Treating anaerobic effluents using forward osmosis for combined water purification and biogas production

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Published in:
Science of the Total Environment

Link to article, DOI:
10.1016/j.scitotenv.2018.08.036

Publication date:
2019

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Treating anaerobic effluents using forward osmosis for combined water purification and biogas production

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Editor: Zhen (Jason) He

Abstract

Forward osmosis (FO) can be used to reclaim nutrients and high-quality water from wastewater streams. This could potentially contribute towards relieving global water scarcity. Here we investigated the feasibility of extracting water from four real and four synthetic anaerobically digested effluents, using FO membranes. The goal of this study was to 1) evaluate FO membrane performance in terms of water flux and nutrient rejection 2) examine the methane yield that can be achieved and 3) analyse FO membrane fouling. Out of the four tested real anaerobically digested effluents, swine manure and potato starch wastewater achieved the highest combined average FO water flux (>3 liter per square meter per hour (LMH) with 0.66 M MgCl2 as initial draw solution concentration) and methane yield (>300 ml CH4 per gram of organic waste expressed as volatile solids (VS)).

Rejection of total ammonia nitrogen (TAN), total Kjeldahl nitrogen (TKN) and total phosphorous (TP) was high (up to 96.95%, 95.87% and 99.83%, respectively), resulting in low nutrient concentrations in the recovered water. Membrane autopsy revealed presence of organic and biological fouling on the FO membrane. However, no direct correlation between feed properties and methane yield and fouling potential was found, indicating that there is no inherent trade-off between high water flux and high methane production.

Keywords: Water reclamation; Biogas production; Fouling; Anaerobic digestion; Wastewater treatment

1.1 Introduction

Access to safe and clean drinking water as well as sustainable energy is a basic human necessity, contributing to human health, poverty reduction and environmental sustainability (Luo et al., 2016; WWAP, 2015).

Despite intense efforts in recent years to increase water supply, sanitation and hygiene for people in water-stressed areas, 663 million people still remain without access to drinking water sources and the population growth outpaces the progress made (WWAP, 2015). Water scarcity is not limited to developing and third world countries, but affects industrialized nations as well. This makes it one of the major challenges of this century and raises the need to develop new sources of water (Shannon et al., 2008).

In addition, the quest to provide sustainable energy sources to satisfy a rapidly increasing global energy consumption while alleviating climate change has yet to be solved (McGinnis and Elimelech, 2008).

One possible solution is the combined reclamation of water and energy from municipal or industrial wastewater sources (Shannon et al., 2008). In recent years, the perception of wastewater has changed. It is no longer considered as waste, but a resource of nutrients (N, P and K), water and energy in form of biogas (Ansari et al., 2017; Lutchmiah et al., 2011).

Biogas can be produced via anaerobic digestion (AD), which converts complex organic matter mainly to methane and carbon dioxide. AD is widely used for the treatment of wastewater because it generates less sludge than
conventional aerobic processes and is also more cost-efficient, since aeration is not required and energy can be partly recovered by utilizing the produced biogas (Ansari et al., 2017). In recent years anaerobic membrane bioreactors (AnMBR) that combine biogas production with low-energy wastewater treatment using porous microfiltration (MF) or ultrafiltration membranes (UF) have raised increasing interest. The advantages of using AnMBR systems include improved effluent quality, lower sludge production and improved biogas yields by increasing the retention time of anaerobic microorganisms in the bioreactor (Gu et al., 2015; Wang et al., 2017).

However, conventional AnMBRs face some challenges that are rooted in their reliance on pressure-driven membrane processes and porous membranes (Stuckey, 2012). Less readily biodegradable soluble organics, dissolved solids (Lay et al., 2010) and trace organic pollutants, such as pharmaceuticals and endocrine disrupting compounds (EDC) (Clara et al., 2005) are washed out through the pores of MF and UF membranes, lowering the effluent quality and negatively affecting the biogas yield (Gu et al., 2015). Further on, fouling results in rapid flux decline and reduces the overall performance (X. Wang et al., 2016). These problems could potentially be solved by replacing MF/UF membranes with tight forward osmosis (FO) membranes.

