i la producció de metà van disminuir amb la temperatura més baixa. El metà dissolt en el permeat va ser baix i no va canviar significativament amb la temperatura, probablement a causa de l'alta eficiència de l’

agitació. Després de 2 mesos de funcionament a 15 °C, la temperatura es va incrementar progressivament, el que va resultar en un augment immediat de la producció de metà i l'eficiència d'eliminació de DQO. L'anàlisi microbià va mostrar canvis importants en la comunitat d'arquees del sistema quan la temperatura va canviar de 34 a 23 ° C. No obstant això, la població d'arquees mesofílica sempre es va mantenir present, fet va permetre una recuperació ràpida de sistema una vegada que la temperatura va tornar a temperatures més altes. El segon capítol d'aquesta tesi va investigar per primera vegada a escala pilot, la viabilitat de concentrar les aigües residuals municipals reals d'entrada utilitzant un mòdul FO de placa i marc submergit per arribar al 70% de recuperació d'aigua. Es va examinar el rendiment de la membrana, el comportament d'incrustació i la concentració efectiva de compostos d'aigües residuals, així com l'ús de dos soluts d'extracció diferents (NaCl i $MgCl_2$) que funcionen amb concentració d'extracció constant o amb dilució d'extracció al llarg de el temps. També es va avaluar l'impacte de la formació de gas a l'embrutiment i la polarització de la concentració externa. A l'utilitzar aigües residuals reals, el mòdul de FO submergit va demostrar ser resistent a l'obstrucció, el que fa viable la seva aplicació en aigües residuals municipals. Es van obtenir fluxos d'aigua elevats, en línia amb els resultats anteriors obtinguts amb membranes a escala de laboratori. El factor de concentració de DQO total i soluble va augmentar, fent que les aigües residuals concentrades siguin més adequades per al tractament anaeròbic.

Finalment, les tecnologies FO i AD es van combinar com es mostra en el tercer capítol d'aquesta tesi, per comparar el tractament anaerobi d'aigües residuals municipal i el tractament de les aigües concentrades a 25ºC. Primer, es van realitzar proves de producció bioquímica de metà (BMP) amb aigua residual municipal i amb dos aigües concentrades. L'ús d'aigua residual concentrada va resultar amb una major producció de metà, però va presentar una fase de retard més llarga probablement a causa de la inhibició provocada per la major salinitat de la WW concentrada. En segon lloc, es va operar un AnMBR en continu mostrant eficiències d'eliminació de DQO similars a les obtingudes al tractar aigua residual municipal (a les 12 i 8 hores de temps de retenció hidràulica (HRT)) i l'aigua concentrada (a les 24 i 12 hores HRT). No es va observar inhibició metanogènica a causa d'una major salinitat al reactor quan va operar amb agua concentrada com ho demostra la baixa concentració d'àcids grassos volàtils en el permeat.

En general, els resultats obtinguts en aquesta tesi demostren la viabilitat de combinar ambdues tecnologies per a un tractament més sostenible de l'agua residual i estableix les bases per una recerca futura a major escala.

General Introduction

Wastewater treatment

The problem of wastewater (WW) disposal started in the early 20th century when the increasing number and dimensions of cities made evident the risks that uncontrolled WW discharges posed to humans and the environment. Since that moment, sewage has been considered a waste to be treated before its discharge into a water body. Usually, wastewater treatment plants (WWTP) are centralized facilities that treat WW generated by an area/city. They include different treatment levels, from preliminary and primary treatments for the removal of WW constituents and a portion of the suspended solids and organic matter, secondary treatment for the removal of biodegradable organic matter and nutrients and in some cases tertiary treatment for the removal of residual suspended solids and water disinfection (Metcalf and Eddy, 2003). The most common treatment technology in a WWTP is the conventional activated sludge (CAS) processes. Despite its high energy demand (50% of the whole WWTP (McCarty et al. 2011)), it features the ability to treat high amounts of WW with low hydraulic retention times (HRT) while achieving good quality effluent, removing organic matter and nutrients. Concerns in WW treatment include the changing nature of the WW to be treated, the emerging contaminants that have been found, and the problem of industrial wastes. However, the scarce availability of freshwater in many locations has triggered the need for WW reclamation and reuse. Indeed, the increasing demand for water and a decrease in water quality due to the combined effects of the increasing urbanization and climate change are forcing many countries to consider significant policy changes and expensive measures for water reclamation and WW treatment (Sowers et al. 2011). Two of the solutions being considered to tackle this challenge are lowering potable water consumption and reusing WW from various sources, such as municipal WW, especially considering the extended use of high-quality water for uses such as water irrigation and toilet flushing which do not require it. WW has also a high content of other valuable products besides water like nutrients such as phosphorus and nitrogen and chemical energy contained in the organic matter. Since most of the sewer systems were not conceived to separate black waters, industrial waters and rain waters, the result is a diluted WW stream from which the recovery of these products is often not profitable and hard to achieve. However, during the last two decades, the introduction of new technologies for water and WW treatment along with the water scarcity have changed the classical concept of WW treatment and pollution removal towards treatment lines and processes that promote the recovery of water, energy, and chemical compounds (Gao et al. 2014). These technologies make possible to rethink WW treatment from a centralized to a decentralized treatment for water reuse and energy recovery. To this end, sewer mining technologies have been introduced as a transition point between centralized and decentralized systems, recovering water where is needed during long dry periods while still taking advantage of the existing WWTP, especially to return the produced waste streams for further treatment. Among others, forward osmosis (FO) and anaerobic digestion (AD) are WW treatment technologies that produce, on one side, high-quality water appropriate for reuse, for example, in irrigation and on the other side, energy in the form of methane-rich biogas (Lei et al. 2018; Lin et al. 2013; Korenak et al. 2017).

AD has been traditionally implemented to treat high strength wastewaters or to digest sludge produced during the CAS process and primary sedimentation at mesophilic or thermophilic temperature ranges. However, during the last decade, it has also been successfully implemented for municipal WW treatment at ambient temperatures achieving good removals in terms of organic matter, similar to aerobic treatment but with lower biomass production and smaller footprint (Bandara et al. 2011; Adam L. Smith et al. 2013), This has been possible by using anaerobic membrane bioreactors (AnMBR) where the sludge retention time (SRT) is decoupled from the HRT, avoiding losing the slow-growing anaerobic biomass.

The combination of FO as a pre-concentration process for anaerobic treatment was introduced by Ansari et al. (2017) within the sewer mining concept. Low strength WW could be concentrated by FO up to approximately eightfold, significantly reducing the waste volume and increasing the COD. This increase in COD concentration makes the FO reject stream more suitable than municipal WW for anaerobic treatment, enhancing the recovery of energy in the form of biogas.

FO for WW treatment and current state of the art

In the last 20 years, a growing interest has been observed in osmotically driven processes. In such systems, the solute concentration gradient (also called osmotic pressure differential, $\Delta\pi$) acts as the driving force between two liquids separated by a selectively permeable membrane. As a result, permeation of water occurs through the membrane from the lowest to the highest solute concentration solutions (i.e. feed and draw solutions respectively), while most of the solute molecules or ions are rejected (Cath et al. 2006) (Figure 1).

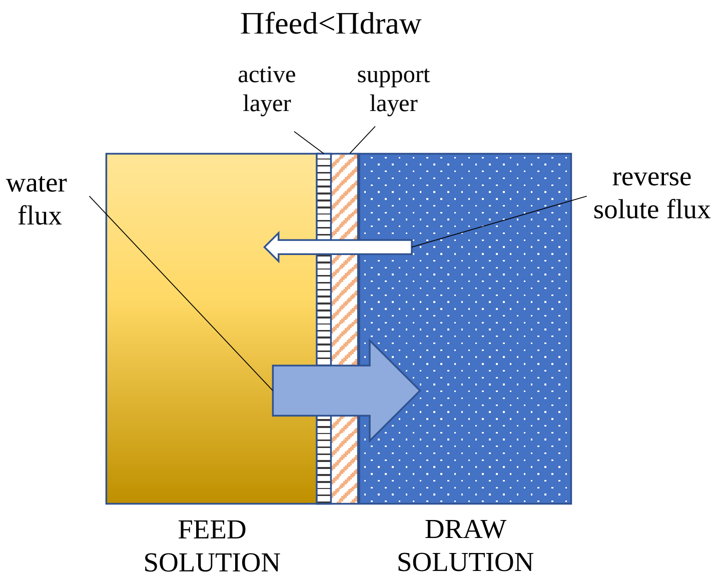


Figure 1: *Basic principle of forward osmosis concentration process.*

This mechanism closely follows Fick's law, with the phenomenological coefficients being the diffusivity and the solubility of the component in the membrane. The permeation flux (Jw) is directly connected to a driving force and the phenomenological coefficient (A). Adapted to osmotic and hydraulic pressure driven processes, the equation to calculate water flux becomes (Lee et al. 1981):

$$J_W = A \cdot \left(\Delta P - \Delta \pi_m \right) \qquad \text{(Eq. 1)}$$

Where J_w is the water flux ($L.m^{-2}.h^{-1}$), A is the membrane-specific pure water permeability ($L.m^{-2}.h^{-1}.\ bar^{-1}$), ΔP is the applied hydraulic pressure differential (bar) between the feed (P_F) and the draw (or permeate for RO) (P_D) and $\Delta\pi_m$ is the osmotic pressure differential (bar) between the feed (π_{Dm}) and the draw (π_{Fm}) across the active layer of the membrane. FO membranes are asymmetric, classically schematised as a dense active layer and a porous support layer. In addition to external concentration polarisation (ECP) observed in other dense membrane processes, reverse salt diffusion (RSD) and internal concentration polarisation (ICP) limits osmotic pressure efficiency (Tang et al. 2010).

The first work of Loeb in the late 1970s (Loeb 1976; Loeb et al. 1997) on osmotic processes remained relatively unexplored until new semi-permeable membranes, tailored-made for osmosis applications were developed in the early 2000s, and commercialized by Hydration Technologies Innovations (Cath et al. 2005). The two main osmotically driven processes that were initially considered were defined as forward osmosis (FO) and pressure retarded osmosis (PRO). Both FO and PRO sparked intense research being seen respectively as novel and highly promising technologies for seawater desalination and energy production (McGinnis et al. 2008).

However, following signs of progress in the development of the technology from initial laboratory proof of concept towards full-scale implementation in those targeted applications, both FO and PRO faced challenges in term of technical limitations, efficiency limitations and competitive advantages versus existing and other growing technologies especially with regards to initial applications forecasted by FO and PRO, i.e. seawater desalination and energy production (Shaffer et al. 2015). Thus, and despite significative advances in membrane and modules development and operation, so far, those applications of engineered osmosis remain mostly at the pilot scale.

Intense research following the FO boom led however to broader the interest and scope of potential FO applications. Low fouling propensity, high rejections of most contaminants present in wastewater, possibly to concentrate streams at low temperature and pressure were among the new advantages offer by FO. Thus, new applications where current technologies showed limitations for extraction and purification of water such as food concentration or complex streams to be treated like brines or highly charged WW were envisioned (Coday et al. 2014). Another potential advantage of FO is to make use of saline sources and the potential hybridization with other processes or applications to get synergies like combining desalination and water reuse or application in fertigation where energy-intensive draw reconcentration process is not required (Blandin et al. 2016; Phuntsho et al. 2011). Following the intense FO research activities of the last decades, several specific publications discussed the interests, principles, limitations, and challenges for future development of the FO process for mass transfer limitations (Zhao et al. 2012; Chung et al. 2012), membrane developments (Zhao et al. 2012; Klaysom et al. 2013), fouling (She et al. 2016), rejection of trace organic contaminants (Coday et al. 2014), optimized draw solutions (Zhao et al. 2012; Chekli et al. 2012; Qin et al. 2012) energy aspects (Shaffer et al. 2015; Chung et al. 2012) potential applications (Shaffer et al. 2012; 2015; Chekli et al. 2016; Xie et al. 2014) and prospects including WW treatment, (Lutchmiah et al. 2014), desalination (Qin et al. 2012) and hybridization of FO with other processes (Chekli et al. 2016).

Specific properties

Unique properties of FO rely on the fact that it features:

- Dense membrane with high selectivity and rejection of most compounds (like reverse osmosis (RO) membrane) so to extract only (mostly) the water while other compounds are concentrated.
- Does not require hydraulic pressure for permeation and therefore the feed solution to be treated will not be affected by the treatment.
- Lack of hydraulic pressure also allows for easier operation and does not require pressure vessels; FO can even be operated in submerged mode offering several design possibilities.
- No thermal treatment which also avoids degradation of feed compounds and at minimized energy costs. FO is also called cold concentration.
- Possible operation at very high osmotic pressure allowing to treat already concentrated streams and reaching high concentration ratios.
- Treatment of viscous or charged/challenging feeds due to the lack of pressure or operation in submerged mode.
- Minimized fouling rate when operated at low flux and easy cleaning since the fouling layer is not compacted on the membrane like in pressurized process.

Water reuse and nutrient recovery

The use of FO within the WW treatment line has been extensively studied in the last decade with the primary objective to promote a water reuse scheme; FO acts as a strong barrier that allows purification of water to the highest quality to be later reused. FO relies on an osmotic gradient, its implementation can be favorable especially if a saline stream is available (seawater, fertilizer, industrial brine…) (Phuntsho et al. 2011; Lutchmiah et al. 2011; Valladares Linares et al. 2013). Using FO to combine water reuse and desalination (FO-RO hybrid) already demonstrated several advantages like the double barrier protection (FO and RO are dense membranes) and can have positive economics compared to stand-alone seawater RO desalination, due to energy savings (osmotic dilution) and maintenance savings resulting from lower fouling tendency estimated from laboratory or pilot scale testing (Sangyoup Lee et al. 2010; Teusner et al. 2017). However, so far most of these studies considered untreated municipal WW as a cost for water production (due to required pre-treatment) without looking to the benefits of concentrating WW while considering more tertiary treated WW as the feed of the FO-RO hybrid. FO has been demonstrated to be a robust and simple process allowing to treat difficult streams such as anaerobic digester centrate or sludge (Holloway et al. 2007; Nguyen et al. 2013). Thus, instead of using tertiary or secondary treated wastewater, new concepts have emerged to consider the implementation of FO upstream in the wastewater treatment scheme (Figure 2).

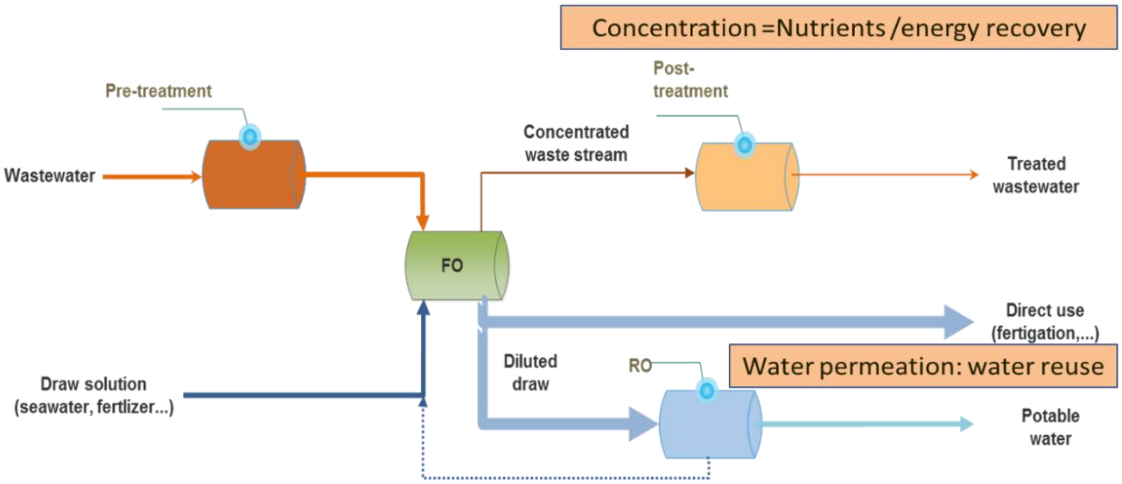


Figure 2: *Scheme of the new concept for WW treatment using FO as a primary treatment.*

Primary treated WW and raw sewage concentration

FO treatment was envisioned even further upstream, for example in the treatment of municipal wastewater after primary treatment or on raw sewage (sewer mining) (Butler et al. 1996; Lutchmiah et al. 2011). FO offers a double advantage here: not only can high-quality water be recovered, but also the concentrated sewage stream can be more easily treated. The first study by Zhang et al. achieved a 6-fold concentration of primary treated WW using a lab-scale cellulose triacetate (CTA) cross-flow module, leading also to a 3.1 fold COD concentration (Zhang et al. 2014). Ansari et al. demonstrated the feasibility to concentrate by 10 fold WW and to reach 1000 mg/L COD concentration which is suitable for downstream anaerobic digestion (Ansari et al. 2016). Moving to pilot scale, water concentration factor of 5 was achieved with a spiral wound membrane (Zhiwei Wang et al. 2016). One of the limitations of raw WW concentration is the incomplete and heterogeneous recovery of nutrients (nitrogen (N), phosphorus (P), COD). COD is generally well rejected by the FO membranes (COD removal>97%), but both studies showed that 19.2% of the COD entering the system was lost due to degradation during the filtration process or attached to the membrane surface. If P recovery is high due to high rejection by the FO membranes, lower N recovery is generally observed resulting from poor membrane rejection (up to 50-60%) (Bao et al. 2019; Zhang et al. 2014; Zhiwei Wang et al. 2016).

Fouling is the main concern in membrane processes and especially when treating challenging feeds. Fouling was observed in most studies and especially when reaching a high concentration factor (Ansari et al. 2016). However, initial experiments using FO on primary treated (screened) wastewater demonstrated that the accumulated fouling layer was loose and easily reversible (Lutchmiah et al. 2011). Another limitation of FO process concentration can be the toxicity of some compounds for downstream treatments, i.e. anaerobic digestion inhibitors such as SO_4^{2-}, NH_3, and salts. Apart from limiting the concentration factor, organic draw solution (sodium acetate or EDTA-2Na) with lower reverse solute flux (RSF) and biodegradability potential might be used (Ansari et al. 2016).

FO Contaminant rejection (COD, NH_4^+, PO_4^{3-})

While FO systems treating WW have always demonstrated high COD and PO_4^{3-} rejection (Table 1), different cations rejections have been reported depending on membrane kind, active layer characteristics, feed solution pH, and draw solutes. Mainly FO membranes are divided into CTA and TFC Polyamide membranes. TFC FO membranes have better performance in terms of higher water flux, higher lifespan better pH stability and resistance to hydrolysis and biological degradation (Gu et al. 2013) compared to CTA FO membrane under the same test conditions due to its lower structural parameter and the higher water permeability of the polyamide material. When considering ions rejection, an important difference between CTA membranes and TFC membranes is the number of fixed charge groups contained in the active layer (Irvine et al. 2013; Qiu et al. 2020). While CTA membranes have a negligible charge, the TFC membrane surface has carboxyl groups, which could serve as fixed ionic group, thereby conferring the membrane a cation exchange feature (Lu et al. 2014). For this reason, ions rejection and reverse solute flux are very different depending on the membrane material and is also influenced by the pH of the solution facing the active layer and the type of draw solute used. Among cations, Thin Film Composite (TFC) membranes poor NH_4^+ selectivity is of major concern due to the extremely similar polarity and hydraulic radius between NH_4^+ and water molecules (Ansari et al. 2017; Hou et al. 2017). In FO system treating streams with high fouling propensity, the active layer is positioned facing the feed solution because it has been confirmed to be more efficient for decreasing membrane fouling compared to the other orientation, active layer facing draw solution (Mi et al. 2008; Wang et al. 2010; Cornelissen et al. 2008). While the pH of the solution facing the active layer does not affect water fluxes for CTA nor TFC membranes, it does have a role in ion transport for TFC membranes. As explained in the study by Lu et al. (2014) when the pH of the solution facing the active layer increases from pH 3 to pH 6, protonated carboxylic groups are substituted for deprotonated carboxylic groups which make the membrane surface more negatively charged (Lu et al. 2014). For this reason, when a cation passes from the draw solution to the feed solution due to its high concentration and the attraction with the negatively charged membrane surface the system tries to maintain solution electroneutrality by transporting the coupled anion to the feed side. This mechanism is hidden by the negatively charged membrane which instead absorbs feed cations that diffuse to the draw solution. This mechanism led to increasing interest in TFC membrane properties and the possibility of pretreating the membrane to confer a more neutral charge to the active layer keeping the same water fluxes. Several studies have proven that modifying the active layer with Polyethylenimine (PEI), due to its abundant positively charged amines, the NH_4^+ removal efficiency increased by 15-25% (Bao et al. 2019). Another of TFC membrane is the Aquaporin. This membrane has incorporated selective water channel proteins, which only allow water to pass through and reject ions. Aquaporin membranes achieve NH_4^+ rejection of 97%, comparable with CTA membranes (Song et al. 2018), without losing the higher water fluxes that characterize TFC membranes.

AnMBR technology for municipal WW treatment: challenges

Aerobic membrane bioreactor (AeMBR) is a well-established technology that couples a micro or ultrafiltration module to an aerobic reactor and has the benefit of creating a high-quality effluent while having a lower footprint compared to CAS. Due to the high energy demand of AeMBRs, AnMBR technology has emerged because of its capability to produce methane-rich biogas treating streams with lower organic matter concentration and at a lower operational temperature which could not be applied without a membrane retaining the biomass. Furthermore, AnMBR technology has the benefits of lower sludge production and high-quality effluent. For these reasons, AnMBR is becoming popular for municipal WW treatment in recent years. There are different configurations depending on whether the membrane module is placed inside the anaerobic reactor (submerged membrane configuration) or in an external reactor (side or external membrane configuration). AnMBR technology has demonstrated at lab and pilot scale to be able to biodegrade the organic matter contained in sewage while producing methane-rich biogas and a nutrient-rich permeate (Giménez et al. 2011). However, there are still several problems that still must be addressed. Those include high volumes that have to be heated compared to the amount of produced biogas, the high percentage of methane that is lost in dissolved form with the permeate, a high energy demand related to fouling prevention (gas sparging), the low P and N removals, and problems in process operation related to sulfate (SO_4^{2-}) concentration in the WW to be treated.

Several configurations have been developed principally to tackle the energy consumption related to fouling prevention (Stazi et al. 2018). While the most considered configuration has been the combination of a membrane with an upflow anaerobic sludge blanket (UASB) reactor because it avoids the contact between the membrane module and the majority of solids present in the system, in the staged anaerobic fluidized bed membrane bioreactor (AFMBR) and integrated anaerobic fluidized bed membrane bioreactor (IAFMBR) the scouring effect of fluidized GAC acts to maintain clean the membrane surface, rather than gas sparging or chemical cleaning, and has also the advantage to represent a support media for the anaerobic biomass (Gao et al. 2014; Kim et al. 2011). Other AnMBR configurations developed to lower fouling issues are gas-lift AnMBRs (Gl-AnMBRs) (Dolejs et al. 2017), anaerobic dynamic membrane bioreactors (AnDMBRs) (Alibardi et al. 2016) and granular AnMBRs (G-AnMBRs) (Chen et al. 2017).

Seasonal temperature

In recent years, many studies have examined the treatment of municipal WW with AnMBR, and several of them have studied the effect of different temperatures on process performance to reduce the energy consumption related to the heating of the system. Microbial cell membrane is mainly composed of a lipid bilayer, a colloidal solution of proteins and phospholipids. Appropriate fluidity of the membrane lipid bilayer is essential to keep the permeability and movement of crucial membrane proteins. Low temperatures cause physical damage and the malfunctioning of the membrane properties disturbing the liquid-crystalline phase. This alteration of the membrane functions inhibits the uptake of important substrates into the cell, by active and inactive and passive transport mechanisms, and is the main causes of the limit of growth and biological inactivity at lower temperatures. Only psychrophiles can maintain membrane fluidity at low temperatures by transforming the lipid composition (Dev et al. 2019). Different COD removal efficiencies and CH_4 were obtained depending on system configuration, operational temperature, inlet WW COD, membrane characteristics and operational parameters such as HRT and SRT (Lei et al. 2018). In the study by Chu et al. (2005) COD removal efficiencies varied from 95 to 76% using a in a membrane-coupled expanded granular sludge bed (EGSB) when temperature was changed from 25 to 11 °C while in the study by Smith et al. (2013) averaged 92% when temperature was maintained at 15 ºC. Temperature has an effect not only on anaerobic biomass activity, lower activity with lower temperatures (Agler et al. 2010), but also on the solubility of CH_4, that increases when temperature is decreased and can represent up to 50% of the generated methane (Crone et al. 2016; Giménez et al. 2011; Hu et al. 2006; Shin et al. 2014; Stuckey 2012). This not only limits the recovery of energy from the system but also poses a potential threat to the environment, with the release of this dissolved methane that can be fugitively emitted to the atmosphere, contributing to global warming.

Sulfate

SO_4^{2-} concentration in the WW is also a parameter that must be considered in anaerobic treatment. Due to the high presence of sulfate-reducing bacteria (SRB) in anaerobic conditions, SO_4^{2-} is converted into sulfide (H_2S) using the COD present in the WW. The increasing concentration of H_2S, because of its corrosive nature, makes essential the scrubbing of the biogas and the use of non-corrosive materials. Especially when treating low-strength WW this results in a major problem with a great percentage of the COD contained in the feed solution being reduced by the SRB instead of being converted into valuable CH_4 (Giménez et al. 2011).

Salts

Salts concentration in WW is another inhibitory factor when dealing with biological processes and it is also related to the complexity of the WW. In the study by Lefebvre et al. (2007) is reported that NaCl inhibition is observed at lower concentration for complex substrates which is likely related to the high number of intermediate stages needed for its biodegradation and the higher probability of inhibition of one of these stages. For the less complex investigated substrate (ethanol) the specific methanogenic activity started lowering for NaCl concentrations of 5 g/L. Salinity concentrations have an impact on the anaerobic biomass composition being the key factor in driving compositional and functional transitions in microbial community (Wu et al. 2017). Higher salinity implies a decrease in the methane producing archaea abundance, especially hydrogenotrophic and acetoclastic methanogens, becoming less competitive than SRB and resulting in a reduced methane yield.

Emerging chemical contaminants - Pharmaceutical compounds

If not treated, PhACs make their way into water bodies through WW with their potential risk to humans and ecosystems. Different removal efficiencies of PhACs are achieved depending on the technology used for treatment as several removal mechanisms can occur (coagulation/flocculation, volatilization, biodegradation, chemical oxidation, liquid/liquid separation (membrane)). For the biodegradation mechanism in membrane bioreactors, bacterial population and compound properties are the most important factors for the PhACs removal with some compounds being more degraded in anaerobic conditions than aerobic conditions. Despite the reported removal rates of PhACs during anaerobic digestion are low (Lin et al. 2013), the relatively long HRT (30 d) applied in standard anaerobic systems make that some PhACs (acetylsalicylic acid, ibuprofen, fenofibrate) are significantly degraded. PhACs removal has been attributed to biodegradation and the enhanced adsorption process into the biomass (Abargues et al. 2018; Cheng et al. 2018). Operational conditions have also an important role in PhACs removal. HRT defines the time that the system has to remove the compounds and tends to be of very few hours in AnMBRs. The higher SRTs that characterize AnMBR on the other hand, have as consequences a change in the microbial community composition, an increase biomass concentration which has demonstrated to cause membrane fouling issues and the deterioration of the effluent quality over time but also, an increase in the removal of certain compounds due to the fouling layer (Cheng et al. 2018). In general, anaerobic systems treating sludge or livestock effluent have shown good removals of compounds like sulfamethoxazole, naproxen, atenolol, loratadine, miconazole, tramadol, domperidone, azithromycin, trimethoprim, tylosin and some sulfonamides c with the large variability of the removals depending on experimental conditions. Also, the biodegradation of PhACs is often questioned due to a lack of knowledge of the elimination pathways and because their transformation products are rarely identified.

Combining FO with AnMBR

Treating raw municipal WW directly with AnMBR technology has been widely studied during the last decade at lab and pilot scale (Giménez et al. 2011; Mei et al. 2018; Watanabe et al. 2014), but the low methane production, the energy needed for the membrane operation (biogas sparging and permeate pump) and for maintaining reactor temperature for keeping high COD removal efficiencies limited its broader development (Pretel et al. 2014). Combining FO with AnMBR has developed an increasing interest whether to increase COD load and improve biogas production or for reducing the cost associated with the micro-nanofiltration membranes operation. These technologies can be combined in two different ways: (1) by replacing or coupling the microfiltration or nanofiltration membrane module with a semi-permeable membrane module in an Anaerobic Osmotic Membrane Bioreactor (AnOMBR) system or (2) by using FO to pre-concentrate WW for subsequent anaerobic treatment.

The operation of AnOMBR positively led to almost total removal of COD and P and 62% removal of NH_4^+ which is a bit higher than conventional AnMBR. Also, 0.21 L CH_4 /g COD of biogas was consistently produced even after salinity build-up that did not seem to impact the biological activity (Chen et al. 2014). Overall, similar observations than for an osmotic MBR (OMBR) could be drawn with high rejection rate, moderate fouling but severe salinity build-up overtime when only a FO membrane is used and which can impact permeation flux (Gu et al. 2015). Even if in some cases, biogas production did not seem impacted by salinity build-up, Tang et al. observed that it negatively affect methanogenic growth leading to ousting of methanogens by SRB (Tang et al. 2014). As for OMBR, combining FO and microfiltration (MF) membrane into the AnMBR reactor was also evaluated and positively avoided salinity build-up while assuring the production of high water quality (through the FO membrane), production of biogas and concentration of nutrients (P in the MF permeate) to facilitate its precipitation (Wang et al. 2017).

The other opportunity to couple FO with AnMBR is using FO for the pre-concentration of low strength WW such as municipal WW when combined with anaerobic digestion. This configuration has several benefits when compared to direct WW treatment via AnMBR technology including higher biogas production, recovery of nutrients, lower FO membrane fouling propensity, and smaller digester volume (Ansari et al. 2017). An increase of the water recovery during FO brings the benefit of lower digester volume but at the cost of higher HRT/membrane areas needed for the FO system not only due to the higher water volume that has to pass through the membrane but also due to the increase of membrane fouling and the build-up of salinity in the feed solution associated to the combined actions of reverse salt flux and the lower feed volume. Several studies have already tried to implement FO for pre concentrating WW for subsequent treatment via anaerobic digestion. FO has proven to be able to concentrate WW at several concentration factors. For example, COD contained in the municipal WW was concentrated up to 3.1 fold with a lab-scale cellulose triacetate (CTA) cross-flow module (Zhang et al. 2014). Pilot-scale has also demonstrated to reach a high COD concentration factor with a spiral wound membrane (up to 5) (Wang et al. 2016). One of the major drawbacks of this study at pilot-scale was that the COD concentration factor did not correspond to the theoretical concentration factor. Despite the very low concentration of COD in the final draw solution (COD removal > 98%), in the COD mass balance, 19.2% of the COD entering the system was degraded during the process or attached to the membrane surface. Finding the water recovery to optimize power and membrane area requirements is of primary interest in the FO-AnMBR configuration. In a study in which an FO-RO system was used to treat centrate at several water recoveries, modeling results indicated that the FO system should be operated at approximately 70% water recovery to achieve maximum efficiency (Holloway et al. 2007). Considering that this result depends on the characteristic of the feed solution, the achievable water flux of the membrane, and that membrane technology is in constant change due to the increasing interest which it produces, the optimal water recovery is intended to increase. Also, when coupling FO and AD the amount of biogas that can be produced from the concentrated WW (related to the concentration of organic matter and anaerobic digestion inhibitors such as SO_4^{2-}, NH_3, and salts) has also to be assessed. In the study by Gao et al. (2019) municipal WW was concentrated using a CTA with embedded polyester screen crossflow module resulting in COD and NH_4^+ concentration factors up to 6 fold and 5 fold respectively. Also, different concentrations of NaCl and NH_4^+ were dosed to study their inhibitory effect on the anaerobic process in the short term. Results showed that maximum COD removal efficiency was 80% and that NH_4^+ concentration higher than 200mg/L and the presence of NaCl had an inhibitory effect on the biogas production especially when combined. The AD performance treating the substrate with 200 mg/L of NH_4^+ and 5 g/L of NaCl could be highly recovered when using acclimated sludge as inoculum suggesting that continuous treatment might have better performance.

The cost associated with the combination of FO-RO-AnMBR for municipal WW treatment and water production was reported for the first time in Vinardell et al. (2020).

This combination was analyzed for four different scenarios, AnMBR directly treating WW and FO-RO- AnMBR with different FO water recoveries (50, 80, 90%). The lowest WW treatment cost was obtained when FO recovery was restricted to 50% and increasing the FO flux to 10 LMH would significantly improve the competitiveness of the combination of these two technologies.

Table 1. *Contaminant rejection results in FO studies treating WW.*

Process	membrane type	DS	TOC	COD	NH_4^+	TN	TP	Reference
			Removal or CF					
Ae-OMBR	CTA (cross-flow)	NaCl 1M	98%	-	99%	-	-	(Xinhua Wang et al. 2016)
	TFC (cross-flow)	NaCl 1M	96%	-	99%	-	-	(Xinhua Wang et al. 2016)
	CTA (sub-FO P&F)	NaCl 42 g/L	-	>99%	-	>82%	>99%	(Holloway et al. 2014)
	CTA (sub-FO P&F)	NaCl and $MgCl_2$	98%	-	80-90%	-	>99% (P-PO_4)	(Qiu et al. 2015)
	CTA (sub-FO P&F)	NaCl	>98%	-	>98%	-	-	(Qiu et al. 2013)
	CTA (cross-flow)	Synthetic sea water (24.5 NaCl, 5.2 MgCl2 etc)	80%	-	88%	-	92% (P-PO_4)	(Yan Sun et al. 2018)
An-OMBR	CTA (sub-FO P&F)	-	-	>95%	70-80%	-	>99%	(Gu et al. 2015)
	CTA (sub-FO P&F)	NaCl	-	96.7%	60%	-	99%	(Lin Chen et al. 2014)
	TFC (Aquaporin Inside)	$MgSO_4$	-	>95%	>95%	-	>95%	(Chang et al. 2019)
	CTA (sub-FO P&F)	NaCl and Na_2SO_4	92.9%	-		-	-	(Tang & Ng, 2014)
	CTA (sub-FO P&F)	NaCl 0.5M	>96%	-	39-50%	-	-	(Xinhua Wang et al. 2017)
WW pre concentration	CTA (sub-FO P&F)	-	-	99%	-	56-59%	99% (P-PO_4)	(Linares et al., 2013)
	CTA (pilot-scale spiral wound)	0.5 M NaCl	-	99.8%	48.1%	67.8%	99.7%	(Zhiwei Wang et al. 2016)
	TFC (cross-flow)	Synthetic sea water (49.06 NaCl, 10.4 MgCl2 etc)	-	2.38 and 2.67 CF	1.31and 1.75 CF	1.58 and 1.94 CF	3.28 and 3.50 CF	(Shihui Yang et al. 2019)
	CTA (cross-flow)	Synthetic sea water (24.5 NaCl, 5.2 MgCl2 etc)	79.0 %	-	85%	-	93% (P-PO_4)	(Yan Sun et al. 2018)
	CTA-ES (cross-flow)	0.2 M,- 4 M NaCl	-	96.5%	89.4%	93.3%	95.4%	(Yue Gao et al. 2017)
	TFC-Aquaporin (cross-flow)	1.5 M $MgCl_2$	-	99%	CF 1.32	-	68-74%	(Singh et al. 2019)
	TFC (cross-flow)	-	-	93.0- 97.5	<59.06%	-	93.71-98.53% (P-PO_4)	(Bao et al. 2019)
	CTA (cross-flow)	1M NaCl	-	97%	-	96%	>99%	(Song et al. 2018)
	Aquaporin (cross-flow)	1M NaCl	-	97%	-	96%	>99%	(Song et al. 2018)
	CTA (cross-flow)	35g/L NaCL	98%	-	70%	-	90%	(Li et al. 2018)
	CTA (cross-flow)	Synthetic seawater	80-95%	-	80-89.2%	-	95-99%	(Yan Sun et al. 2016)
liquid digestate pre-conc.	TFC – Aquaporin sub-FO P&F	1.1 M and 3.5 M NaCl	-	-	>95.5% (TAN)	-	-	(Camilleri-Rumbau et al. 2019)

Where Ae-OMBR stands for aerobic osmotic membrane bioreactor, An-OMBR anaerobic membrane bioreactor, sub-FO submerged forward osmosis configuration, CTA cellulose triacetate, TFC thin film composite, P & F plate and frame module.

Objectives

The general objective of this thesis is the development and optimization of the combination of FO and AnMBR technologies for WW concentration and treatment to simultaneously obtain high-quality water and methane-rich biogas recovery.

To achieve this goal, the following sub-objectives were pursued:

- Unraveling the effect of seasonal temperature variation on the operation of an AnMBR treating concentrated WW.
    - To determine the effect of temperature on CH_4 production, COD removal efficiency, and reactor stability.
    - Determine biomass recovery due to the increase of operational temperature after the operation at 15°C.
    - To study changes in microbial population due to changes in operational temperature.

- Exploring the performance of a TFC submerged plate and frame pilot-scale FO module.
    - To assess the effect of different salt used as draw solute in terms of water fluxes and reverse solute flux.
    - To determine the capability of the system for concentrating real raw municipal WW treatment.
    - To compare the effect of different gas sparging procedures on water fluxes.
    - To determine the rejection and concentration factors of COD, main ions, and PhACs.
    - To determine the effect of osmotic backwash as a membrane cleaning procedure.

- Exploring the combined performance of FO and AnMBR system for municipal WW treatment.

- To study the effect of concentrated WW from FO processes with different water recoveries on anaerobic digestion.
- To study the effect of anaerobic digestion on the removal of PhACs concentrated during the FO process.
- To compare COD removal efficiencies of an AnMBR system treating raw WW and concentrated WW at different HRTs.

THESIS OUTLINE

According to these objectives, the research work of this thesis has been distributed along the following 3 chapters of results:

CHAPTER 1: Anaerobic membrane bioreactor for biogas production from concentrated sewage produced during sewer mining.

CHAPTER 2: Exploring submerged forward osmosis for water recovery and pre-concentration of wastewater before anaerobic digestion: a pilot-scale study.

CHAPTER 3: Exploring the performance of anaerobic treatment for real concentrated raw municipal WW

Materials and methods

Chemical analysis

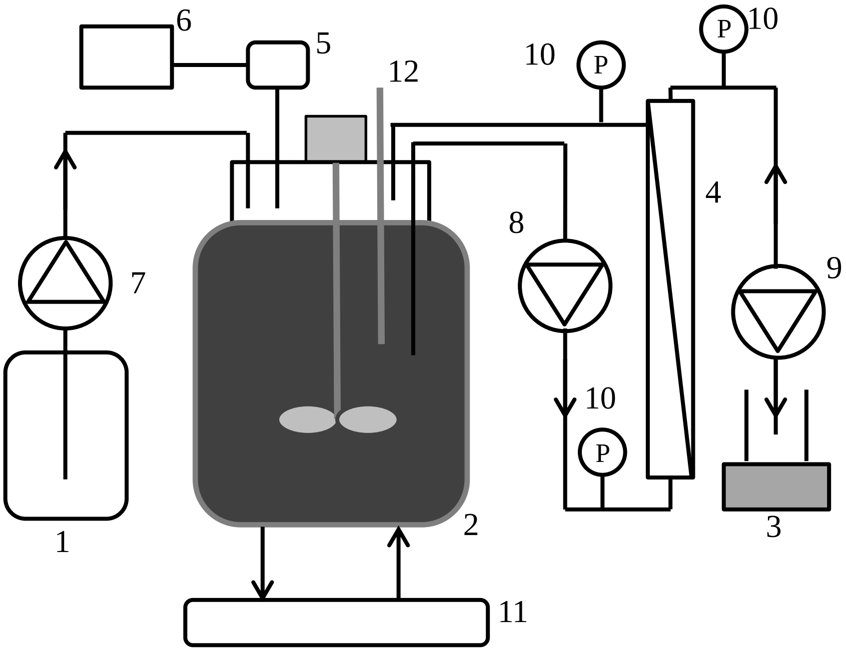
pH, conductivity, Total Solids (TS), and Volatile Solids (VS) were analyzed according to the Standard Methods (APHA 1998). Ions were analyzed via ion chromatography (ICS5000, DIONEX) after sample filtration with 0.2 mm Millipore filters. Volatile Fatty Acids (VFAs) and dissolved CH_4 were analyzed via gas chromatography (Trace GC Ultra ThermoFisher Scientific, US). Total COD and soluble COD concentrations were measured using test kits (Hach Lange, Germany). Total organic carbon (TOC) concentration was analyzed by a TOC analyzer (TOC-V_{CSH}, Shimadzu, Japan). Total and partial alkalinity and IA/TA ratio were measured by pH titration (endpoints 5.75 and 4.3) using a 0.1 N solution of H_2SO_4. CH_4 fraction in the biogas was measured with a Hydrocarbon detector Gir-3000 (GAS TECH, Australia) and biogas composition was analyzed with gas chromatography (Trace GC Ultra Thermofisher Scientific). Analysis of aqueous PhACs was realized according to Gros et al. (2012) method and they were analyzed by chromatographic separation with an Acquity ultra-high-performance-liquid chromatography (UHPLC) system (Waters Corporation, MA, USA) coupled to a 5500 QTRAP hybrid quadrupole-linear ion trap tandem mass spectrometer (AB Sciex, Foster City, USA) and analyte quantification was performed by IS calibration. For accurate quantification, total recoveries were determined for the WW matrix and applied for antibiotic concentration calculations. Quantification of the PhACs in the samples was performed by internal calibration with isotopically labeled standards.

Microbial analysis

Total genomic deoxyribonucleic acid (DNA) was extracted with FAST DNA Kit for Soils (MP Biomedicals, USA) following the manufacturer's instructions. DNA concentration and purity were checked in all samples by Qubit fluorometer (Thermo Scientific) and Nanodrop 2000 UV- VIS spectrophotometer (Thermo Scientific) respectively. Genomic DNA from each sample was submitted to BMR Genomics (Padua, Italy) for sequencing. The V3-V4 hypervariable regions (Pro341F/Pro805R) of the 16S ribosomal ribonucleic acid (rRNA) gene were amplified using universal prokaryotic primers, whose amplicons were sequenced on an Illumina MiSeq instrument (Illumina, San Diego, USA) using 2×300 bp paired-end reads. Sequences were quality trimmed using the MOTHUR software package (Schloss et al. 2009) and aligned using the SILVA reference database (Quast et al. 2013). Subsequently, sequence libraries were randomly subsampled to contain the same number of sequences (14,374) for α- and β-diversity comparisons. The Ribosomal Database Project (RDP) pipeline and Classifier function was used to assign identities at a confidence threshold of 80% (Qiong Wang et al. 2007). Sequences were assigned to operational taxonomic units (OTUs) based on a 97% sequence similarity. Selected OTUs were also identified using the EzBioCloud database (Yoon et al. 2017). A heatmap showing the relative abundance of selected OTUs was generated using the gplots package in R, version 3.1.0 (http://www.r-project.org/). The Shannon diversity index (H') and the Chao1 richness estimator were also calculated as implemented in MOTHUR (Schloss et al. 2009). The unweighted and weighted UniFrac tests were applied to determine whether two or more communities have the same structure (Lozupone et al. 2007). Raw sequences have been submitted to the Sequence Read Archive (SRA) with Accession number PRJNA525616.