In FO, a draw solution (DS) is used to induce a net flow of water through a semipermeable membrane into the DS from a feed solution (FS). The flow is driven by the transmembrane osmotic pressure gradient \( \Delta \pi \) between the DS and FS and will occur as long as \( \pi_{DS} > \pi_{FS} \). The \( \pi_{DS} \) arises from the DS osmolyte where seawater, by-products from industrial processes, and inorganic salts (e.g. NaCl, MgCl\(_2\)) all have been evaluated in previous studies. This emerging membrane technology can be used to extract water from wastewater streams while efficiently retaining organic matter and microorganisms (York et al., 1999). FO membrane systems are able to treat complex wastewater streams of varying composition (Lutchmiah et al., 2014), such as landfill leachate (York et al., 1999), municipal wastewater (Hey et al., 2017; Z. Wang et al., 2016), or wastewater from oil and gas separations (Hey et al., 2017). The diluted DS from FO can be re-concentrated by reverse osmosis (RO) (Holloway et al., 2007) or membrane distillation (MD) (Liu et al., 2016), while simultaneously producing high quality water.

Taking all of these considerations together, the integration of FO membranes into an osmotic anaerobic membrane bioreactor (FO-AnMBR) can be seen as a promising technology for wastewater treatment, water reclamation and simultaneous biogas production (Chen et al., 2014; Gu et al., 2015; Li et al., 2017; Tang and Ng, 2014). However, this concept has to our knowledge so far not been tested for high-strength wastewater sources, such as agricultural wastewater and cattle manure.

In this study the membrane performance of a novel biomimetic FO flat sheet membrane is evaluated for the treatment of AD effluents. Eight types of effluents were selected: potato starch wastewater, swine manure and two types of cattle manure (thermophilic and mesophilic), as well as four effluents based on basal anaerobic medium (BA): synthetic sugars, synthetic lipids, synthetic proteins and synthetic mixture. The synthetic effluents were chosen in addition to the real effluents due to their known composition. This should help to find possible correlations between the effluent composition, biogas potential and fouling propensity.

The objective of the present study is to answer the following questions:

1) What is the FO membrane performance of the selected AD effluents, with regards to water flux and nutrient rejection?
2) What is the methane yield achieved by these wastewaters during AD? This aspect is especially important with respects to reduction of operational expenditure.
3) What is the extent and the nature of the fouling and how does the composition of the AD effluents affect the membrane fouling?

Taken together, the results from this study can be used towards the development of an integrated FO-AnMBR-MD/RO process, and will help to improve understanding regarding which types of wastewater can be treated successfully, providing a compromise between high biogas production, good FO-based water extraction and low fouling potential. The scope of the article is depicted in Figure 1.
2. Material and methods

2.1. FO membrane

The thin film composite (TFC) flat sheet FO membranes used herein are Aquaporin Inside™ membranes provided by Aquaporin A/S, Denmark. They are composed of a polyethersulfone (PES) support layer and a polyamide active (PA) layer with incorporated Aquaporin proteins reconstituted in spherical polymer vesicles. (Habel et al., 2015; Zhao et al., 2012). Membrane thickness is 110 μm (+/-15 μm). The isoelectric point lies at approximately pH 2.9 and the zeta potential is between -80 mV and -90 mV at pH 7 (Singh et al., 2018).