AnMBR set-up

The AnMBR set up was comprised of a 5.4 L working volume reactor that was connected to an external membrane module of 0.125 m^2 of membrane area (0.15 L module volume. 2.1 cm internal diameter) built using polyvinylidene difluoride fibers of 0.04 µm nominal pore size of a ZeeWeed10 module (ZENON) in which the mixed liquor recirculation flow was kept at 0.83 L/min to avoid fouling problems without gas-sparging (4.6 cm/s of mixed liquor speed inside the module) (Figure 3). The reactor was equipped with pH and oxidation-reduction potential probes (CRISON) and a temperature sensor (SELECTA) and was continuously mixed at 35 RPM with a stirrer (RZR-1 Heidolph). Permeate flux was controlled by a peristaltic pump while the reactor liquid level was controlled by a scale (KERN) which measured permeate volume. A pressure sensor was positioned on the permeate line



1 Influent tank
2 Anaerobic reactor
3 Scale, permeate tank
4 Membrane module
5 Biogas counter
6 Biogas bag
7 Influent pump
8 Recirculation pump
9 Permeate pump
10 Pressure sensor
11 Water bath
12 pH probe

Figure 3: *Schematic diagram of the AnMBR lab-scale set-up.*

FO pilot set-up and operating conditions

The pilot set-up was composed of three units: (1) A 150 L storage tank for the WW (Setpar Export, S.L.), (2) an FO vessel, and (3) a tank for the draw solution (Figure 4). The FO module was a U-shaped plate and frame module, assembled as described in (Blandin et al. 2018) using a Kubota plate (Kubota, Japan) and a Toray TFC membrane sheet (Toray, Japan) (pure water permeability coefficient A, salt permeability coefficient B and structural parameter S data are 8.9 ± 0.14 L m^{-2} h^{-1} bar^{-1}, 5.68 ± 0.14 L m^{-2} h^{-1}, and 466 × 10^{-6} m (Jungeun Kim et al. 2017), with a surface area of 0.336 m^2 (Figure 4). The FO module was vertically positioned in the membrane vessel, consisting of a 9 L methacrylate structure equipped with a gas sparging system. The space between the membrane and the structure was 0.5 cm to control particle deposition; fouling and external concentration polarization (ECP) were mitigated through gas scouring (gas bubbles on membrane surface). WW entered from the bottom of the FO module with a flow rate of 1.8 L/min (WW 0.72 m/min cross-flow velocity).

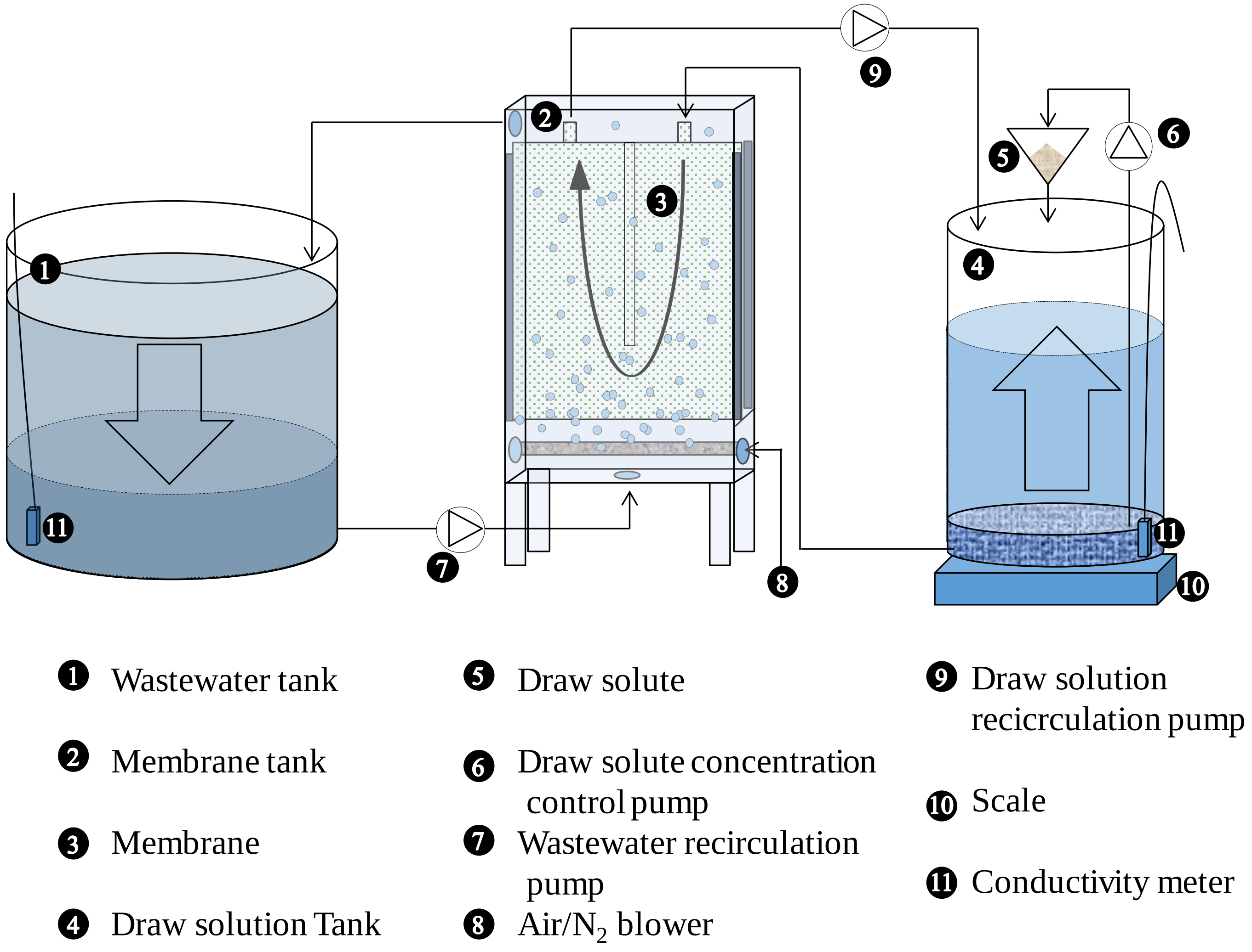


Figure 4: *Schematic diagram of the FO bench-scale set-up. Arrows in the tank describe changes in volumes during the FO concentration process.*

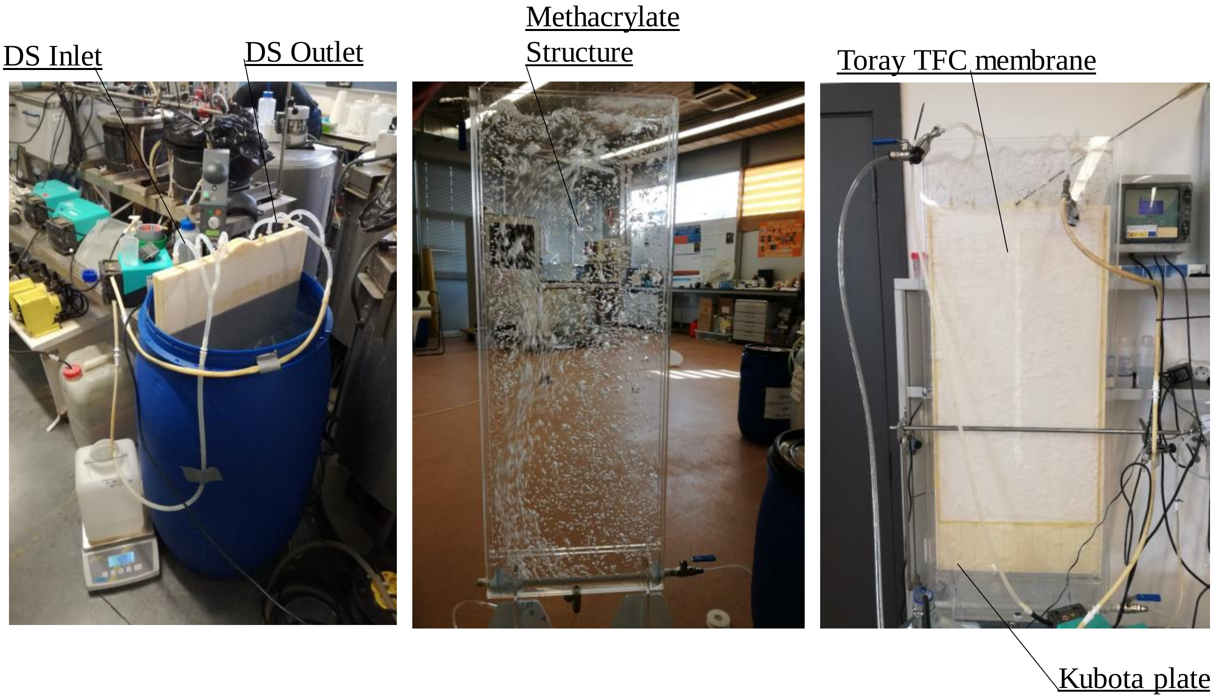
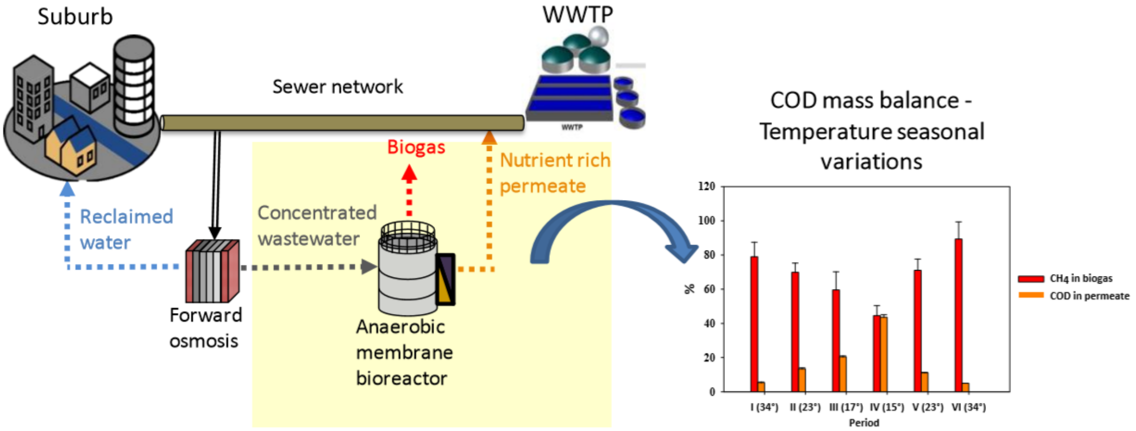


Figure 5: *Membrane module and methacrylate structure.*

Biochemical Methane Potential (BMP) tests

The BMP tests were conducted in 250 mL serum bottles (with a working volume of 150 mL). The ratio Inoculum/ Substrate (I/S, in mg COD/mg COD) was 2, which has been successfully used by others (Basset et al. 2016; Zahedi et al. 2018). The bottles were sealed and stored in a temperature-controlled incubator at 25ºC. All the bottles were continuously shaking at 150 rpm to ensure enough mixing. All tests were conducted in triplicates. The BMP tests lasted for 40 days when no biogas production from any bottle was detected. The biogas production from the WW was obtained by subtracting the biogas production from the inoculum (Blanks). Specific methane production (SMP), milliliters of methane produced per gram of TCOD added, have been expressed under normal pressure (P=1 atm) and temperature conditions (T^a= 0ºC).

Chapter 1: Anaerobic membrane bioreactor for biogas production from concentrated sewage produced during sewer mining



This section examines the effect of seasonal temperature variations on the anaerobic treatment of synthetic concentrated municipal wastewater with an AnMBR. It also assesses for the first time the challenges associated with the operation at relatively low temperatures (15ºC) and the recovery capability of this type of reactors once temperature increases. Changes within the microbial groups were also monitored.

1.1 Materials and methods

1.1.1 AnMBR set-up and operation

The lab-scale AnMBR was operated for 319 days. Permeate flux was set at 2.1 LMH. The reactor was inoculated with 2.5 L of anaerobic sludge (11 g VS/L) coming from the anaerobic digester of Girona's municipal WWTP which operated at 34 °C treating primary and secondary sludge. The sludge was diluted with 2.9 L of synthetic feed. A pressure sensor was positioned on the permeate line and when pressure reached values below -200 mbar, a backflushing of 20 seconds was applied. Membrane was manually cleaned by submerging it into a solution of 1 g/L (NaOH) for 1.5 hours when frequencies of backflushing operations could not keep a constant HRT. After an adaptation period at 34ºC to the synthetic concentrated WW, operational temperature was gradually decreased till 15ºC, as described in Table 1.1, and then gradually increased back to 34ºC during the last month of operation to study the recovery of the system after the period at psychrophilic temperature. Biogas volume was measured through a Milligas counter and collected in a Tedlar bag for the analysis of its composition. SRT was not controlled, being the biomass only removed from the reactor for analysis of solids and during the cleaning of the membrane and was estimated by knowing the volume and concentration of VS in the mixed liquor taken for solid analysis and the VS concentration and volume of water washed during the membrane maintenance.

1.1.2 Synthetic concentrated wastewater

Synthetic concentrated wastewater was made to mimic a concentrated medium-strength municipal wastewater through a forward osmosis process with 80% water recovery (4 times original COD concentrating factor, 1.72 g COD/L). The concentrated synthetic wastewater composition used in this study was modified from Aiyuk et al. (2004) (in mg/L): 312 of NH_2CONH_2, 39 NH_4Cl, 718 CH_3COONa, 86 Peptone, 60 K_2HPO_4, 26 $CaCl_2$ $2H_2O$, 134 $MgSO_4$ $7H_2O$, 60 Starch, 659 skim milk powder, 258 yeast extract, 144 soybean oil and 5mL of trace element solution. The trace element solution included (g/L): 3.8 $KCr(SO_4)_2$ $12H_2O$, 2.1 $CuCl_2$ $2H_2O$, 0.4 $MnSO_4$ H_2O, 0.9 $NiCl_2$ $6H_2O$, 0.4 $PbCl_2$, 1.0 $ZnCl_2$, 0.4 $FeCl_3$ $6H_2O$.

1.1.3 COD mass balance calculation

The COD mass balance was calculated for all the tested temperatures following equation 1.1.

$$COD_{tot} = COD_{CH_4 diss.} + COD_{CH_4 biog.} + COD_{biom.} + COD_{SO_4} + COD_{perm.} \qquad \text{(Eq. 1.1)}$$

It was divided into the contribution of methane present in the biogas ($COD_{CH_4biog.}$), the dissolved methane present in the permeate ($COD_{CH_4diss.}$), the COD lost with the permeate ($COD_{perm.}$), the theoretical COD used for biomass synthesis ($COD_{biom.}$) and the theoretical COD used by sulfate-reducing bacteria (SRBs) for sulfate reduction (COD_{SO_4}).

The COD due to the dissolved methane was calculated by converting the result of dissolved methane analysis of the permeate (1 mg CH_4/L = 4 mg COD/L). The contribution of methane present in the biogas to the COD mass balance was calculated following equation 1.2.

$$COD_{CH_4 biog.} = LCH_{4\,biogas} \;\; / \, Y_{CH_4} \qquad \text{(Eq. 1.2)}$$

Where $LCH4_{biogas}$ are the liters of methane present in the produced biogas and Y_{CH4} is the theoretical COD/CH_4 yield and it is equal to 0.35 (Lier et al. 2008).

The theoretical COD used for biomass synthesis was calculated following equation 1.3.

$$COD_{\,biom.} = Y \;\cdot\; gCOD_{removed} \;\cdot\; 1.42 \qquad \text{(Eq. 1.3)}$$

Where Y is the anaerobic biomass yield and it is equal to 0.1 g VSS/g $COD_{consumed}$ and 1.42 is the conversion unit of VS into COD (Lier et al. 2008).

The theoretical COD used by SRBs for sulfate reduction was calculated following equation 1.4.

$$COD\ for\ SO_4\ reduction = SO_{4\,removed} \cdot 0.67 \qquad \text{(Eq.1.4)}$$

Where 0.67 g COD/g SO_4^{2-} is the COD utilization ratio by the SRBs (Lier et al. 2008).

1.1.4 Microbial analysis

Samples were collected on days 90 (34°C), 184 (23°C), 222 (17°C) and 272 (15°C) and stored at -20°C until DNA extraction.

1.2 Results and discussion

1.2.1 Reactor performance at different temperatures

The AnMBR reactor was operated for 319 days progressively decreasing the temperature from 34°C to 15°C and then increasing it back till 34°C to study the biomass recovery after 2 months of operation at low temperature (15°C). Reactor operation has been divided into five experimental periods depending on the operational temperature (Table 1.1).

Table 1.1. *Process parameters and COD removal efficiencies at the different operating temperatures.*

Operational period	Temperature	Removal efficiency (%)	Biomass concentration (g VS/L)	HRT (hours)	SRT (days)	Operation time (days)
I (0-119 days)	34°C	94.9±1.8	3.7±0.2	30.0±3.1	103	119
II (120-203 days)	23°C	86.6±4.6	5.1±1.3	28.4±2.2	83	83
III (204-224 days)	17°C	76.5±5.7	6.8±0.5	29.6±2.6	120	20
IV (225-284 days)	15°C	58.4±9.0	6.4±0.4	34.1±6.3	118	59
V (285-300 days)	23°C	87.9±3.3	5.7±0.0	34.8±6.0	100	15
VI (301-320 days)	34°C	95.1±0.9	5.4±0.2	24.7±4.8	100	19

During the first period, the reactor was operated at 34°C with an HRT of 30 hours resulting in an organic loading rate (OLR) of 1.30±0.12 g COD L^{-1} day^{-1}. This temperature was chosen to facilitate the adaptation of the anaerobic biomass (which was withdrawn from a local anaerobic digester working at 34ºC) to the operational conditions of the AnMBR. Under this temperature, the reactor displayed high COD removal efficiencies (~95%) (Figure 1.1a). Also, reactor stability was confirmed by the intermediate alkalinity/total alkalinity (IA/TA) ratio which is a parameter commonly used to determine the stability of an anaerobic digestion process (intermediate alkalinity is given by the difference between total and partial alkalinity and it is an approximation of the VFAs concentration). An anaerobic process is considered stable when the IA/TA is below 0.3 (Figure 1.1b). The VFAs concentration in the permeate was very small, averaging 16 mg/L as COD. After temperature was decreased to 23°C on day 104, the reactor continued being stable (IA/TA<0.3) but its performance slightly deteriorated with average COD removal efficiencies decreasing to ~87%. VFA concentration in the permeate also increased resulting in an average effluent concentration of 124.1±70.8 mg/L as total VFAs (calculated using mg to COD conversion factor listed by Williams (1983) during the 81 days of operation under this temperature. The first time in which the IA/TA parameter was higher than 0.3 occurred after temperature was reduced to 17°C on day 201. This was accompanied by an increase in COD and VFA concentrations in the permeate. This condition lasted for only the first 2 days after which stability (IA/TA <0.3) was reached again and COD removal efficiencies increased back to ~82% while maintaining the same OLR as in previous temperatures. When temperature was further decreased to 15 °C on day 222, COD removal efficiencies decreased until reaching an average COD concentration in the effluent of 684.1±165.0 mg/L (average removal efficiencies of 58.4±10.1%). The IA/TA ratio increased exceeding 0.3 and reactor stability was compromised. In this case, the reactor did not recover and on day 256, the OLR had to be decreased to 0.92 g COD L^{-1} day^{-1} by increasing the HRT from 29.6 to 43.9 h to avoid system failure. With this change, COD removal efficiencies recovered achieving 66.3±1.4% and VFA concentration in the effluent decreased to 357.5 mg COD/L as an average concentration. After 2 months operating at 15ºC, temperature was increased back to 23 and 34°C on days 280 and 296 respectively to assess the reactor recovery. COD removal efficiencies, IA/TA ratio, and VFAs concentration in the permeate reached similar levels to the ones obtained in the initial periods at the same corresponding temperatures (Figure 1.1a & b).

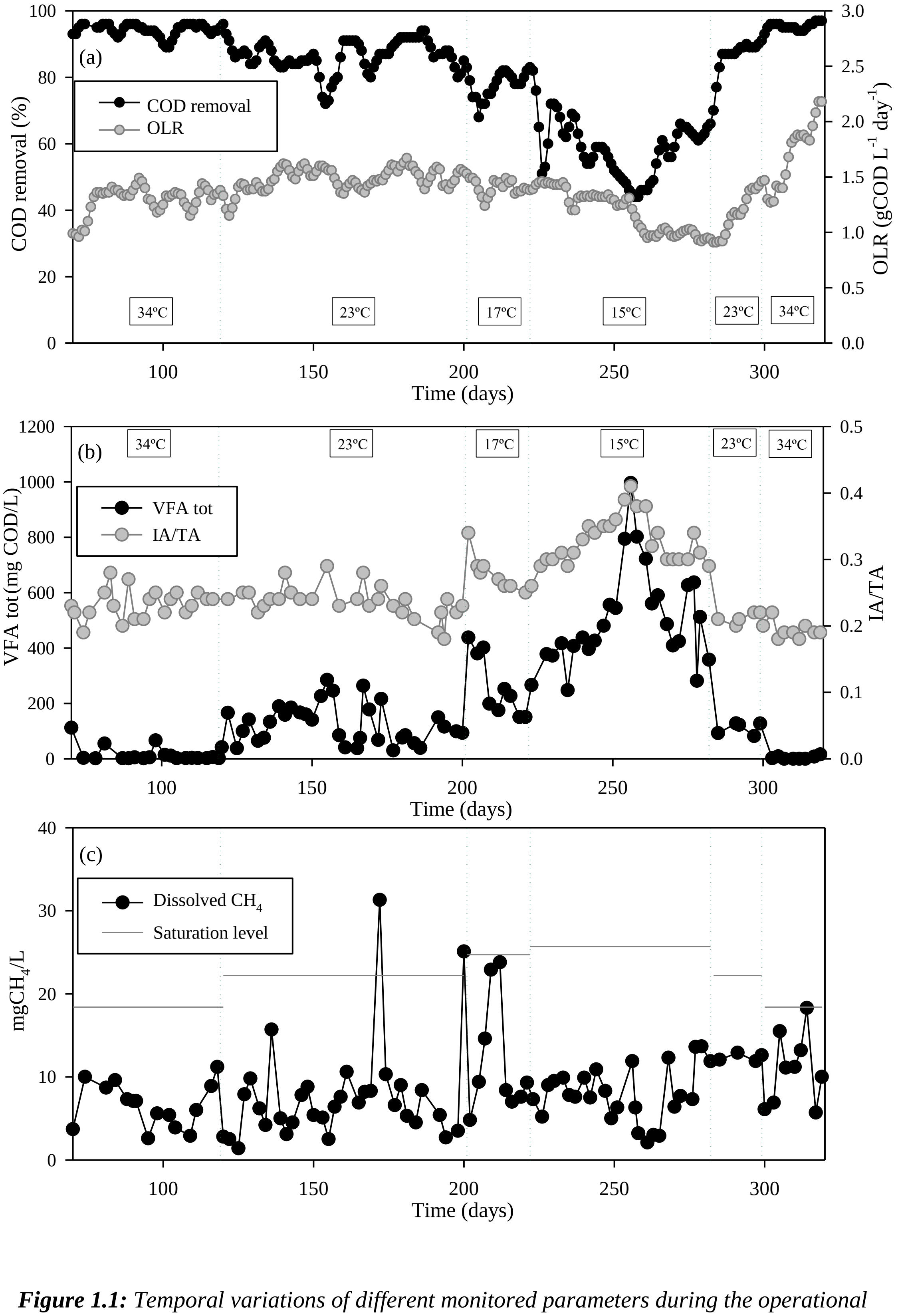


Figure 1.1: *Temporal variations of different monitored parameters during the operational period: COD removal efficiencies and OLR (a); Total VFAs concentration in the permeate and IA/TA ratio (b); dissolved CH_4 in the permeate. Lines indicate saturation level at the different operating temperatures, for 90 % CH_4 content in the biogas at 1.01 atm) (c).*

Interestingly, temperature changes did not affect dissolved methane concentration in the permeate which stayed constant and reached supersaturation only in one case when operating at 23°C (Figure 1.1c). The average dissolved methane concentration during the whole operational period was 8.2±4.9 mg CH_4/L. This differs from other studies that have shown higher dissolved methane concentrations when temperature is decreased (Smith et al. 2015). In our system, the low dissolved methane found in the permeate was probably due to the high mixing efficiency generated by the high flow of the mixed liquor recirculation in the membrane. Indeed our results are comparable to the values obtained by (Yeo et al. 2013), in which, using a 5.7 L AnMBR with 1.6 L/min mixed liquor recirculation, additional gas sparging and working at 23°C, between 4.3±0.3 and 9.9±2.3 mg CH_4/L, were found in the permeate in dissolved form.

Methane fraction in the biogas was very high, always between 85 and 95%, independently of the temperature applied. Also, high methane concentration in the biogas produced by an anaerobic reactor treating municipal wastewater and operating at 15°C was reported by Smith et al. (2015). They suggested that high methane content could be attributed to the low OLR applied the high CO_2 solubility at the psychrophilic temperature, and the feed composition in their system. In our case, however, we did not find any change in the methane content when the OLR was changed, being the methane percentage very high under all temperatures tested. This suggests that the high methane content might be attributed to the highly biodegradable wastewater composition.

The presence of VFA in anaerobic reactors is often associated with a warning signal in the process performance (Ahring et al. 1995). The accumulation of VFAs occurs when acidogenesis is faster than methanogenesis and can cause inhibition to microbial groups responsible for methane production (Ngo et al. 2019). The presence of VFAs in the permeate during the operational period depended mainly on temperature changes. The average concentration of the most abundant VFAs produced (acetate and propionate) present in the permeate is shown in Figure 1.2. Apart from these two VFAs, isobutyric acid also started to accumulate at 23°C while n-butyric was present in the permeate exclusively when temperature was decreased to 15°C (Figure 1.2). However, their concentration was always below 15 mg/L.

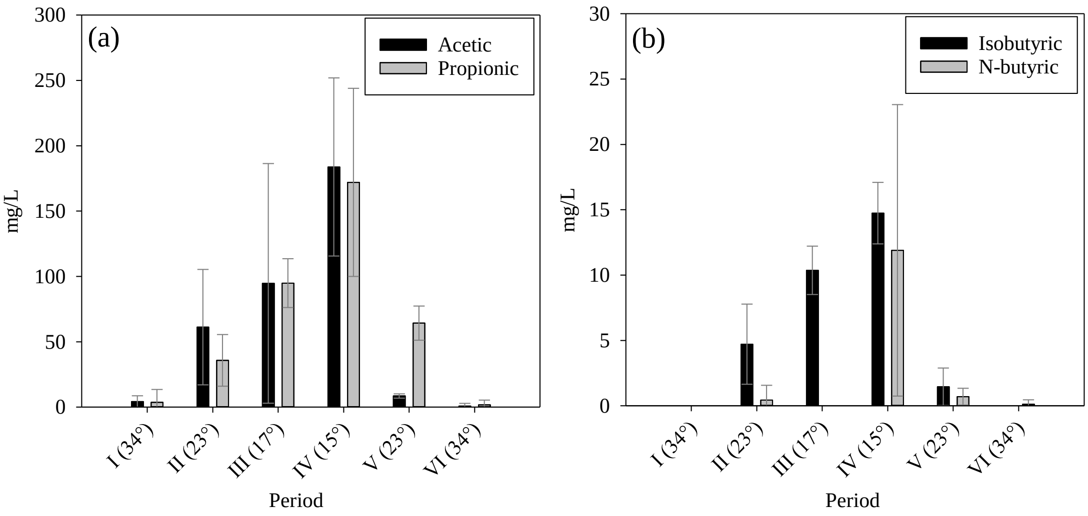


Figure 1.2: *VFA average concentration with standard deviation at the different operating temperatures: Acetic and propionic acids (a); Isobutyric and n-butyric acids (b). Daily VFA's concentrations are shown in Figure 1.4b*

1.2.2 Performance at 15 °C

Low-temperature anaerobic digestion still represents an attractive option for reducing operational costs due to the high energy demand for keeping the anaerobic digester in the mesophilic or thermophilic temperature ranges (Lettinga et al. 2001). In this study, temperature was decreased to 15°C to study the effect that this temperature has on methanogenesis and system performance. When system temperature was dropped to 15°C (Figure 1.3a), methane production rapidly decreased but never ceased. With the HRT set at 28 hours, the system faced a gradual lowering of performance leading to system instability which was firstly evidenced by the IA/TA ratio that kept increasing reaching a value of 0.41 on day 256. There was a significant decrease in COD removal efficiencies from 80 to 43% because of the increase in the VFAs concentration in the permeate, especially acetic and propionic acids. The isobutyric acid concentration was always in the range of 10-20 mg/L and n-butyric acid concentration started fluctuating reaching values up to 40 mg/L. As reported in the study Ahring et al. (1995) the increase of n-butyrate and isobutyrate is associated with process instability. In our study, these VFAs were mainly present when operating the system at 15°C. In the case of isobutyric acid, its concentration was over 5.28 mg/L that was reported as a threshold for process imbalance (Hill et al. 1988). Despite the increase in VFAs in the effluent and the decrease in COD removal efficiencies, the reactor maintained its anaerobic activity and the production of biogas. This result contrasts with the study of Dolejs et al. (2017) in which a decrease of temperature from 34 to 15°C in an AnMBR treating synthetic municipal WW led to complete inhibition of the biological processes after two weeks of operation at this temperature, confirmed by the absence of both biogas production and VFA accumulation. To restore process stability, the OLR was stepwise decreased from 1.44±0.02 to 0.92±0.03 g COD L^{-1} day^{-1} by increasing the HRT from 28 to 43 hours from day 257. This increase of HRT was progressively applied for 3 weeks increasing it to 36 hours during the first week, 40 hours during the second week, and 44 hours in the third week. Methane production was constant even when the OLR was decreased, indicating that methanogenesis was the rate-limiting step in the process. The constant methane production at lower OLR improved the COD removal efficiencies from the reactor from 43% on day 256 to 60% (day 265), 63% (day 274) and 68% (day 282) which occurred simultaneously with a quick decrease in acetic and propionic acids concentration. Isobutyric and n-butyric acids were not affected by the change of HRT and their concentration was constant during the operation at 15°C. It is important to highlight that the stability of the reactor was compromised when temperature was decreased from 17ºC to 15ºC, suggesting this temperature as a minimum threshold under which the microbial processes are most severely affected.

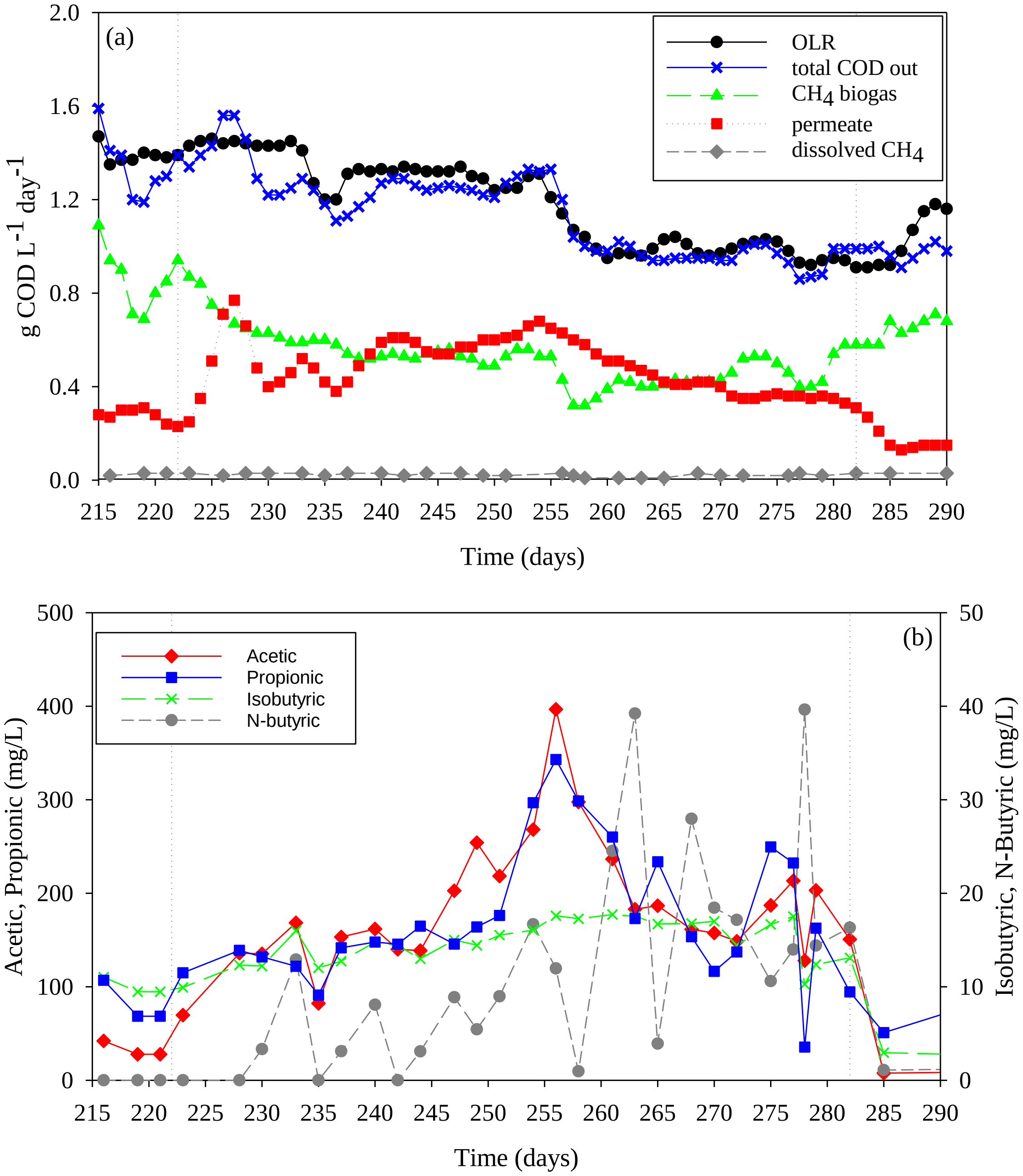


Figure 1.3: *Temporal variations of different monitored parameters when operating at 15°C: COD mass balance (a); Acetic, propionic, isobutyric, and n-butyric acid concentrations (b). (Temporal variations of COD mass balance and VFAs for the entire experiment duration are reported in Figure 1.4 a and b).*

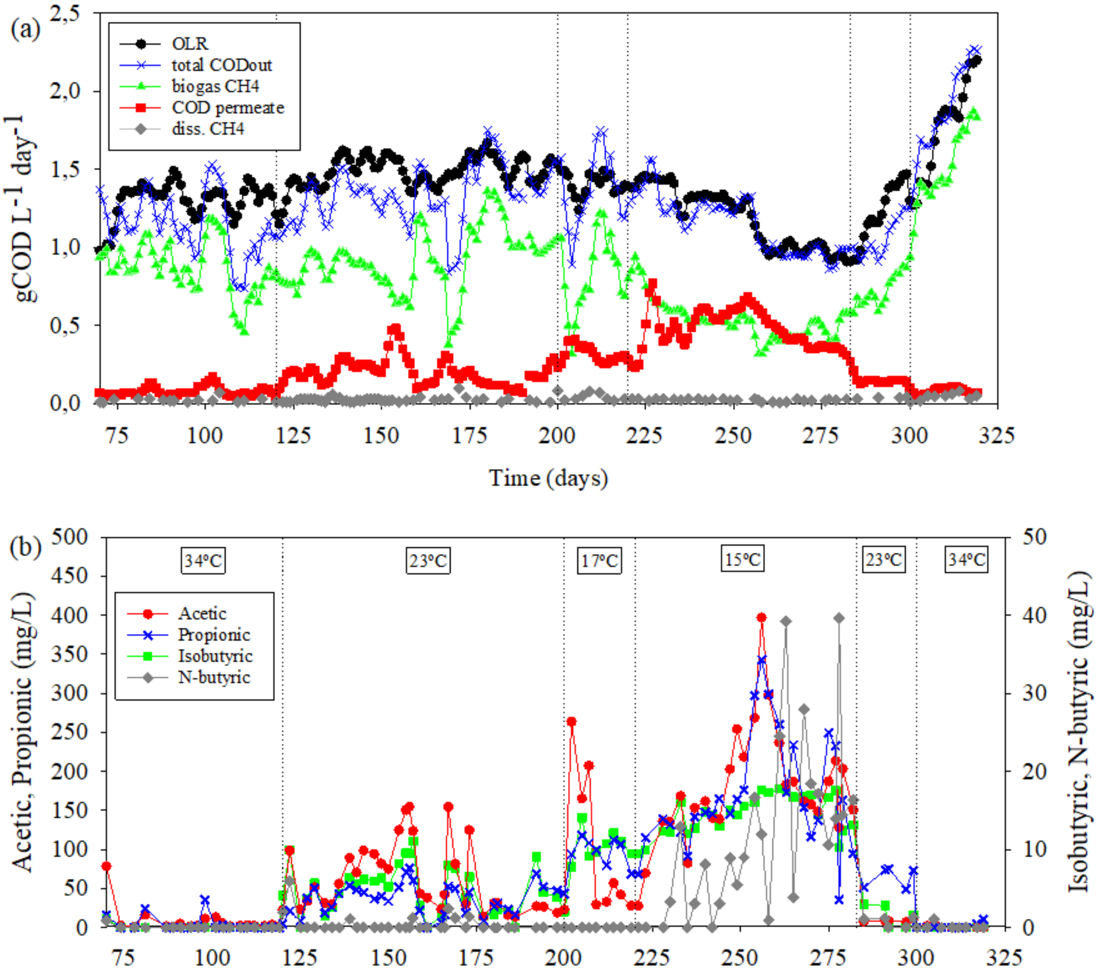


Figure 1.4: *Temporal variations of different monitored parameters: COD mass balance (a); Acetic, propionic, isobutyric, and n-butyric acid concentrations (b).*

1.2.3 COD mass balance

Figure 1.5 depicts the changes in the COD mass balance distribution under the different temperatures tested. The parameters which changed the most by changing the temperature were the contribution of methane present in the biogas and the COD lost with the permeate. Lower temperatures led to lower methane production and higher COD concentration in the permeate. COD mass balance during period II and IV (23°C) was very similar to results obtained by Sunaba et al. (2012) with an AnMBR treating synthetic wastewater at 25°C and 1.1 g COD L^{-1} day^{-1} of OLR. In their study, the percentage of COD due to the dissolved methane was very low (3%) compared to the percentage of

COD due to the methane in the biogas (72%) and was also attributed to the high mixing conditions through biogas recirculation which facilitated the release of dissolved methane to the gas phase.

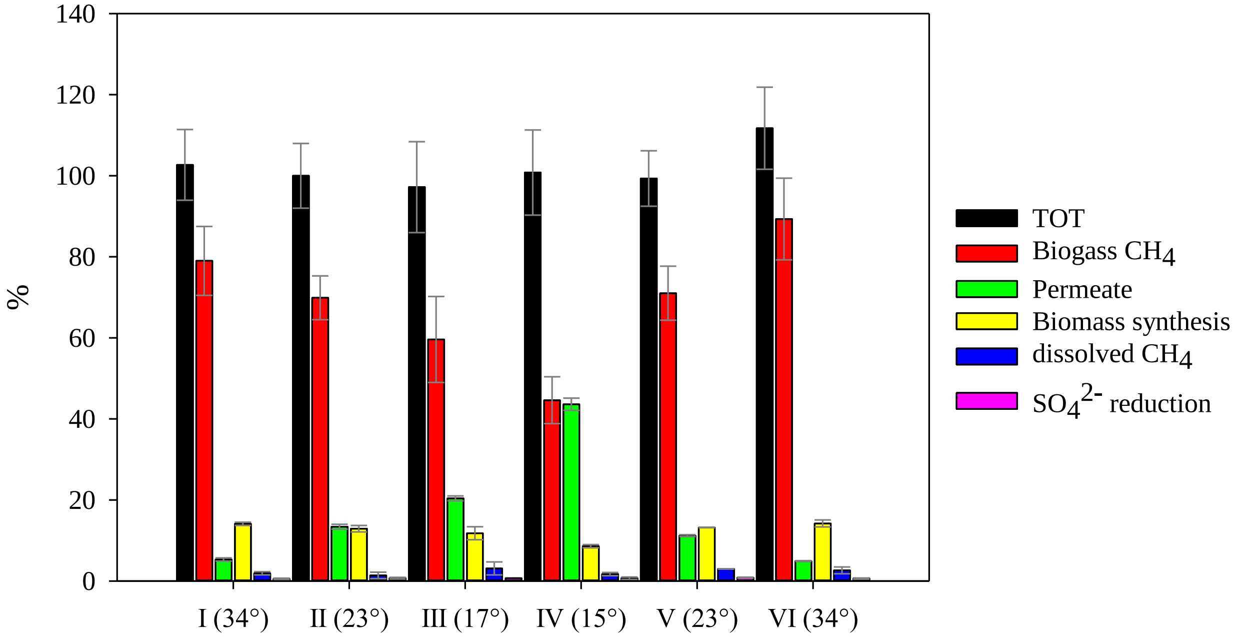


Figure 1.5: *Average COD mass balance under different operating temperatures.*

The COD associated with biomass synthesis represented 14.1±0.3% of the total COD during the first period of operation and lowered with temperature to 12.9±0.5, 11.8±0.5 and 8.6±1.2 % at 23, 17, and 15°C respectively. When the temperature was increased the biomass synthesis also increased achieving similar results to the ones obtained at the beginning at the corresponding temperature (13.2±0.2% during period V and 14.2±0.1 during period VI). Sulfate reduction was constant and almost complete (95-99%), contributing to the mass balance in less than 1% of the total COD entering the system. Dissolved CH_4 contribution to the carbon balance was also very low averaging 2% of the entering COD and remained constant despite the changes in temperature.

1.2.4 Microbial analysis

The microbial community was analyzed using high throughput 16S rRNA gene sequencing to identify if changes in microbial community structure and composition were related to temperature changes. In general terms, the number of OTUs was the highest in period I (565), whereas other periods contained between 405 and 425 OTUs (Table 1.2). Shannon diversity index and Chao richness estimators also demonstrated that period I had higher microbial diversity and richness than those samples collected at periods II, III, and IV.

Table 1.2. *Measures of α diversity.*

Period (T°C)	Total no. of OTUs	Shannon diversity index	Chao1 richness estimator
I (34°C)	565	4.21	1128
II (23°C)	422	3.18	952
III (17°C)	405	3.30	970
IV (15°C)	425	3.43	1094

The library size of each sample was normalized to the smallest number of sequences (14374) to minimize any bias due to the difference in the total number of sequences. Sequences were then assigned to operational taxonomic units (OTUs) based on a 97% sequence similarity.

Differences in the microbial community composition were determined using the unweighted (sensitive to rarer taxa) and weighted (sensitive to abundances of taxa) UniFrac tests (Table 1.3), as implemented by MOTHUR, which showed that while samples taken during period III and IV had similar memberships (pairwise unweighted UniFrac test, $p=0.933$), the relative abundances of each OTU were different (Table 1.3). Bacteria was the dominant domain in all samples (Figure 1.6), with the most abundant phyla in the sample of period I (34°C) being Bacteroidetes, Chloroflexi, and Firmicutes. When the temperature was lowered to 23°C, the greatest microbial community change took place, particularly in the relative abundance of the phylum Bacteroidetes which increased considerably at the expense of the phylum Chloroflexi and the archaeal community. Since operating at 23 ºC and for the lower temperatures, phyla percentages did not change as much after the first temperature change and Bacteroidetes, Firmicutes, and Synergistetes were the most dominant. Candidatus Saccharibacteria relative abundance changed, increasing with decreasing temperature. *Desulfomicrobium escambiense* was detected at every temperature but a very low abundance (always < 0.5%) and similar values were detected for every temperature (Figure 1.8). Probably this was due to the constant and not high concentration of sulfate. The percentage of the archaeal community compared to the overall microbial community decreased from 17% to 10% when lowering the temperature from 34 to 23ºC remaining stable when further decreasing the temperature (Figure 1.6).