2.2. Anaerobic digestion effluents

Effluents were collected from eight lab-scale bioreactors at steady state conditions and frozen immediately at -20 °C until used. The total amount of effluents collected, as well as additional information about the bioreactors, can be found in the Supplementary data. The anaerobic reactors were fed with four types of real wastewater (potato starch wastewater, swine manure, cattle manure from a thermophilic reactor and cattle manure from a mesophilic reactor) and four types of synthetic wastewater, based on BA medium (Angelidaki et al., 1990) supplemented with sugars (glucose), proteins (casein), lipids (glycerol triolride, GTO) and a mixture of the aforementioned. To ensure that the collection of effluents was taken from a process operated at steady state conditions, the biogas production of bioreactors was measured daily via a water-displacement gas meter (Kougias et al., 2013) and other biochemical parameters (i.e., pH, volatile fatty acids (VFA), CH₄ content in the biogas (Tsapekos et al., 2017)) were monitored at least twice a week. The methane yield per gram volatile solids (VS) [mL CH₄/g VS] was daily calculated taking into consideration the biogas production [mL], the organic loading rate (OLR) [g VS/L] and CH₄ content [%] in the biogas:

\[
\text{methane yield} = \frac{\text{biogas production} \times \text{CH}_4\text{content}}{\text{OLR} \times V_L}
\]

where \(V_L\) is the reactor volume.

Further information about the bioreactors can be found in the Supplementary data and in previously published studies (Bassani et al., 2016; Mahdy et al., 2017; Tsapekos et al., 2017).

Prior to use, the effluents were unfrosted and sieved in three steps, using sieves with a mesh size of 1 mm, 250 μm and 125 μm. The characteristics of the effluents are given in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Effluent characteristics.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Real effluents</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
</tbody>
</table>

Figure 1 Scope, process outcome and analyses in this study. Effluents from anaerobic digestion (AD) reactors were treated using forward osmosis (FO). The FO membrane performance of the effluents and the methane yield during anaerobic digestion were evaluated. Furthermore, fouled membranes were analysed to gain insight into fouling properties.

alt-text: Fig. 1
<table>
<thead>
<tr>
<th></th>
<th>Swine manure wastewater</th>
<th>Cattle manure, thermophilic</th>
<th>Cattle manure, mesophilic</th>
<th>BA medium + GTO</th>
<th>BA medium + glucose</th>
<th>BA medium + mixture</th>
<th>BA medium + casein</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC [g/L]</td>
<td>1.51±0.01</td>
<td>1.37±0.12</td>
<td>4.55±0.00</td>
<td>7.11±0.05</td>
<td>1.95±0.15</td>
<td>1.42±0.15</td>
<td>1.18±0.01</td>
</tr>
<tr>
<td>TS [g/L]</td>
<td>7.73±0.00</td>
<td>8.68±0.35</td>
<td>6.51±3.18</td>
<td>8.27±0.26</td>
<td>7.06±0.02</td>
<td>18.55±0.04</td>
<td>6.72±0.30</td>
</tr>
<tr>
<td>VS [g/L]</td>
<td>3.21±0.33</td>
<td>1.82±1.57</td>
<td>4.26±2.84</td>
<td>3.7±0.25</td>
<td>3.53±1.83</td>
<td>10.91±0.99</td>
<td>4.15±2.92</td>
</tr>
<tr>
<td>TSS [g/L]</td>
<td>11.92±0.33</td>
<td>13.70±1.57</td>
<td>23.17±2.84</td>
<td>23.02±0.25</td>
<td>21.03±1.83</td>
<td>14.12±0.99</td>
<td>19.35±2.92</td>
</tr>
<tr>
<td>TKN [g/L]</td>
<td>1.68±0.01</td>
<td>1.19±0.09</td>
<td>3.34±0.00</td>
<td>2.20±0.00</td>
<td>5.97±0.01</td>
<td>4.84±0.01</td>
<td>3.80±0.00</td>
</tr>
<tr>
<td>TAN [g/L]</td>
<td>2.08±0.00</td>
<td>0.91±0.06</td>
<td>3.41±0.00</td>
<td>1.66±0.00</td>
<td>5.80±0.00</td>
<td>4.46±0.01</td>
<td>3.24±0.00</td>
</tr>
<tr>
<td>Ortho-P [g/L]</td>
<td>0.12±0.00</td>
<td>0.19±0.06</td>
<td>0.31±0.00</td>
<td>0.28±0.01</td>
<td>0.59±0.00</td>
<td>0.67±0.00</td>
<td>0.57±0.00</td>
</tr>
<tr>
<td>Density [kg/L]</td>
<td>1.00±0.00</td>
<td>1.00±0.00</td>
<td>1.02±0.00</td>
<td>1.01±0.00</td>
<td>1.00±0.00</td>
<td>1.00±0.00</td>
<td>1.00±0.00</td>
</tr>
<tr>
<td>Dynamic viscosity μ [mPa·s]</td>
<td>1.35±0.00</td>
<td>1.15±0.00</td>
<td>2.00±0.00</td>
<td>1.39±0.00</td>
<td>1.44±0.00</td>
<td>1.24±0.00</td>
<td>1.45±0.00</td>
</tr>
<tr>
<td>Kinematic viscosity [mm²/s]</td>
<td>1.35±0.00</td>
<td>1.15±0.00</td>
<td>2.00±0.00</td>
<td>1.37±0.02</td>
<td>1.44±0.00</td>
<td>1.23±0.02</td>
<td>1.43±0.00</td>
</tr>
</tbody>
</table>