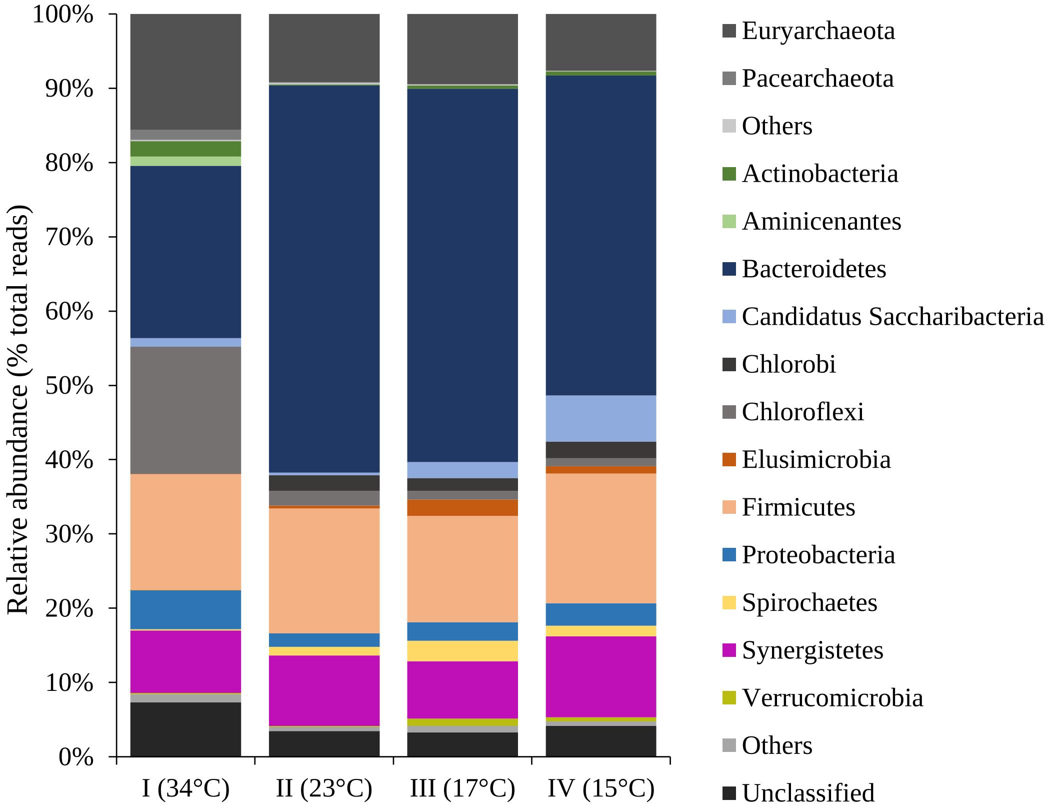


Figure 1.6: *Relative abundance of archaea and bacteria at the phylum level.*

Table 1.3. *Comparison of p-values obtained using the unweighted and weighted UniFrac tests.*

Period (T°C)	Unweighted UniFrac							
	Score				*p*-values			
	I(34°C)	II(23°C)	III(17°C)	IV(15°C)	I(34°C)	II(23°C)	III(17°C)	IV(15°C)
I(34°C)	–	0.76	0.78	0.78	–	<0.001	<0.001	<0.001
II(23°C)	0.76	–	0.74	0.75	<0.001	–	0.015	<0.001
III(17°C)	0.78	0.74	–	0.72	<0.001	0.015	–	0.933
IV(15°C)	0.78	0.75	0.72	–	<0.001	<0.001	0.933	–

Period (T°C)	Weighted UniFrac							
	Score				*p*-values			
	I(34°C)	II(23°C)	III(17°C)	IV(15°C)	I(34°C)	II(23°C)	III(17°C)	IV(15°C)
I(34°C)	–	0.37	0.36	0.36	–	<0.001	<0.001	<0.001
II(23°C)	0.37	–	0.16	0.23	<0.001	–	<0.001	<0.001
III(17°C)	0.36	0.16	–	0.12	<0.001	<0.001	–	<0.001
IV(15°C)	0.36	0.23	0.12	–	<0.001	<0.001	<0.001	–

Figure 1.7 shows the relative abundance of different archaeal species found within the archaeal community under each temperature. Four archaeal species were found, being two of them acetoclastic methanogens (*Methanothrix soehngenii* and *Methanosaeta* sp. represented by OTU 3 and OTU 8, respectively) and the other two hydrogenotrophic methanogens (*Methanospirillum hungatei* and *Methanobacterium subterraneum* represented by OTU 20 and OTU 22, respectively) (Figure 1.8).

A shift in the predominant archaeal species was observed when the temperature was decreased from 34ºC to 23ºC. At 34°C, *Methanosaeta* sp. (OTU 8) was the dominant species of the archaeal community with an abundance of 96.8 %. This percentage dropped to 7.9%, 1.1 % and 0.7% at 23, 17 and 15°C, respectively. This species was replaced by *Methanothrix soehngenii* (OTU 3), a mesophilic acetoclastic methanogen that belongs to the genus *Methanothrix*. Its abundance within the archaeal community increased from 2.9% at 34°C to 76.5, 86.5, and 85.4% at 23, 17, and 15°C, respectively. The lowering percentage of *Methanosaeta* sp. is in line with results obtained by Smith et al. (2015a) in which *Methanosaeta* sp. was replaced by *Methanosarcina* sp. when lowering the temperature form 15 to 3ºC. This change of microbial population was attributed to the capability of the *Methanosarcina* sp to perform both hydrogenotrophic and acetoclastic methanogenesis. The other two archaeal species present in the AnMBR reactor were mesophilic hydrogenotrophic methanogens which slightly increased their percentage with lower temperatures. *Methanospirillum hungatei* (OTU 20) increased from 0.2% at 34°C to 9.4, 6.1 and 7.0% at 23, 17 and 15°C, respectively, while *Methanobacterium subterranum* (OTU 22) increased from not detectable levels at 34°C to around 6% of the archaeal community at other temperatures. Acetoclastic methanogens dominated in the AnMBR under all tested temperatures but the percentage of the hydrogenotrophic methanogens increased by 15% when lowering temperature from 34 to 23°C. This increase of the hydrogenotrophic population is in line with the study from Lettinga et al. (2001) that suggested that lower temperatures may not offer a considerable energetic advantage to the hydrogenotrophic methanogens. Overall, the decrease in methane production obtained at the lowest temperature tested and the increase in acetic acid concentrations confirms that acetoclastic methanogenesis is treated as a rate-limiting step for methane fermentation process (Nozhevnikova et al. 2007). Mesophilic psychrotolerant populations dominated in the AnMBR making possible the increase of their activity once the temperature was increased to 23 and 34°C as shown also by the rapid increase of treatment performance once temperature increased.

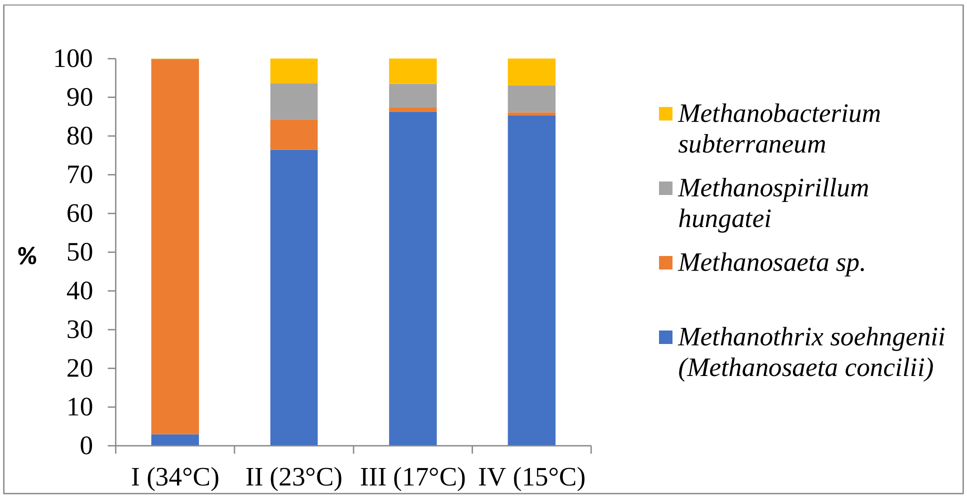


Figure 1.7: *Percentages of archaeal species at the different temperatures tested in this study.*

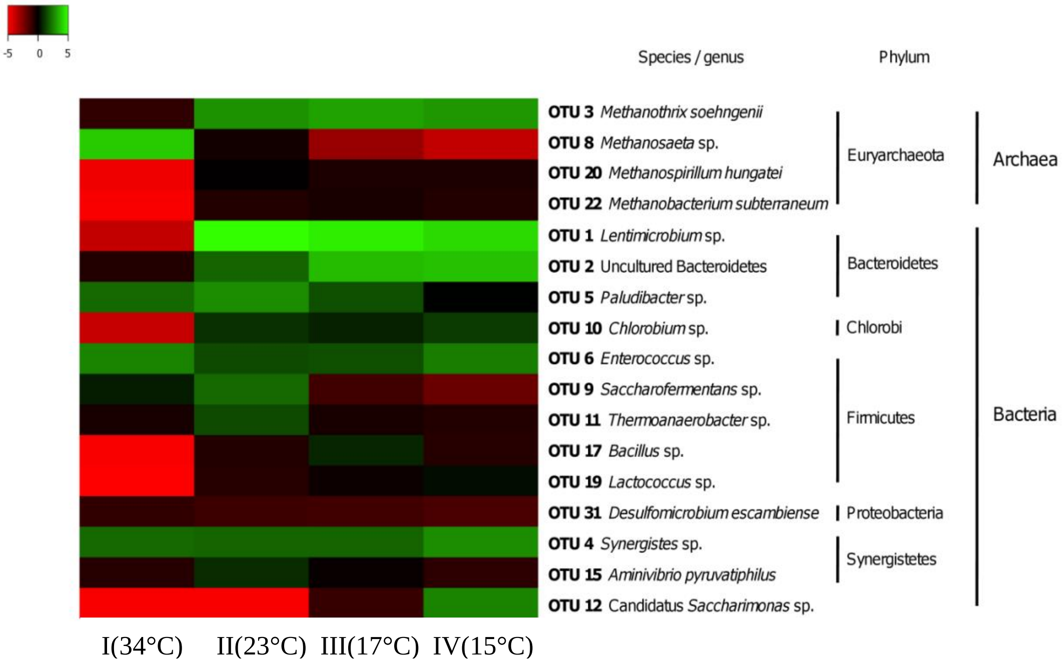
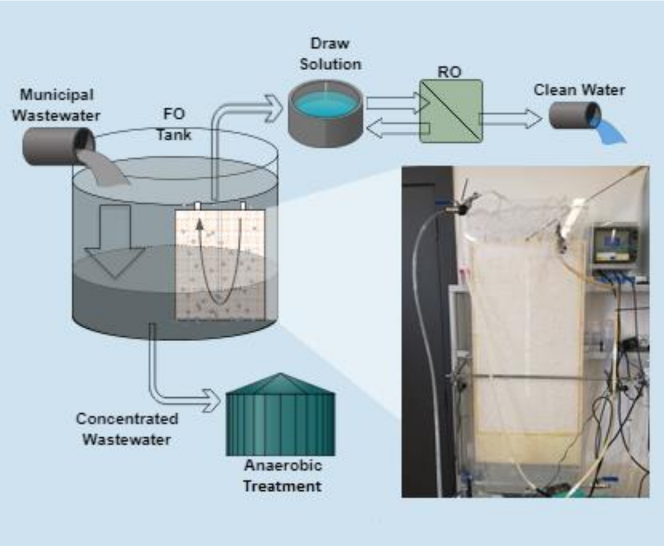


Figure 1.8: *Heatmap of species of the four samples. Comparison of the presence of the relative species among the four samples. Lower concentration is represented in brighter red colors higher concentrations in brighter green.*

1.2.5 Concluding remarks

The treatment of concentrated synthetic municipal wastewater with an AnMBR at 1.38±0.25 gCOD/dayL-1 OLR at different operating temperatures was feasible and resulted in high levels of methane production. Reactor stability was compromised at 15ºC but was restored by reducing the OLR. Dissolved methane was under saturation level averaging 6.18 mgCH4/L and remained constant across the different tested temperatures probably due to the high mixing efficiency applied. Microbial analysis showed mesophilic populations dominated in the AnMBR making possible the increase of their activity once temperature was brought back to 23 and 34°C, confirmed by the complete recovery of system performance.

Chapter 2: Exploring submerged forward osmosis for water recovery and pre-concentration of wastewater before anaerobic treatment: a pilot-scale study



This section presents the results obtained with a novel, upscaled, and newly designed sub-forward osmosis (FO) pilot-scale system for raw municipal wastewater (WW) concentration. In the first step, the system was optimized using: (1) Tap water, (2) tap water with salt (to mimic the concentration of salt in a typical municipal WW), and (3) municipal WW. Then, tests were conducted to concentrate municipal WW to reach 70% water recovery. The effect of different gas sparging procedures on membrane performance and concentrated WW characteristics were also assessed.

2.1 Material and methods

2.1.1 Filtration tests

Four different sets of tests were conducted. The first three sets of tests were conducted to evaluate the impact of operating conditions, i.e., draw solution type, cross-flow velocity (CFV), air sparging, feed conductivity, and draw concentration on water flux. In the fourth set of tests, the optimum operating configuration was chosen and tested with real WW. A description of each set of tests is presented below.

Impact of draw solution type on water permeation flux: The first set of tests was conducted using 60 L of tap water as feed solution and 2 L of 35 g/L of salt as draw solution. NaCl and $MgCl_2$ were tested to study the dependence of water flux on the salt used as draw solute.

Impact of CFV and air sparging on water flux: The second set of tests was done using 60 L of tap water as a feed solution and 2 L of a solution containing 70 g/L of sea salt (>99.4% NaCl), provided by Vicens I Batllori S.L. (Banyoles, Spain), as a draw solution, letting it dilute as the test progressed. Tests lasted for 2 h. Two CFVs (0.27 and 0.72 m/min) were tested by changing the section of the methacrylate structure, both with and without air sparging.

Impact of feed water salinity and draw concentration: The third set of tests was conducted using 113 L of tap water with a conductivity of 0.6 mS/cm as a feed solution. Tests were stopped when they reached 62% water recovery (the draw solution recirculation pump stopped once the draw solution reached the volume associated with 62% water recovery, measured through a scale connected to a programmable logic controller (PLC)). Two draw solution configurations were tested: (1) 30 L with an initial salt concentration of 35 g/L (which was diluted during the filtration time), and (2) 20 L with an initial salt concentration of 11.7 g/L (which was kept constant by adding salt during the experiment by recirculating the draw solution through a filter containing salt with a recirculation pump, controlled via a conductivity probe (Crison, Spain) as detailed in (Sauchelli et al. 2018). Both configurations resulted in the same amount of salt utilization at the end of the concentration test. Conductivities of the feed and draw solutions were continuously monitored. Two different feed solutions were used: tap water and saline water with a conductivity of 1.9 mS/cm, as to mimic ions and conductivity from a real municipal WW. The saline water composition used was (in mg/L): 183 of NH_4Cl, 280 of $NaHCO_3$, 750 of $MgSO_4 \cdot 7H_2O$, 118 of $CaCl_2 \cdot 2H_2O$.

Impact of real municipal WW: In the fourth set of tests, 50 L of municipal WW collected from the inlet of a local WWTP (Quart WWTP, Spain) and prefiltered with a 5 mm mesh sieve was used as a feed solution, and 10 L of sea salt solution (11.7 g/L) was used as a draw solution. Tests finished once 70% of water recovery was reached. Three different gas sparging procedures were studied: (1) continuous air sparging, (2) intermittent nitrogen gas sparging (1 min on/15 min off), and (3) absence of gas sparging. The operating temperature was set at 17 °C. After each test, 2 L of distilled water was recirculated inside the membrane and purged to manually clean the membrane surface, as described in two recent studies (Blandin et al. 2018; Blandin et al. 2019) WW composition at the beginning and the end of the tests was analyzed to determine any possible chemical oxygen demand (COD) degradation in real WW. Triplicates were conducted for each test.

2.1.2 Assessment of membrane integrity and performance

A two hours flux test was carried out to assess membrane integrity before each test. For the third set of tests, the same flux test was conducted after each test, and after the cleaning procedure, to respectively quantify the fouling effect after each WW concentration process and the cleaning efficiency. For this purpose, 25 L of tap water and 20 L of sea salt solution (35 g/L) were used as feed and draw solutions, respectively. The conductivity of the feed solution was monitored to quantify the reverse solute flux (RSF) and draw solution conductivity was not controlled. Osmotic backwash (OBW) cleaning was also conducted after the assessment of the membrane performance. To this end, 20 L of salt solution (35 g/L) was placed in the WW tank and 25 L of tap water in the draw solution tank; the FO unit was operated for two hours in OBW mode. The whole system was then rinsed using tap water.

2.1.3 Chemical analysis

Municipal WW (feed) and draw solution samples were taken and immediately filtered through 0.2 µm filters before and after each test conducted with municipal WW for subsequent analysis. Ions, total COD, soluble COD, and total organic carbon (TOC) were measured in the raw WW, concentrated WW, final draw solution, and in a sample of raw WW at the end of the test to check its degradation.

2.1.4 Jw and WR calculations

Jw (L/m^2 h) was calculated using equation 2.1.

$$J_w = \frac{\text{Change is DS volume (L)}}{A_m(m^2) \times \Delta t\ (h)} \qquad \text{(Eq.2.1)}$$

where A_m is the effective membrane surface area (m^2), and Δt is the operation time (h). RSF was determined using equation 2.2.

$$\text{RSF} = \frac{\text{Change is DS conductivity (mS/cm)} \times \text{FC (g/(mS/cm))}}{A_m(m^2) \times \Delta t\ (h)} \qquad \text{(Eq.2.2)}$$

where FC is the calibration factor for the draw solute concentration versus conductivity (FC_{MgCl2} = 0.46 g/(mS/cm), FC_{NaCl}= 0.51 g/(mS/cm)) obtained using calibration curves.

WR was defined as described in equation 2.3.

$$\text{WR} = \frac{\text{Permeated volume (L)}}{\text{Initial feed volume (L)}} \times 100 \qquad \text{(Eq.2.3)}$$

2.2 Results and Discussion

2.2.1 Tests with tap water

FO tests with tap water and an initial draw solution concentration of 35 g/L of salt (dilution overtime) were conducted to study the impact of the type of salt used as draw solute ($MgCl_2$ and sea salt) on water flux. Figure 2.1 shows the results obtained in these tests.

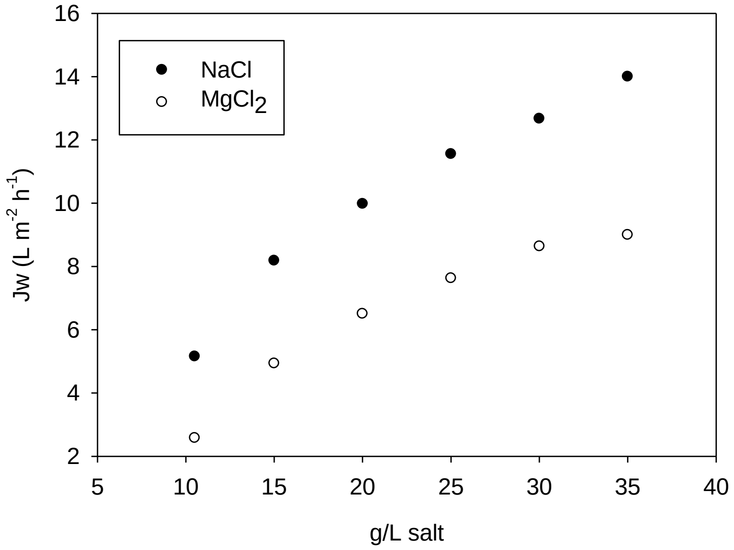


Figure 2.1: *Water flux dependence on the draw solute concentration and the type of salt used.*

Water fluxes were generally high (starting from 14.1 and 8.2 L m^{-2} h^{-1} for 35 g/L of sea salt and $MgCl_2$, respectively) and in line with results obtained in a previous study (Blandin et al. 2018) with smaller FO modules (0.05 m^2 of surface area), proving the good functioning of the Sub-FO plate design even at a larger scale. The lower Jw using $MgCl_2$ led to longer filtration times as compared to the test with sea salt (42.9 and 25.6 h, respectively). Surprisingly, the use of $MgCl_2$ as draw solute was also accompanied by a higher RSF, averaging 7.6 g m^{-2} h^{-1}, compared to sea salt with 6.7 g m^{-2} h^{-1}, leading to final salt concentrations in the feed solution of 3.16 and 2.24 g/L for $MgCl_2$ and NaCl, respectively. The resulted RSF/Jw ratio (0.95) was the same as the one obtained in a previous study (Blandin et al. 2018) with a smaller TFC Sub-FO module after 8 days of permeation in an osmotic membrane bioreactor (OMBR) and using NaCl as draw solute. The original salt present in the feed accounted for 26% and 40% of the final concentration for $MgCl_2$ and NaCl, respectively. With this membrane module, NaCl resulted in a more appropriate draw solute compared to $MgCl_2$, not only thanks to the higher water flux obtained and its lower price but also the lower final salinity in the concentrated feed solution, which must be considered for its potential inhibitory effect in a downstream biological system.

Figure 2.2 shows the results of the second set of tests conducted to assess the effect of CFV (0.27 and 0.72 m/min) and air sparging (with/without) on Jw.