*Viscosity could not be measured due to high TS content.

### 2.3.2 Forward osmosis experimental setup

All FO experiments were conducted in a lab-scale FO cross-flow setup with the active layer facing the feed solution (AL-FS). The membranes were pre-soaked in MilliQ water for 45 min before each FO experiment.

A schematic representation of the setup can be found in the Supplementary material.

The flat sheet module was manufactured by Mikrolab Aarhus A/S (Denmark) and consisted of two symmetrical flow chambers with the dimensions 175 mm (length), 80 mm (width) and 1.3 mm (height) and an effective membrane area of 140 cm².

Feed and draw solution were recirculated by gearing pumps ( Longer Precision Pump Co., Ltd, China) at 500 mL/min, corresponding to a crossflow velocity of 8 cm/s. A draw-side mesh spacer was used to facilitate stirring close to the membrane surface.

As a feed solution, 2 L of anaerobic digestion effluents were used. The pH was adjusted to 6.7 with H₂SO₄ (6 M) to improve total ammonia nitrogen (TAN) retention by reducing the fraction of TAN present as NH₃ (Camilleri-Rumbau et al., 2015). For the draw solution, 4 L of 0.66 M MgCl₂ (analytical grade, Sigma-Aldrich, USA), was prepared by dissolving the salt in MilliQ water.

The concentration of the draw solute was chosen using the van't Hoff equation for dilute and ideal solutions in order to yield a theoretical osmotic pressure of 49 bar.

The feed solution bottle was placed on a balance (Kern, Germany) and the draw solution was mixed continuously to avoid the formation of a concentration gradient inside the draw solution bottle due to returning the diluted draw solution.

The water flux $J_w$ [Lm⁻²h⁻¹] was determined by recording the weight decrease of the feed solution, based on

$$J_w = \frac{(m_0 - m_t)}{A_m \Delta t}$$

(2)

where $A_m$ is the membrane surface in m², $\rho$ the density of the feed [kg m⁻³] and $m$ the mass of the feed solution [kg] recorded at the times $t_1$ and $t_2$ (Bowden et al., 2012). Weight data was logged automatically every 5 minutes throughout the entire duration of the experiments.

The concentration of the draw solution was not kept constant, meaning it decreased over time due to the water transport from feed to draw solution.

The reverse salt flux $J_r$ was calculated using

$$J_r = \frac{(m_{0, draw} - m_{t, draw})}{A_M \Delta t}$$
\[ J_{c,ct} / J_{M} = \frac{(V_{0} \beta_{2} - V_{f} \beta_{1})}{At} \]  

With \( \beta_{1} \) and \( \beta_{2} \) as the respective Mg\(^{2+}\) and Cl\(^{-}\) concentrations in the feed solution [mol/L] and \( V_{0} \) and \( V_{f} \) as the volume of the feed solution [L] at \( t_1 \) (beginning of the experiment) and \( t_2 \) (end of the experiment).