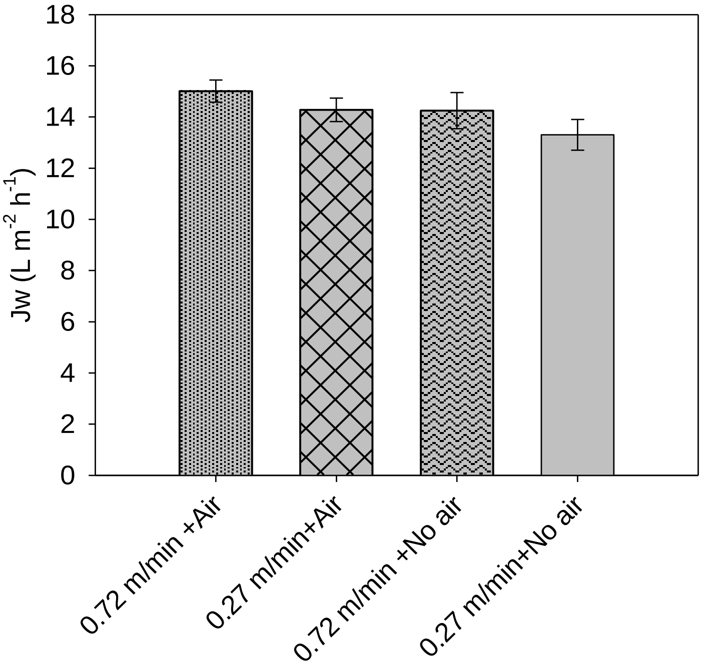


Figure 2.2: *Impact of cross-flow velocity (CFV) and air sparging application on the average initial water flux (first 10 min of operation).*

All tested configurations resulted in slightly different Jw after 10 min but remained mostly within the interval of uncertainty; only the last configuration (no air sparging, low CFV) showed a significantly lower flux. On the other hand, operating the system at 0.72 m/min CFV with air sparging resulted in the highest permeation flux. The two configurations (0.72 m/min CFV without air sparging, and 0.27 m/min CFV with air sparging) had similar results with lower average fluxes. Overall, these results indicate that the higher the shear stress (higher CFV and air sparging), the lower the ECP. However, the effects remained quite mild in the conditions tested and in the first minutes of the filtration tests. Further tests were performed during a longer period (i.e., 2 h); the impact of feed salinity and the application of air sparging for two types of draw solute operations (dilution overtime or constant concentration) is shown in Figure 2.3.

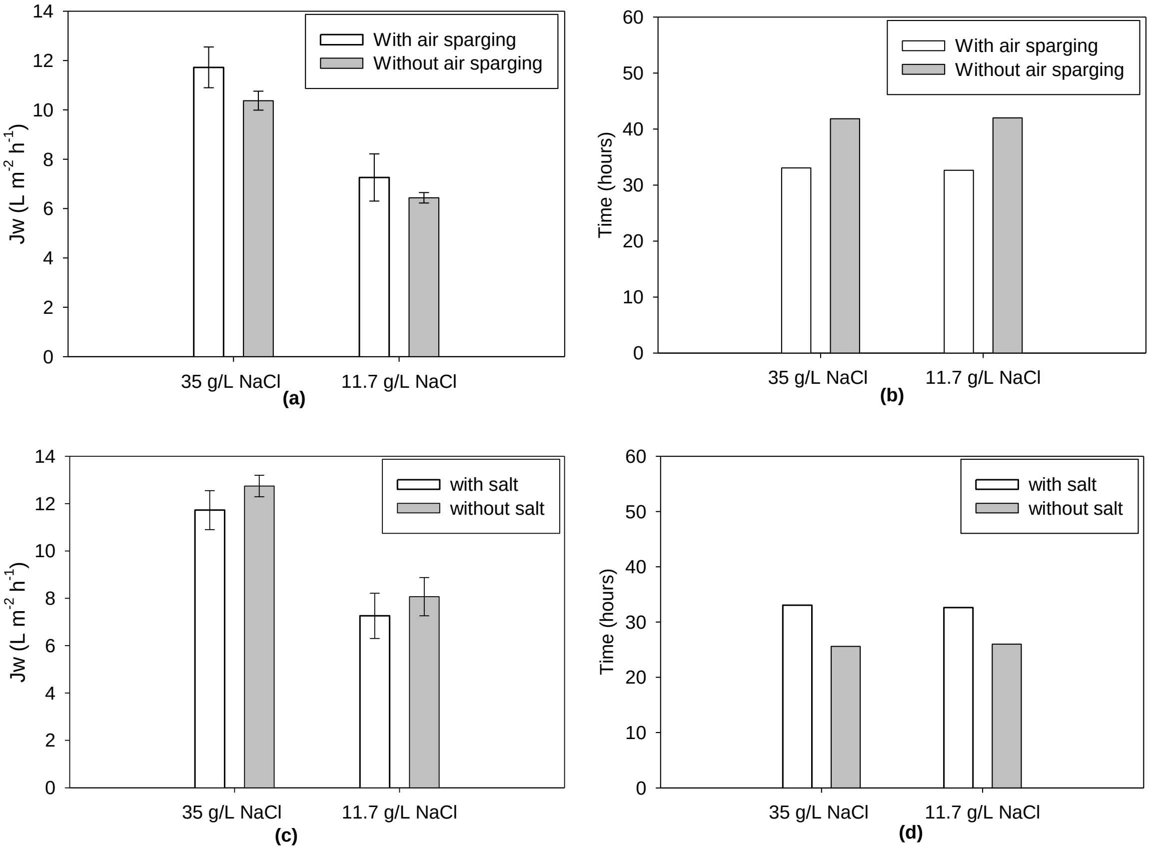


Figure 2.3: *Average water fluxes during the first 2 h of each test (a,c); total filtration time for 35 g/L of draw solute (without re-concentration) and 11.7 g/L constant draw solute concentration under different conditions (b,d).*

When looking at 35 g/L draw solution tests (dilution over time), the application of air sparging resulted in 11.42 ± 0.04 L m^{-2} h^{-1} initial water flux, which was higher compared to the same conditions but without air sparging (11.4% higher for 11.7 g NaCl/L and 11.5% for 35 g NaCl/L). Similar observations could be made with a constant draw operation, confirming the benefits of air sparging in mitigating ECP. In both cases, longer filtration time was needed to achieve the desired concentration rate when no air sparging was implemented. Operating at a constant draw solute concentration of 11.7 g/L of sea salt throughout the test led to 38.01 ± 0.20% lower initial Jw compared to the higher initial draw solute concentration (35 g/L of sea salt, without re-concentration). However, the final test duration to reach the desired water recovery was similar for both configurations. This is due to the sharper flux decrease when the system is operated at a higher initial draw concentration but without re-concentration. With time, permeation flux decreases to very low levels and filtration time is extended. Since both configurations use the same amount of salt and similar filtration time, a system operated with draw re-concentration would be preferred, allowing operation at lower and constant flux and providing lower fouling rate and higher process stability.

Finally, both initial flux and filtration time varied depending on the initial salinity of the feed solution. When feed solution mimicking the WW salinity was used, test duration was 22.8% higher than when using tap water. This is due to the lower initial osmotic pressure driving force as a result of the higher salinity of the feed, which is reinforced by the enhanced salinity increase in the feed over time and the higher overall feed salinity at the end of the concentration process.

2.2.2 Tests with municipal WW

Three tests with real municipal WW were conducted to study the effect of three different gas sparging procedures (continuous air sparging, intermittent N_2 sparging 1 min on/15 min off, and absence of gas sparging) on Jw. Figure 2.4 shows a picture of the raw WW, concentrated WW, and the final DS.

Figure 2.4: *Raw WW, Final DS, Concentrated WW.*

Test duration, COD concentration, and degradation, as well as ion concentrations, were monitored. Figure 2.5 shows the average Jw of the first 2 h of each test (initial flux) and average Jw to reach 70% water recovery.

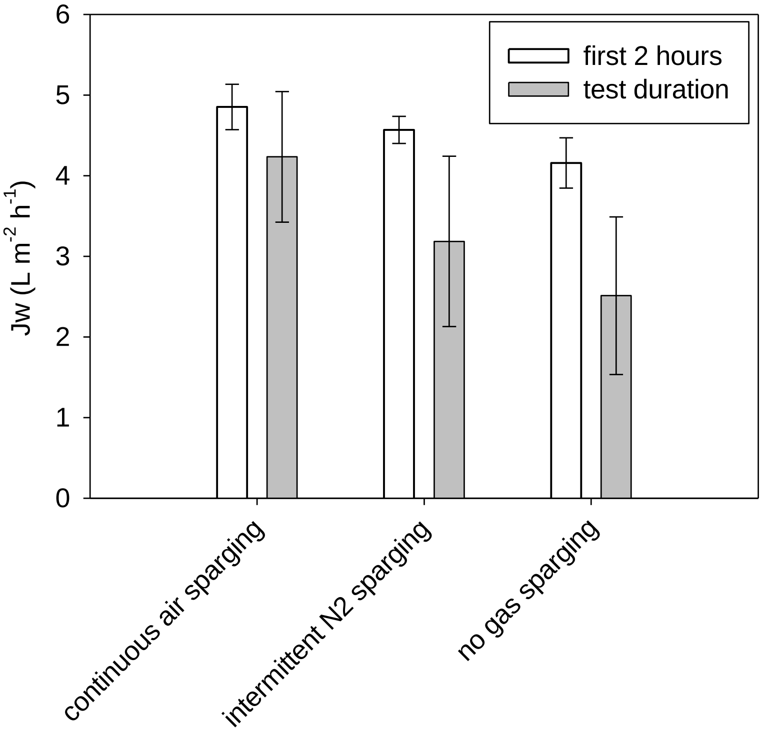


Figure 2.5: *Average water flux with standard deviation during the first 2 h of each test and the whole test duration, under different gas sparging conditions.*

Continuous air sparging and intermittent N_2 sparging led to lower flux declines, and implied 40.1% and 17.4% less time to reach 70% water recovery when compared to the configuration without gas sparging (lasting 23.9, 33.0 and 39.9 h, respectively). The benefits of the application of gas sparging were clear from the beginning of the tests (Figure 2.5) and increased throughout their duration, due to the effect of gas sparging on ECP, as well as on fouling control. RSF was similar for the three sets of tests, being 4.8 ± 2.6, 4.2 ± 2.2, and 3.9 ± 2.4 g m^{-2} h^{-1}, and leading to a final salt concentration in the WW of 5.1 ± 1.7, 6.4 ± 1.2, and 7.2 ± 0.8 g/L of NaCl for continuous air sparging, intermittent N_2 sparging, and no gas sparging, respectively. The highest final salt concentration obtained under the lowest gas sparging intensity can be attributed to the longer test duration necessary to reach 70% water recovery, leading to more salt passage.

The effect of the gas sparging procedure on membrane fouling was also assessed by comparing the flux before (clean membrane) and after each WW test, using tap water as feed solution and with continuous air sparging (Figure 2.6).

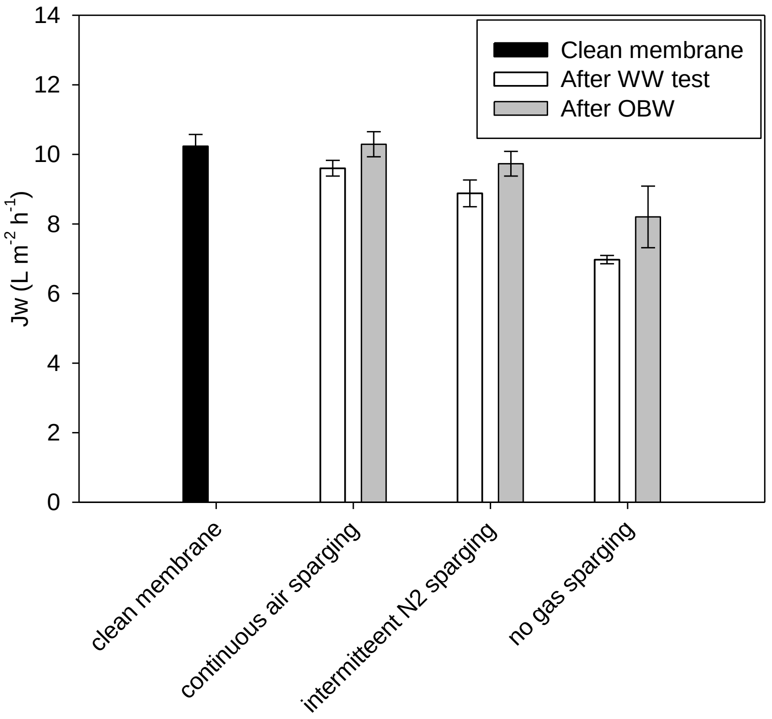


Figure 2.6: *Comparison of water fluxes results of the flux test with clean membrane, after WW tests and after osmotic backwash (OBW). Effect of gas sparging procedure on Jw. (Tests conducted with 35 g/L salt in the draw solution)*

After the filtration batches, a Jw decline of 5.7%, 12.4%, and 31.3% was observed with continuous air sparging, intermittent N_2 sparging, and no gas sparging, respectively, confirming that gas sparging (even if intermittent) has a strong effect on fouling mitigation. On the other hand, the strong flux decline when no gas sparging was applied confirms that operation without gas sparging is challenging. Additionally, OBW allowed for flux recovery in all cases. Full recovery of the initial flux was achieved when OBW was applied after continuous gas sparging and nearly full recovery (95.1%) when applied after intermittent gas sparging. These results indicate that a sustainable procedure for operation and cleaning was found. However, it must be tested for extended filtration times and repeated batches. For the no gas sparging batch, OBW did not allow for the full recovery of the initial flux (only 80%), confirming that operating with gas sparging is preferable. These results are encouraging, especially when air sparging is implemented since it confirms the low fouling potential of Sub-FO and easy cleaning even when treating very complex streams such as raw WW. This is further reinforced by the fact that no problems related to clogging were encountered during the duration of the tests, and that no membrane degradation was detected. These results show that pre-treatment of the WW, which for other membrane configurations such as a cross-flow module is considered as an important procedure to decrease the likelihood of clogging and degradation issues, can be very limited in the case of a submerged plate and frame module. This would further simplify and make economically more attractive this technology, and, in the case of anaerobic treatment of the concentrated WW, it would mean that no COD would be lost in the pre-treatment stages, maximizing its concentration and subsequent conversion into biogas. On the other hand, due to the interaction between gas bubbles and the surfactants present in the WW, white foaming was observed in the membrane tank when operating the system with gas sparging compared to tests in the absence of gas sparging. Surfactants demonstrated to have beneficial effects rather than disadvantages in the conversion process of hydrolysis, acidification, and methanogenesis of AD of sludges (He et al. 2019) and in our study did not imply any issue on the osmotic process. Anyway, the low volume that the foam had at disposition in the membrane tank was the main cause of foam overflowing issues. This issue could be solved by raising the walls/ lowering the exit connection of the membrane tank and by increasing the diameter of the exit connection letting the foam go to the WW tank instead of overflowing.

2.2.3 Consecutive tests with OBW cleaning procedure.

For assessing the effect of osmotic backwash on fouling removal, four consecutive batches were run till reaching 70% water recovery. To this end, between one run and the following, an osmotic backwash was applied by recirculating 25 L distilled water in the membrane and a DS (35 g/L sea salt) in the feed line. Figure 2.7a shows the average Jw for the first 2 hours and the complete duration of the test. While the Jw relative to the first 2 hours of each test decreased 2.1%, 3.8% and 11.5% as compared to test 1 for test 2, 3 and 4 respectively, the effect of fouling on Jw was clearer considering the average Jw of the complete duration of the test being 14.6%, 24.4% and 26.8% lower compared to test 1 for test 2, 3 and 4 respectively. The decrease of the Jw can be partially attributed to the decrease in the concentration of salt between the DS and the feed solution. Feed conductivity increased 5.6-fold during the first test while for tests 2, 3, and 4 the increase of conductivity was higher being 5.9, 7.7, and 8.8-fold. As for the results of different gas sparging procedures, this might be explained by the increase in test duration to achieve 70% water recovery while the average RSF did not decrease. Test duration increased for every batch as a result of the fouling that resisted to the OBW procedure. Test 1 lasted 24.5 h to reach 70% water recovery while lasted 28.3, 33.6, and 37.2 h for tests 2, 3, and 4 respectively.

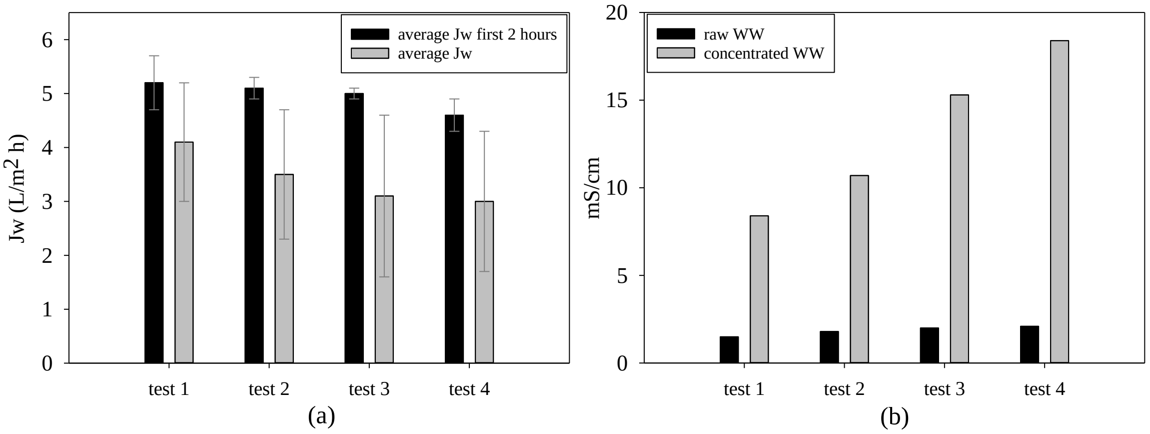


Figure 2.7: *Average water flux with standard deviation during the first 2 h of each test and during the whole test duration (a), raw WW, and concentrated WW conductivities of each test (b).*

2.2.4 COD concentration during the filtration batch

A 70% water recovery (extraction) from WW via FO implies the production of a concentrated stream rich in COD, which can be treated in an anaerobic reactor to recover biogas. However, the effective concentration of COD needed to be assessed, therefore total and soluble COD and TOC were measured in the WW at the beginning of the test and in the concentrate stream at the end of each test (Figure 2.8).

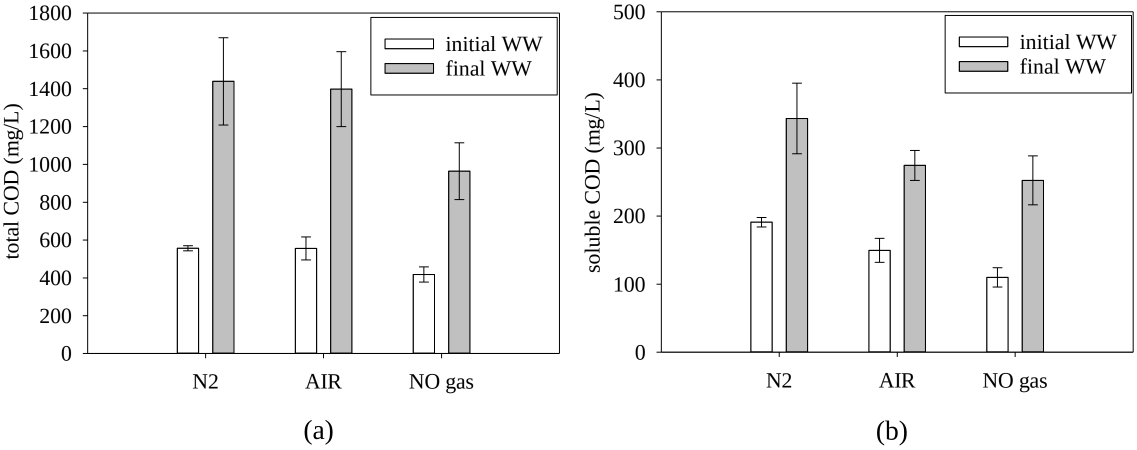


Figure 2.8: *Initial and final WW COD concentration: Total COD (a); soluble COD (b).*

In all tests, independently from the gas sparging configuration, a concentration factor (CF) of 2.47 ± 0.15 and 1.86 ± 0.08 was achieved for total and soluble COD, respectively. These values represent 75 ± 4% and 56 ± 2% of the theoretical CF (3.33), implying a loss of COD was present in the WW. Several hypotheses were formulated to explain the loss, namely: (1) passage in the draw solution, (2) degradation during the filtration due to the presence of air, and (3) natural degradation in the WW due to filtration time. The TOC present in the final draw solution (COD analysis of the draw solution was not reliable due to the interference of the high salt concentration) accounted for 3.7 ± 0.4% of the initial TOC (80.1 ± 7.0 mg TOC/L) and, therefore, potential loss due to lack of membrane rejection remains very limited. The impact of air (vs. N_2) sparging did not show a significant difference and COD losses were observed in both cases. To investigate if COD loss could be attributed to the WW degradation at 17 °C temperature during the filtration time, 100 mL of WW was left outside the WW tank and COD was monitored at the beginning and the end of each test. Results showed that 12% and 36% of the total and soluble COD present in the WW, respectively, was lost in the storage tank. Considering these losses and calculating the theoretical final concentration with the COD concentrations of the biodegraded samples, the real final WW concentration represented 85.5 ± 5.8% and 88.3 ± 6.6% of the theoretical values for the total and soluble COD, respectively. Thus, it indicates that the main cause of COD loss during filtration is the natural raw WW degradation during the time of filtration. Other (minimal) COD losses might have been due to deposition in the reactor (estimated to be up to 3% by collecting and analyzing leftover WW sludge in the bottom of the reactor) and to foaming. Overall, the final COD concentration of the concentrated WW was close to 1500 mg/L, which is considered the lowest COD concentration limit that is needed to produce enough quantities of methane to heat the WW without an external fuel source, and therefore confirms the use of FO for effective concentration of organic matter. Further improvement of the process can be achieved to improve COD recovery by minimizing dead zones and foaming and reducing the filtration time.

2.2.5 Ion concentrations during filtration batch

Analysis of the ions present in the draw and feed solution before and after the tests were performed, showing high differences in the rejection of cations and anions (Figure 2.9).

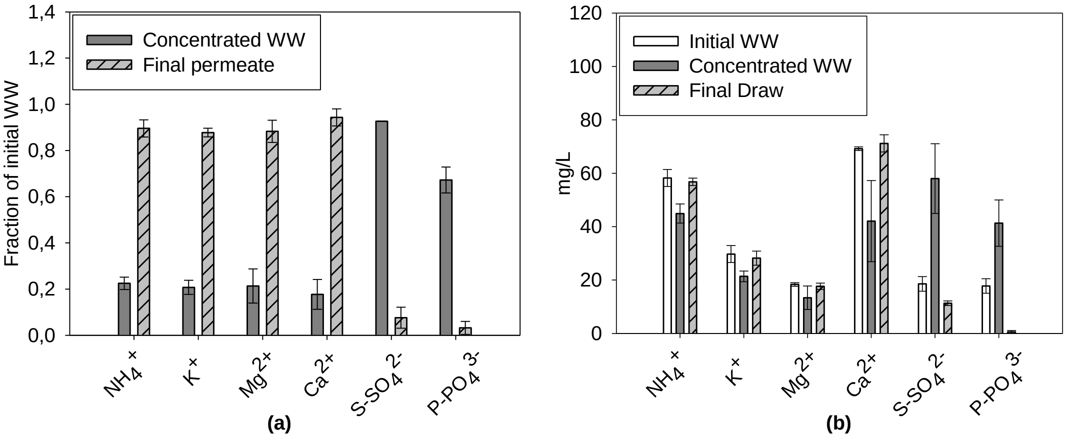


Figure 2.9: *Average ion mass balance with standard deviation at the end of the test with real WW (a). Average ion concentrations with standard deviation of the test with real WW in the original WW concentrated WW and final permeate at the end of test (b).*

The concentration of cations (NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in the WW after each test was lower compared to the original concentration, implying that the retention of cations by the process was negative, with the majority (always more than 80%) ending in the draw solution (Figure 2.9a). The anions (SO_4^{2-} and PO_4^{3-}) followed the opposite trend, with a low fraction passing to the draw solution (always lower than 10%), resulting in a higher concentration, up to 3.3 fold for SO_4^{2-} (same as theoretical CF) and up to 2.6 for PO_4^{3-}, compared to values of the original WW. These results are similar to the results obtained by (Xue et al. 2015). In this article, different membrane materials and orientations were tested to study ion rejection during an FO process. Interestingly, while for Cellulose Triacetate (CTA) membranes high removals were obtained for every ion species studied, in the case of TFC membranes, different results were obtained depending on the orientation (with the active layer facing the feed solution or the draw solution). In the configuration used in our study (active layer facing the feed solution), negative retention was obtained for ammonia rejection, while 90% retention was obtained for phosphate. With the active layer facing the draw solution, the phosphate removal remained the same as for the other configuration, while ammonia rejection increased to 50%. This phenomenon can be explained with two hypotheses, namely: (1) greater ammonium permeability of the TFC membrane compared to the CTA one (one order of magnitude higher); and (2) high negative zeta potential of the TFC membranes, which is at a similar level to that of a cation exchange membrane (cation exchange like mechanism). Other articles with TFC membranes provide the same interpretation (Sauchelli et al. 2018; Geise et al. 2014) but one study (Hu et al. 2017) explains the poor cation retention due to the Donnan equilibrium and the use of sea salt as a draw solute. The high concentration of NaCl in the draw solution and the higher diffusion coefficient of Na^+ compared to Cl^- leads to a higher amount of Na^+ in the feed solution, creating a charge imbalance between the feed and draw solutions. To compensate for this imbalance, more cations diffuse from the feed solution to the draw solution. For further understanding on TFC membrane selectivity, and to confirm whether Donnan equilibrium —in combination with the use of NaCl as a draw solute— is the mechanism which leads to poor cation rejection, future studies are needed to show that electroneutrality is maintained in the final WW solution and the draw solution. The concentrated WW turned out to be more suitable for an anaerobic treatment than before concentration as a result of its higher COD concentration (>1500 mg/L). As a side effect, a high concentration of SO_4^{2-} (Figure 2.9b) was also achieved, resulting in the COD: SO_4^{2-} ratio being slightly lower compared to the original WW (27.5 and 23.3 for raw and concentrated WW, respectively). The NH_4^+ concentration in the concentrated WW was similar to the original WW and remained lower than 200 mg/L, a concentration at which ammonium is considered to be inhibitory for AD (Sung et al. 2003). For the development of FO in combination with AD, future studies should focus on draw solute, such as biodegradable organic solutes, and improvements of FO membrane materials to reduce inhibition of the anaerobic biomass, due to the RSF, and to increase the Jw (Wanying Sun et al. 2018).

2.2.6 PhACs removal

Eighty pharmaceutical compounds were also monitored during the filtration step via FO in the concentrated during an FO batch with air sparging. Figure 2.10 shows the average concentration of the detected antibiotics in the raw WW, concentrated WW, and final DS. Of the 80 compounds analyzed 43 were detected either in the municipal WW, concentrated WW or final DS. 40 were detected in the municipal WW, 40 in the concentrated WW and 24 in the final DS. 31 compounds were concentrated (CF>1) as a result of the FO process while 13 compounds did not concentrate in the concentrated WW because of their high concentration in DS (acetaminophen, salicylic acid, ranitidine) or because their concentration was lower than the limit of detection in both DS and concentrated WW suggesting a process of degradation during the FO process or their attachment in the membrane fouling at the end of the test. It is to be highlighted that some of the PhACs appearing below the detection limit in the municipal WW were found in the DS (i.e. propranolol) or in the concentrated WW (i.e. fluvastatin) or both final DS and concentrated WW (i.e. metoprolol). The highest concentration detected corresponded to acetaminophen (>50000 ng/L) present in the municipal WW and to ibuprofen (71805 ng/L) in the concentrated WW. Figure 2.11 shows the normalized concentration of PhACs in the DS solution. Of the 21 compounds found in the DS solution, only 5 (atenolol, salicylic acid, trimethoprim, ranitidine, levamisole) had a normalized concentration higher than 0.1 even if only salicylic acid and levamisole did not concentrate in the concentrated WW during the FO process. As previously said, acetaminophen concentration was higher than the upper detection limit. The total ng of acetaminophen was 33.7 times higher than the one measured in the concentrated WW meaning that the majority of this compound was not rejected by the membrane probably due to its small dimension (151 Dalton) being the smallest molecule among the 43 compounds detected in this study.

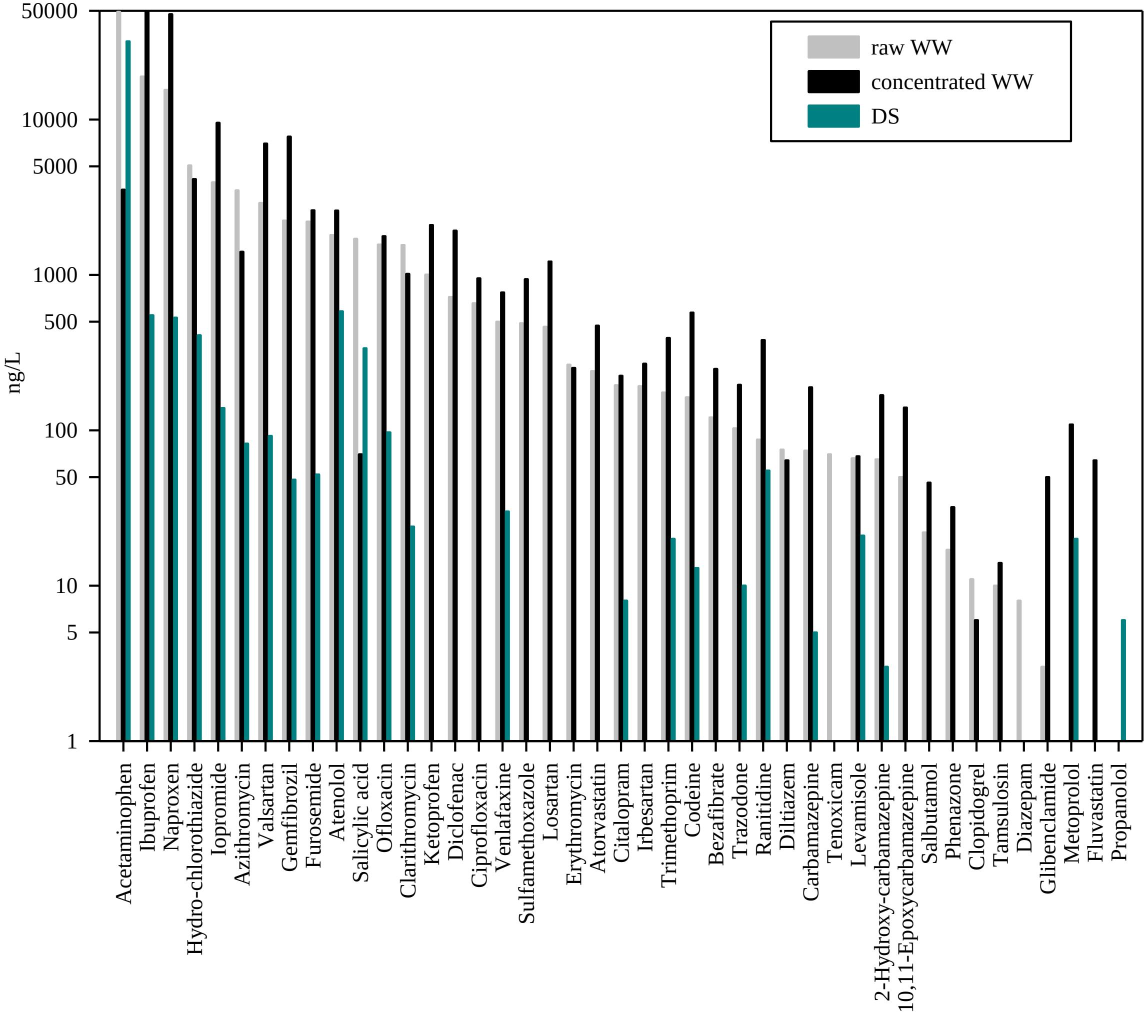


Figure 2.10: *Concentration of PhACs on raw WW, concentrated WW, and final DS.*

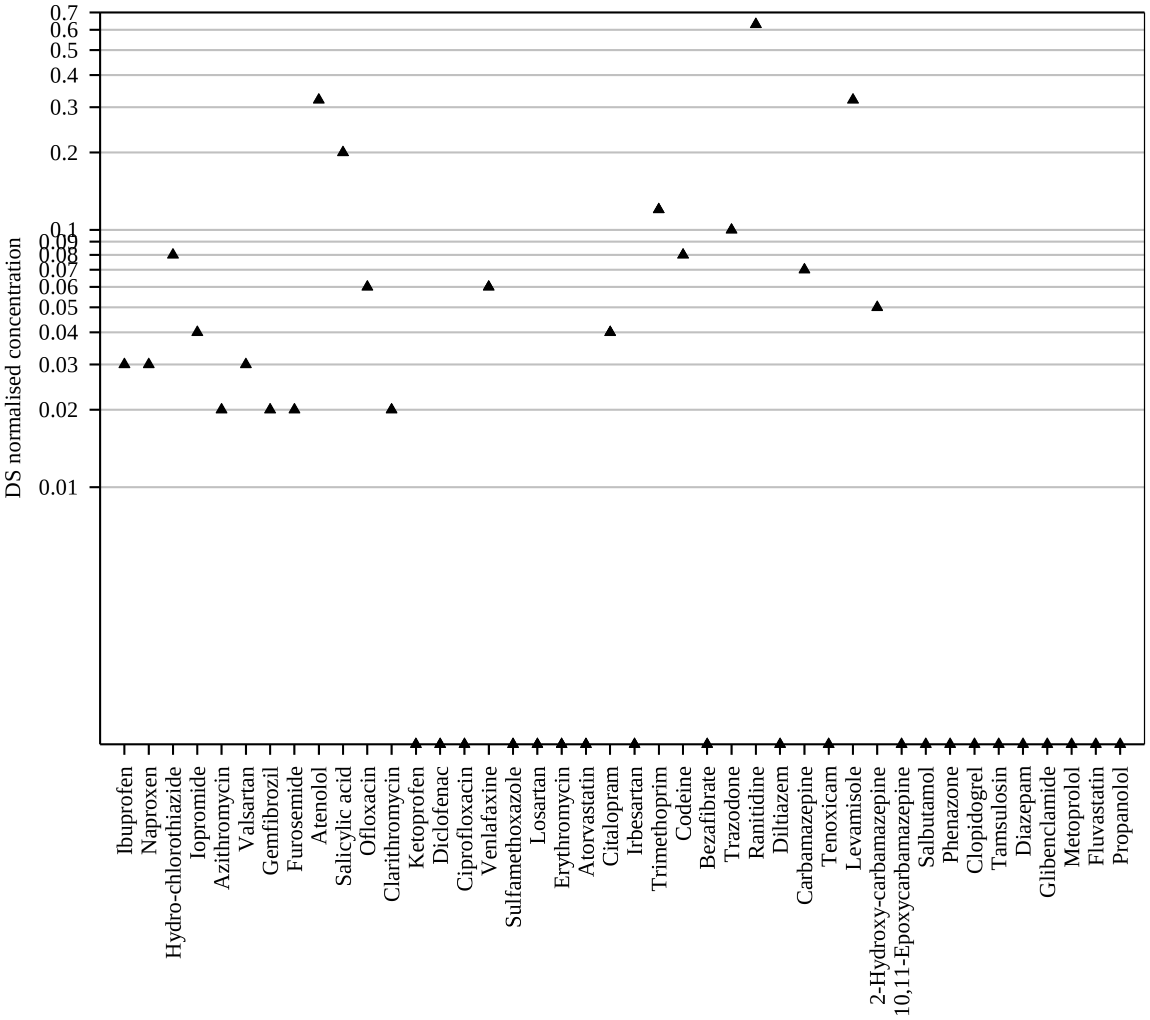


Figure 2.11: *Fraction of PhACs in final DS (ng$_{tot}$ DS /ng$_{tot}$ raw WW)*

In figure 2.12 is presented the mass balance of 15 compounds and their dimension in Dalton. The compounds are ordered from lower charge to higher charge (indicated in brackets following the name of the molecule) of the molecule at the initial pH (7.5). The rejection behavior is related to membrane interfacial properties, physicochemical characteristics of the pharmaceutical molecules (Table 2.1), and feed solution pH (Jin et al. 2012). Correlation between the percentage of these compounds in the final DS and other parameters such as molecule dimension, charge at pH 7.5 and 8.9 (pH of the raw WW and the concentrated WW), biodegradability and distribution coefficient (partition of a chemical compound between the lipid and aqueous phases) was evaluated. Among these, molecule charge provided the highest results. The correlation between the percentage of compounds that ended up in the final DS and the charge of every compound was 0.66 in both cases indicating that membrane selectivity decreases when the compounds are more positively charged. This is in line with results obtained in several studies (Sauchelli et al. 2018; Xie et al. 2013) in which negative charged TFC membranes had a higher rejection of negative charged compounds and was stated that electrostatic interaction is an important rejection mechanism of charged solutes especially for highly charged membrane.

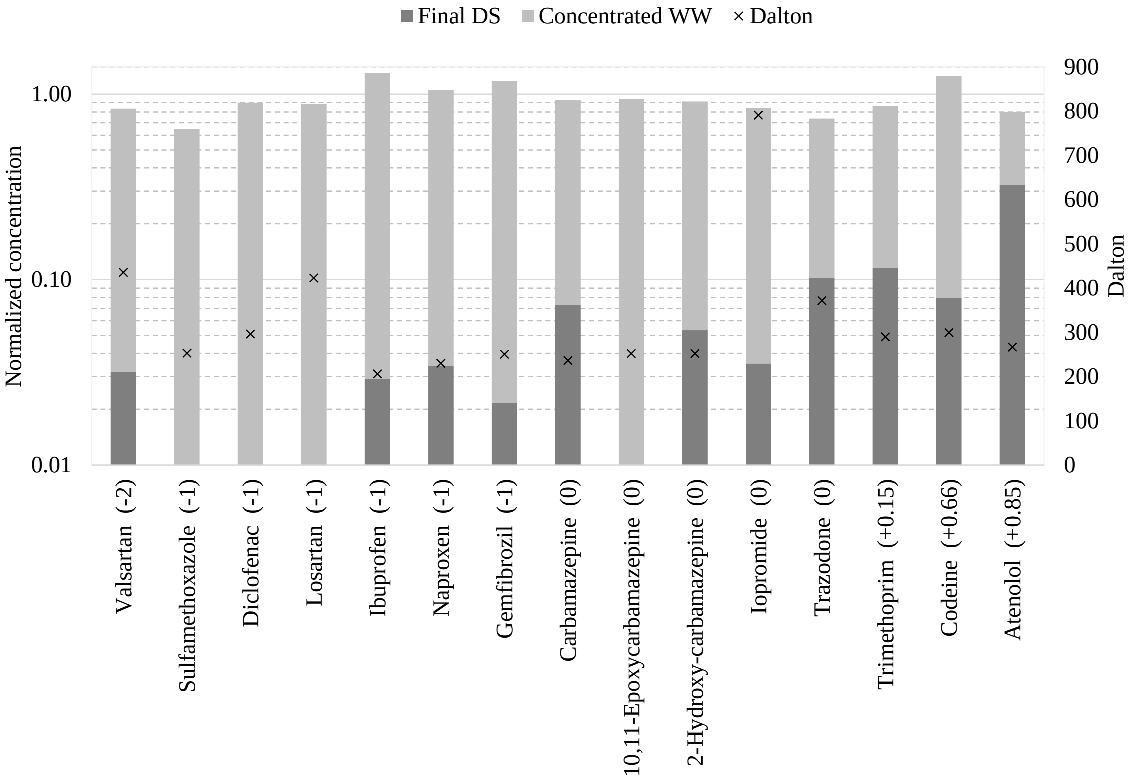


Figure 2.12: *Normalized concentration and molecule dimension (Dalton) and of PhACs with molecule charge at pH 7.5 in concentrated WW and final DS.*

The FO system had a good overall rejection of the PhACs present in the WW. The average removal efficiency was 93.7%. This result was due to the combined effect of membrane rejection and compounds degradation during the process operation. For most of the compounds (70.7%), the FO process resulted in a CF higher than 1 meaning that the membrane was capable to reject them completely or partially. An anaerobic treatment of the concentrated WW could also be used not only to take advantage of the increasing COD concentration but should also be able to further biodegrade the concentrated compounds.

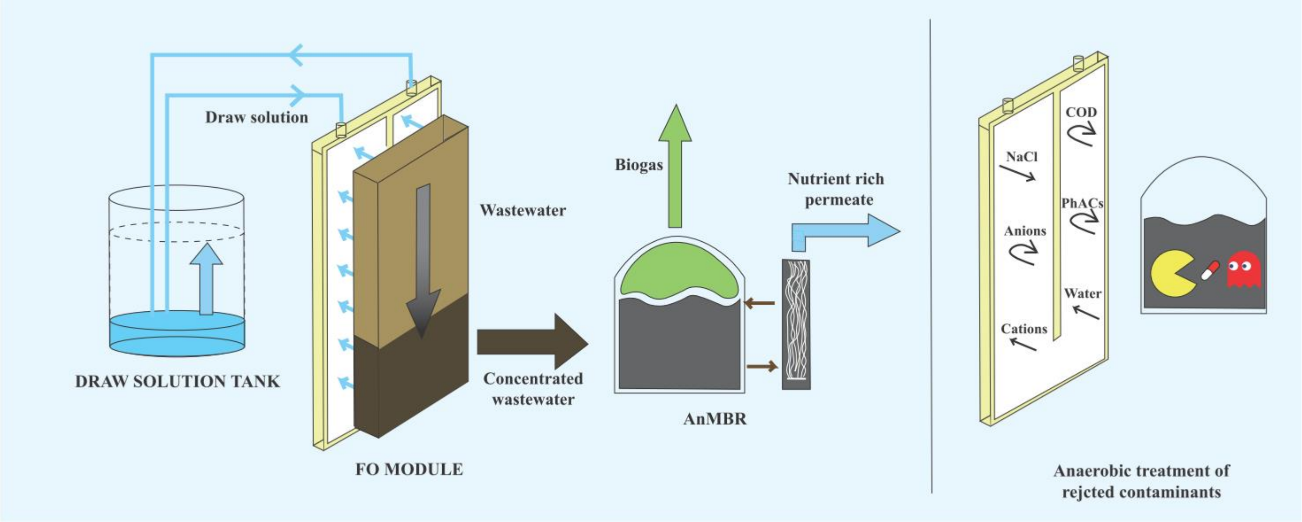
Table 2.1. *PhACs properties. (chemicalize.com)*

PhAC name	Dalton	molecule charge		biodegradability probability	log D	
		pH 7.5	pH 8.9		pH 7.5	pH 8.9
10,11-Epoxycarbamazepine	252	0	0	1		
2-Hydroxy-carbamazepine	252	0	0	1		
Acetaminophen	151	0	-0.21	1	1	1
Atenolol	266	1	0.85	1	-2	-1
Atorvastatin	559	-1	-1	0.89	2	2
Azithromycin	749	-1	-1	0.99	-1	0
Bezafibrate	362	1.95	1.27	0.8	1	1
Carbamazepine	236	-1	-1	0.99	2.77	2.77
Ciprofloxacin	331	0	0		-1	-1
Citalopram	324	0	-0.57	0.99	1	2
Clarithromycin	748	1	0.88	0.67	2	2
Clopidogrel	322	1	0.56		4	4
Codeine	299	1	0.66	1	0	0
Diazepam	259	0.8	-0.57	0.63	3	3
Diclofenac	296	-1	-1	0.99	1	1
Diltiazem	415	0.83	0.16	1	2	2
Erythromycin	734	1	0.56	0.82	1	2
Fluvastatin	267	0	0		1	1
Furosemide	331	-1	-1.1	0.99	-1	-2
Gemfibrozil	250	-1	-1		2	1
Glibenclamide	494	-1	-1	0.99	3	3
Hydro-chlorothiazide	298	-0.03	-0.504	0.97	-1	-1
Ibuprofen	206	-1	-1		1	1
Iopromide	791	0	0		0	0
Irbesartan	429	-0.97	-1	1	4	4
Ketoprofen	254	-1	-1	0.92	0.39	0.18
Levamisole	204	0.23	0	0.67	2	2
Losartan	423	-1	-1		4	4
Metoprolol	267	0.99	0.85	0.97	0	0
Naproxen	230	-1	-1	0.99	0	0
Ofloxacin	361	-0.84	-1	0.51	-1	-1
Phenazone	188	0	0	0.99	1	1
Propanolol	411	0.99	0.85	0.97	0	1
Ranitidine	314	0.66	0		0	1
Salbutamol	239	0.98	0.68	1	-1	-1
Salicylic acid	138	-1	-1		-2	-2
Sulfamethoxazole	253	-1	-1	0.99	0	0
Tamsulosin	409	1	0.57	2	0	1
Tenoxicam	285	0.96	0.56		0.99	0.64
Trazodone	372	0.28	0	1	3	3
Trimethoprim	290	0.82	0.15		1	1
Valsartan	436	-1.97	-2	0.97	1	1
Venlafaxine	277	0.96	0.5	1	1	2

2.2.7 Concluding remarks

The present chapter showed the performance of a pilot scale submerged plate and frame FO module for the treatment of real municipal WW, and its concentration for a subsequent anaerobic treatment. The water fluxes obtained were high and in-line with previous results obtained with a lab scale module. Applying continuous air sparging helped maintain a high water flux and a lower fouling propensity and WW salinity. Compared to the initial WW, the final concentrated WW proved to be more suitable for an anaerobic treatment because of the increase of COD concentration (always higher than 1200 mg/L). This work has also demonstrated that for this sub-FO module, there were neither clogging nor degradation issues, making it more economically reasonable and more attractive for a scale up without the need of WW pre-treatment. The FO system had a good overall rejection of the PhACs present in the WW. The average removal efficiency was 93.7%. This result was due to the combined effect of membrane rejection and compounds degradation during the process operation. For most of the compounds (70.7%), the FO process resulted in a CF higher than 1 meaning that the membrane was capable to reject them completely or partially.