Nutrient rejection is calculated based on the feed side mass balance as

\[ R = \left( \frac{V_{0} C_{t} - V_{f} C_{t}}{V_{f} t} \right) 	imes 100\% \]

With \( c_{t} \) and \( c_{t0} \) as the respective TAN, TN and TP\(^{-}\) concentrations in the feed solution [mol/L] at \( t_1 \) (beginning of the experiment) and \( t_2 \) (end of the experiment)]

The duration of the experiments was 24 h to allow formation of a fouling layer.

### 2.4.2.4 Analytical methods

The AD effluents and the draw solution were analysed at the beginning and at the end of each FO experiment, namely: Total solids (TS), volatile solids (VS) and total suspended solids (TSS) were determined according to the APHA standard methods (2005). Total Kjeldahl Nitrogen (TKN) and total ammonia nitrogen (TAN) were analysed using a Kjeldahl distillation unit (FOSS, Denmark). Total organic carbon (TOC) was determined with a TOC analyser (LECO, USA). Orthophosphate-P and Cl\(^{-}\) concentrations in the feed were analysed using ion chromatography (IC) (Thermo Fisher Scientific, USA). Mg\(^{2+}\) concentrations in the feed were analysed with, inductively coupled plasma optical emission spectrometry (ICP-OES).

Viscosity and density of the samples was measured using a viscosity meter (Anton Paar, Austria).

### 2.5.2.5 Membrane autopsy for analysis of the fouled membrane

Membrane autopsy methods include scanning electron microscopy (SEM) to determine the overall morphology of the fouling layer, energy-dispersive X-ray spectroscopy (SEM-EDS) to analyse the elemental composition of the fouling layer, Fourier-transform infrared spectroscopy (FTIR) to identify organic foulants, Ion chromatography (IC) for the determination anionic foulants, Inductively coupled plasma optical emission spectrometry (ICP-OES) for the determination cationic foulants and Adenosine Triphosphate (ATP) analysis to analyse biological fouling.

Before SEM and SEM-EDS (FEI, USA), fouled membrane coupons were soaked in 2.5% glutaraldehyde for 1 h (Sigma-Aldrich, USA) to fixate bacteria on the membrane surface, followed by dehydration in an ethanol dilution series (50% (v/v), 60% (v/v), 70% (v/v), 80% (v/v), 100% (v/v)) by immersion in for 5 min each. The samples were kept at 4 °C until analysis. Both fouled and virgin membrane coupons were sputter coated with gold (Morrow et al., 2017).

SEM samples were analysed at a 10 mm working distance, at an acceleration voltage of 10.0 kV and a spot size of 3.0.

For FTIR, fouled and virgin membrane coupons were analysed in an attenuated total reflectance (ATR-FTIR) spectrometer (PerkinElmer, USA), equipped with a diamond crystal. Four scans per measurement point were collected.

To determine the inorganic components on the fouling layer, the foulants were extracted from a membrane coupon of the size 3.5 cm \( \times \) 3.5 cm. The fouled membrane coupons were immersed in MilliQ water (for IC) or 0.8 M HNO\(_3\) (for ICP-OES) for 24 h followed by ultrasonification for 180 min. The extracts were kept at 4 °C until analysis. An ICP-OES scan included Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Si, Sr and Zn and was carried out using a Vista MPX spectrometer (Varian, USA). IC analysis included chloride, bromide, nitrate and sulfate was analysed on a Thermoscientific Dionex AS-AP (Thermo Fisher Scientific, USA).

Prior to ATP analysis, the biomass was extracted from membrane coupons of the size 5 cm \( \times \) 5 cm defined size by immersing them in MilliQ water, followed by ultrasonification for 5 min in order to keep the microbial cells intact. The samples were kept at \( 80\) °C until analysis. To determine the ATP concentration, a luciferase assay was used, following the procedure described by Vang et al. (2014). In short, to determine the total ATP, the samples were lysed before adding luciferase. For free ATP, no cell lysis was conducted and luciferase was added directly. Microbial ATP was calculated as the difference between free ATP concentrations and total ATP concentrations. Bioluminescence was measured in a luminometer (Charles River, USA) and microbial ATP was determined indirectly by subtracting free (extracellular) ATP from total ATP.