Chapter 3: Exploring the performance of anaerobic treatment for real concentrated raw municipal WW.



This section presents the results obtained when using concentrated municipal wastewater (WW) in an anaerobic treatment process. First, the effect of concentrated WW on the anaerobic process was assessed with biochemical methane potential (BMP) tests. Three different types of municipal WW were tested: i) municipal wastewater (WW0), ii) concentrated WW generated via a FO process with a 50 % water recovery (WW1), and iii) concentrated wastewater via FO process with a 70 % water recovery (WW2). Also, a continuous lab-scale AnMBR was operated with concentrated wastewater via FO with a 70% water recovery at 25ºC.

ARTICLE IN PREPARATION. EMBARGO UNTIL PUBLICATION DATE

General discussion

Anaerobic treatment and operational parameters.

Operational temperature is one of the key factors for controlling the performance of AD. For AD treating primary and secondary sludges a small variation of temperature if not quickly adjusted can lead to system failure. Several studies have tried to operate systems at a lower temperature (low mesophilic and psychrophilic ranges) to reduce the energy demand due to the heating system. This is of main importance when treating streams with a low concentration of COD for achieving a net-neutral or net-positive energy system. In the study by Martin et al. (2011), it is reported that the influent of an AnMBR must be characterized by concentrations higher than 4-5 g/L of COD to achieve enough CH_4 to heat the bioreactor and maintain system temperature at mesophilic range and that net energy recovery from wastewater can only be feasible at low temperatures.

Several studies were conducted with synthetic low strength WW (Smith et al. 2013; Smith 2014) obtaining COD removal efficiencies of 92% at 15ºC even if high percentages of the CH_4 produced were not recovered because dissolved in the permeate. With our AnMBR system, we wanted to investigate if such removals could be obtained even with a concentrated WW coming from a FO process with 80% WR being this characterized by a higher concentration of COD, so increasing the OLR under the same HRT. WW temperature ranges from 8 to 25 ºC in temperate climates (Martin et al. 2011) and from 15 to 29 ºC in Mediterranean regions (Giménez et al. 2014). In this thesis the aim was to address system efficiency with temperature fluctuation that mimicked the Mediterranean temperature range.

Results reported in Chapter 1 showed different removal efficiencies and CH_4 production depending on the operational temperature both decreasing when temperature was decreased. CH_4 production lowered only by ~10% when temperature was lowered from 34 to 23 ºC while the decrease was especially high when the temperature was decreased to 15 ºC. At this temperature, the low stability of the system was evident by the increasing concentration of VFAs, including isobutyric and n-butyric acids, that were found in the permeate. To repristinate the stability the OLR was lowered by almost doubling the HRT. This result suggested that an AnMBR system treating concentrated WW could not be run at psychrophilic temperature (T<17 ºC) without facing real stability issues or by increasing the HRT at levels that would make lose one of the main benefits of the AnMBR technology. Even if the seasonal temperature fluctuation implied a change in the COD removal efficiency and CH_4, lower at lower temperatures, when temperature was increased back to 23 and 34 ºC system quickly recovered to the same performance that it showed before lowering the temperature. This recovery might be attributed to the dominance of mesophilic psychrotolerant methanogens in the system at every temperature. A shift in the predominant archaeal species was observed when the temperature was decreased from 34°C to 23°C. At 34°C, *Methanosaeta* sp. (OTU 8) was the dominant species of the archaeal community with an abundance of 96.8 %. This percentage dropped to 7.9%, 1.1 % and 0.7% at 23, 17 and 15°C, respectively. This species was replaced by *Methanothrix soehngenii* (OTU 3), a mesophilic acetoclastic methanogen that belongs to the genus *Methanothrix*. Its abundance within the archaeal community increased from 2.9% at 34°C to 76.5, 86.5, and 85.4% at 23, 17, and 15°C, respectively. The high removal efficiencies and CH_4 production of the AnMBR at both 34 and 23 ºC with methane production not to low, was the reason behind the decision, for Chapter 3, to run the BMPs test and the continuous AnMBR system at 25 ºC when treating real raw municipal WW and real concentrated WW. Both tests resulted in high COD removal efficiencies which were confirmed by the very low concentration of VFAs found at the end of the test and in the permeate, respectively. The biogas production in the BMPs showed a high difference depending on the substrates. Indeed, the highest specific CH_4 production in the BMPs treating concentrated WW was found at the highest concentrated WW.

FO+AnMBR combination for municipal WW treatment

COD

FO process showed a high rejection of COD. The final concentration found in the concentrated WW was lower than the theoretical concentration factor in most of the tests. This was attributed to the partial degradation of the biodegradable fraction of the COD. Several studies of FO treating synthetic and real WW could not close the COD mass balance and attributed it to a partial loss of the COD that remained attached to the membrane surface in form of fouling (Ansari et al. 2016; Wang et al. 2016). Even if a small amount of the COD could have been retained in the membrane surface, this effect cannot explain the high percentage (25%) of the COD that was not present at the end of the tests in the concentrated WW or the final DS. Analyzing samples of the same WW that was used for these tests after test duration and at the same temperature, it appeared that a fraction of the COD was degraded. Considering this fraction, it was possible to close the COD mass balance. Temperature had an important role in preventing this degradation. In Chapter 3 temperature of the feed tank for the BMPs test was set at 15ºC. This was the lowest temperature tested for the FO process and led to COD CFs that were very similar to theoretical values.

IONS

Ions rejection was one of the main results of this thesis. In every test, independently from the draw solute concentration in the DS, ions were rejected depending on their charge. Our FO system showed a high rejection of anions with over 90% of anions staying in the concentrated WW and the rest 10% passing to the DS. Rejection of cations was very low with final concentrations in the concentrated WW being lower compared to the original WW. A separate discussion has to be made for Na^+ and Cl^-. Since NaCl was the main salt present in the sea salt used as draw solute, their high concentration, and the RSF were the causes of the high amount of these ions to pass from the DS and accumulated in the concentrated WW. These results were due to the combined effect of Donnan equilibrium and the membrane that was used to build the submerged module of this study. The TFC membrane has a highly negatively charged active layer that attracts positively charged compounds and rejects negatively charged compounds. The high amount of Na^+ that passed from the DS to the WW due to the highly concentrated DS solution pushes cations to pass from the feed solution to the DS to achieve the electroneutrality of the system. Even if the same happens with Cl^- and the anions present in the feed, the charged active layer repels the anions not permitting their diffusion to the DS.

The concentrated WW resulted in a higher concentration of SO_4^{2-} that negatively affects the anaerobic digestion due to competition between methanogens and SRB on a common substrate and the production of hydrogen sulfide H_2S which reduces the quality of the biogas. When changing the feed from raw municipal WW to concentrated WW the SO_4^{2-} removal decreased. This decrease could be attributed to the higher NaCl concentration and its inhibitory effect of SRBs. On the other hand, the concentration of NH_4^+ decreases in the concentrated WW reducing inhibitory issues related to high NH_3 concentration on the anaerobic biomass.

PhACs

High rejection of PhACs was obtained by the FO system (>93%). The size and charge of these compounds have an important role in their rejection. Compounds that were more present in the final DS were compounds with lower size (<300Da) and that was more positively charged.
In Chapter 3, the removal of the compounds by AD that were concentrated via an FO process at 70% WR, was studied via the BMP test at 25 ºC. While some compounds were efficiently removed from the liquid phase like antibiotics (100% removal) the removal pathway is still unclear. This could be the adsorption into the solid phase, biodegradation of the compound by the anaerobic biomass or the transformation to other product which were not detected by our systems.

RSF and Salinity

One of the main issues related to the combination of FO with AD both in AnOMBR and in the FO+AnMBR scheme is the increasing concentration of salinity which is an inhibitor for the anaerobic biomass. In our study, the RSF increased with increasing concentration of NaCl in the DS with RSF up to 7.4 and 19.8 g m^{-2} h^{-1} for 11.7 and 35 g/L of sea salt respectively. However, even if a huge difference in RSF resulted in the final concentration of Na^+ and Cl^- in the concentrated WW was of 3.1±0.1 g/L of Na^+ and 4.0±0.1 g/L of Cl^- for both DS. Even if higher RSF were obtained when using a higher concentration of salt for the DS this led also to lower test duration to reach 70%WR. The high similarity of the final concentration of Na^+ and Cl^- in the concentrated WW also suggests that it is proportional to the amount of water that passes through the membrane when the other operational conditions are the same. Also, the ratio Cl^-/Na^+ changed between the initial DS and the final concentrated WW being 1.51 and 1.29, respectively. These results suggest that a higher amount of Na^+ is responsible for the RSF compared to the Cl^- and which is in accordance with the results discussed previously. The salt concentration is probably the main cause of the different lag phases of the BMPs with different substrates. BMPs with the concentrated WW from the FO process with the higher WR (70%) took 15 days to start producing CH_4. This effect was not noticed in the continuous AnMBR of Chapter 3 when the substrate was changed from raw WW to concentrated WW possibly due to the increase of the HRT (from 8 to 24 hours) and/or to the biomass that was already used to the operational temperature. The COD in the permeate and its VFAs content did not increase during the whole experiment duration.

Submerged FO membrane module and Jw

The Jw is an important parameter and one of the limitations for the widespread of FO system. A recent techno-economic analysis of FO-AnMBR (Vinardell et al. 2020) showed that concentrating the WW till reaching 50%WR was the best configuration in terms of operational costs and that achieving Jw of 10 LMH with the FO system would make this process more attractive. This study was based on calculations made with cross-flow module which needs WW pretreatment and higher WW flow rates to avoid clogging and reduce fouling issues respectively. The novel submerged module used in this thesis had no clogging issues without pretreating the WW and air sparging was applied to reduce fouling formation on the membrane surface instead of high WW flow rates. The module used showed also that Jw up to 7.9±0.7 LMH were achievable when a solution of 35 g/L was used as DS. A comparison of cross-flow module and submerged modules has also to be considered in terms of cleaning procedure, durability. Submerged modules must be placed in a tank in contact with the WW. This module anyway gives the possibility of a water rinse at low pressure that is very efficient due to the low fouling propensity of FO module. The integrity of the membrane is also more easily detectable in submerged module compared to cross-flow modules since in the seconds the module must be opened in order to examine the membrane. Also, the high shear force due to the high flow rates needed in cross-flow modules might decrease the durability of this module which is considered the major OPEX contributors in an FO-AnMBR configuration along with energy consumption when WR is equal to 50% (Vinardell et al. 2020). However, the membrane replacement OPEX contribution outweighing the energy consumption when WR is increased from 50 to 80 and 90%.

Conclusions

Results obtained in this thesis demonstrate the feasibility of combining forward osmosis and anaerobic membrane bioreactor technologies for a more sustainable treatment of WW and set up the basis for further investigations at a larger scale.

CHAPTER 1: Anaerobic membrane bioreactor for biogas production from concentrated sewage produced during sewer mining:

- The treatment of concentrated synthetic municipal wastewater with an AnMBR at 1.38±0.25 g COD/day L^{-1} OLR at different operating temperatures (34, 23, 17, 15ºC) was feasible and resulted in high levels of methane production.
- Average COD removal efficiencies were 95, 87, 76 and 67% at 34, 23, 17 and 15°C respectively, obtaining lower biogas production and lower COD removal at lower temperatures.
- Dissolved methane in the permeate averaged 8.2±4.9 mg CH_4/L and did not significantly change with temperature probably due to the high mixing efficiency applied.
- Reactor stability was compromised at 15ºC showed by increasing concentration of VFAs found in the permeate (including isobutyric and N-butyric acids) and increasing values of VFA/TA ratio (over 0.3) but was restored by reducing the OLR.
- After 2 months operating at 15°C, temperature was progressively increased, resulting in an immediate increase of methane production and COD removal efficiencies. Microbial analysis showed important changes in the archaeal community when temperature was changed from 34 to 23°C.
- Microbial analysis showed mesophilic populations dominated in the AnMBR making possible the increase of their activity once temperature was brought back to 23 and 34°C, confirmed by the complete recovery of system performance.

CHAPTER 2: Exploring submerged forward osmosis for water recovery and pre-concentration of wastewater before anaerobic digestion: a pilot-scale study:

- The water fluxes obtained were high and in-line with previous results obtained with a lab-scale module.
- Applying continuous air sparging helped to maintain a high-water flux and a lower fouling propensity and WW salinity.
- Compared to the initial WW, the final concentrated WW proved to be more suitable for an anaerobic treatment because of the increase of COD concentration TCOD CF=2.5 (always higher than 1200 mg/L).
- Ions rejection proved to be dependent from the ion charge with anions rejection being higher than 90% and cations rejection averaging 20%. This result was probably due to the combined effect of the positive charged active layer of TFC membranes and Donnan equilibrium.
- For this sub-FO module, there were neither clogging nor degradation issues, making it more economically reasonable and more attractive for a scale-up without the need for WW pre-treatment.
- Test with tap water demonstrated that OBW had good results for repristinating the Jw especially after test with continuous air sparging where same Jw were obtained.
- When subsequent batch tests with WW were run without flux test with tap water, OBW did not show same degree of restoring capacity resulting in a progressive decrease of the average flux to reach 70% WR.
- The FO system had a good overall rejection of the PhACs present in the WW. The average removal efficiency was 93.7%. This result was due to the combined effect of membrane rejection and compounds degradation during the process operation. For most of the compounds (70.7%), the FO process resulted in a CF higher than 1 meaning that the membrane was capable to reject them completely or partially.
- Molecule charge seemed to affect molecule rejection with the most positively charged molecule having higher normalized concentrations in the DS.

CHAPTER 3: Exploring the performance of anaerobic treatment for real concentrated raw municipal WW:

- BMPs with concentrated WW (WW1 and WW2) through FO proved to have higher methane production compared to BMPs with municipal WW.
- BMPs with concentrated WW produced with higher WR (WW2) resulted in the highest cumulative methane production, higher SMP but longer lag phase due to the inhibitory effect of the salt concentration in the feed solution.
- PhACS measurement showed that after AD, high removal efficiencies from the liquid phase were obtained for several compounds especially for the 6 species of antibiotics (100% removal).
- The submerged FO system was able to achieve 70% WR in 15 consecutive tests without any cleaning procedure between one test and the following.
- The average Jw of the first test was 7.9±0.7 LMH while being 4.3±1.2 LMH in the last test. This led to different test duration 12.3 and 23 hours for test 1 and test15 respectively.
- The final Na^+ and Cl^- concentration was the same for FO process with 11.7 g/L and 35.0 g/L of sea salt as DS demonstrating that the solute passage from the DS to the feed solution does not depend on the concentration of solute in the DS.
- Continuous AnMBR showed similar COD removal efficiency when treating municipal WW (12, 8 hours HRT) and concentrated WW (24, 12 hours HRT) with no inhibition by the salt concentration in the feed.
- Low concentrations of VFAs in the permeate were found (acetic acid was the only present along the test) when treating municipal WW and concentrated WW at the two studied HRTs.
- AnMBR permeate was characterized by lower concentration of N and higher concentration of P compared to the municipal WW. However, the high salinity makes it not suitable for direct irrigation.
- Higher COD removal was achieved when the AnMBR feed had higher COD concentrations probably due to the higher ratio of biodegradable COD independently from treating municipal WW or concentrated WW.

Future perspective

This thesis has been mainly focused on having a clearer understanding of the potential of combining FO with AnMBR technologies for municipal WW concentration and anaerobic treatment. In previous studies, this combination was tested only with BMPs with synthetic WW leaving many research questions that had to be addressed. The first part of the thesis studied the two technologies individually with a lab-scale AnMBR treating synthetic concentrated WW with seasonal variation in the operational temperature and with a novel submerged pilot-scale TFC membrane for the concentration of raw WW.

The last part of the thesis reported the direct anaerobic treatment of municipal WW with the combination of the two technologies above mentioned.

Overall, the outcomes of this PhD thesis provide new knowledge and better understanding of the direct treatment of WW via FO combined with AnMBR technologies but more research is still needed to tackle remaining questions and implement robust and reliable operational parameters at a larger scale.

AnMBR treating concentrated WW via FO

Dissolved CH_4 is considered one of the potential limitations for the widespread of AnMBR systems treating low strength WW. In this thesis, mixing efficiency has proven to be an important parameter that should be optimized because of its potential to lower the CH_4 that is present in dissolved form. Further studies should be carried out to compare the energy efficiencies of the system with improved mixing efficiencies and system with lower mixing efficiencies but with membrane contactors on the permeate line for dissolved CH_4 recovery. Also, the dissolved CH_4 in the permeate of the FO-AnMBR system should be compared to the use of AnMBR. In the case of equal concentration of dissolved CH_4 in the permeate the FO- AnMBR system would have the benefits of a greater percentage of the produced CH_4 that ends up in biogas (due to the higher overall produced biogas per treated volume) decreasing the amount of CH_4 lost via permeate per volume of raw WW in dissolved form because of the lower volume of water that is treated thanks to the FO system.

The efficiency of the AnMBR system relies on the capacity of the membrane module to maintain high Jw with at low applied pressure. To be able to fully comprehend the potential of the FO-AnMBR system, a comparison of the fouling propensity of membranes treating concentrated WW and raw WW should be addressed.

Further studies are needed at pilot scale. While the FO system used in this study operated in batch mode, in a continuous mode, membranes would be continuously in contact with a partial concentrated streams which might have the benefits of decreasing the COD degradation during the process but also decrease the average water flux due to the continuous presence of higher salinity in the WW and to the higher fouling issues due to the lower dilution of the fouling compounds in the WW.

The novel module used in this thesis might reduce the energy consumption of FO modules due to the only use of gas sparging on the membrane instead of the combination of prefiltration and high flow rates to prevent fouling and clogging issues. A new economical comparison of AnMBR treating municipal WW with FO-AnMBR-RO system should be studied. Gas sparging results in high energy expenditure that should be reduced. On the other hand, biogas is a methane rich product that needs an expensive upgrading process to remove CO_2, H_2O H_2S, NH_3, particle and siloxanes before converting it into energy. New more efficient and less expensive treatments are based on the absorption-adsorption of these impurities when gas is passed through a pressurized WW volume (De Godos et al. 2015). The combination of FO technology with this biogas upgrading technology would convert our system in a pressure enhanced osmosis configuration taking advantage of both the pressure used by the upgrading system for increasing the Jw and the biogas recirculation for gas sparging purpose and further decreasing the overall energy requirement of the FO-AnMBR system.

The FO system due to the negatively charged TFC showed different rejections of ions depending on their charge with cations being poorly rejected. This characteristic of the process combined with its capability of treating WW with complex matrix opens new possibilities to solve other problems related to cations concentration and anaerobic digestion such as manure treatment. NH_4^+ concentration in manure represents an important issue in the anaerobic digestion of these streams since NH_4^+ was found to be inhibitory already at concentrations higher than 200 mg/L (Gao et al. 2019). The FO system would increase de COD/NH_4^+ ratio improving the anaerobic digestion of the concentrated streams.

Anaerobic treatment of municipal WW showed that high removal of some PhACs is possible. However, the elimination pathway is still not clear with several alternatives being possible like adsorption into the solid phase which could mean that for longer operation after an initial accumulation, PhACs could be released back into the liquid phase or be present in the anaerobic sludge without being biodegraded compromising the use of the produced sludge and permeate as amendment and irrigation respectively. Also, further studies need to investigate potential transformation products which can affect the removal efficiencies since many molecules once transformed into another product are difficult to identify.

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