### 3.3 Results and Discussion

#### 3.3.1 FO performance and methane yield of AD effluents

\( J_{c} \) for all tested AD effluents is displayed in Fig. 2. Since the draw solution concentration was diluted over time, data is displayed as a function of feed recovery. This way, it is possible to compare flux decline at a given level of draw solution dilution (Blandin et al., 2016) The duration of the experiments was 24 h each.
The initial $J_w$ ranges from $4.3 \pm 4.8$ LMH for the real effluents and from $4.3 \pm 5.1$ LMH for the synthetic effluents. Even though the initial $J_w$ for all effluents was within a comparable range, decline over time differs substantially. While potato starch wastewater and swine manure reached 30% feed recovery within 12 h, thermophilic cattle manure and mesophilic cattle manure required 16 h and 21 h, respectively. As the impact of the draw solution dilution is the same at this point, the differences can be attributed to fouling and ICP effects (Blandin et al., 2016). Further on, differences in reverse salt flux of draw solution ions, reducing the osmotic pressure difference over the membrane, could influence the results as well. However, there seems to be no direct correlation between flux decline and $J_{w,ave}$ or $J_{w,av}$. 

As can be seen in Table 2, $J_{w,av}$ exceeds $J_{w,ave}$ substantially. This is in agreement with previous studies, that found that is mainly governed by the anion transport rather than the paired cations (Achilli et al., 2010; Coday et al., 2013).

### Table 2 FO performance. $J_{w,GTO}$ was calculated as a mean value of $J_w$ during the entire duration of the experiment. Flux decline is calculated over 24 h.

<table>
<thead>
<tr>
<th>Effluent Type</th>
<th>Real Effluents</th>
<th>Synthetic Effluents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_{w,ave}$ [L/(m²·h)]</td>
<td>$J_{w,ave}$ [L/(m²·h)]</td>
</tr>
<tr>
<td>Swine manure</td>
<td>3.3 ± 0.10</td>
<td>2.9 ± 0.38</td>
</tr>
<tr>
<td>Potato starch wastewater</td>
<td>3.0 ± 0.22</td>
<td>2.9 ± 0.15</td>
</tr>
<tr>
<td>Cattle manure, thermophilic</td>
<td>2.4 ± 0.01</td>
<td>2.4 ± 0.63</td>
</tr>
<tr>
<td>Cattle manure, mesophilic</td>
<td>1.9 ± 0.17</td>
<td>2.9 ± 0.10</td>
</tr>
<tr>
<td>BA medium + GTO</td>
<td>3.1 ± 0.07</td>
<td>2.9 ± 0.15</td>
</tr>
<tr>
<td>BA medium + glucose</td>
<td>66.12 ± 4.03</td>
<td>71.03 ± 0.94</td>
</tr>
<tr>
<td>BA medium + mixture</td>
<td>56.09 ± 5.53</td>
<td>74.88 ± 19.81</td>
</tr>
<tr>
<td>BA medium + casein</td>
<td>59.92 ± 10.50</td>
<td>76.16 ± 4.85</td>
</tr>
</tbody>
</table>

The differences in FO performance are listed in Table 2 and compared with effluent properties, such TOC, TS and dynamic viscosity (see Table 1). An increase in viscosity of the feed solution can lead to decreased water diffusivity over the membrane and thus decreased $J_w$ (McCutcheon and Elimelech, 2006; Phuntsho et al., 2012).

Flux decline can also be caused by the formation of an organic fouling layer on the membrane, leading to increased hydraulic resistance (Lee et al., 2010; Parida and Ng, 2013). Organic foulants are often measured as TOC, therefore the organic matter content of each tested effluents was assessed.

In these experiments, $J_{w,ave}$ of the real effluent, except for potato starch wastewater, generally declined with increasing dynamic viscosity and TOC content. The synthetic effluents, on the other hand, showed the opposite trend. The highest average $J_w$ of 3.3 LMH was achieved for swine manure, which has a dynamic viscosity of 1.35 mPa·s, closely followed by potato starch wastewater with an average $J_w$ of 3.0 and a dynamic viscosity of 1.1 mPa·s. Overall, no clear correlation between feed characteristics and FO performance was found.

In order to decide on a suitable wastewater source for the use in an osmotic anaerobic bioreactor, both membrane performance (in terms of $J_w$) and methane yield must be considered to yield an economically viable process (Fig. 3). Overall, the synthetic BA medium effluents achieve a higher methane yield, because their macro- and micronutrients have been optimised for biogas production. GTO gives a high methane yield, since lipids are very energy-intensive.
rich, while glucose is easily processed by AD, making it a very efficient substrate.

Cattle manure and swine manure, on the other hand, contain lignocellulosic material which is recalcitrant to AD (Tsapekos et al., 2015). The swine manure has been sieved before AD, thus removing large parts of the lignocellulosic material and achieving a higher methane yield than cattle manure. However, the methane yield is also influenced by differences in the operation conditions of the bioreactors, such as HRT and OLR (see Supplementary data).

Out of the real effluents, potato starch wastewater and swine manure achieve both a high $J_w$ and higher methane yield, combined with a moderate flux decline, making them interesting wastewaters candidates for the use in an osmotic anaerobic bioreactor to produce clean water and energy in the form of methane. Unsurprisingly, the methane yield of the synthetic effluents exceeds that of the real effluents, as BA medium has been specifically optimised for AD.

### 3.2.3.2 Nutrient rejection

The TFC membrane achieves remarkable results in terms of TAN, TKN and orthophosphate rejection, as shown in Table 3. Rejections were calculated using the initial and final concentrations in the feed solution.

![Table 3 TAN, TKN and orthophosphate rejection](alt-text: Table 3)

<table>
<thead>
<tr>
<th>Effluent Type</th>
<th>TAN</th>
<th>TKN</th>
<th>Orthophosphate-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swine manure</td>
<td>92.34</td>
<td>88.62</td>
<td>98.74</td>
</tr>
<tr>
<td>Potato starch wastewater</td>
<td>85.53</td>
<td>82.95</td>
<td>99.18</td>
</tr>
<tr>
<td>Cattle manure, thermophilic</td>
<td>96.95</td>
<td>93.83</td>
<td>99.56</td>
</tr>
<tr>
<td>Cattle manure, mesophilic</td>
<td>95.34</td>
<td>95.87</td>
<td>99.52</td>
</tr>
<tr>
<td>BA medium + GTO</td>
<td>81.25</td>
<td>81.08</td>
<td>99.74</td>
</tr>
<tr>
<td>BA medium + glucose</td>
<td>96.55</td>
<td>82.84</td>
<td>99.78</td>
</tr>
<tr>
<td>BA medium + mixture</td>
<td>80.76</td>
<td>68.69</td>
<td>99.74</td>
</tr>
<tr>
<td>BA medium + casein</td>
<td>85.38</td>
<td>81.84</td>
<td>99.83</td>
</tr>
</tbody>
</table>

The orthophosphate rejection is consistently high for all effluents (>99%), which is consistent with previous results for TFC membranes (Xue et al., 2015). Xue et al. (2015) found that TAN was not effectively retained. This was not observed in this study. Although rejection of TAN and TKN is lower than the orthophosphate rejection, TAN rejection ranges from 80.76% (in BA medium + mixture) up to 96.95% (in thermophilic cattle manure) and TKN rejection ranges from 68.69% (in BA medium + mixture) up to 95.87% (in thermophilic cattle manure). The similar TKN and TAN rejections can be explained by the fact that TAN made up between 66 and 100% of the measured TKN content in...
all effluents. In semipermeable membranes, ion rejection is governed by electrostatic repulsion between ions and the membrane as well as steric hindrance depending on the hydration radii of the ions (Cornelissen et al., 2008; Xue et al., 2015). Since the experiments were carried out at pH 6.7 and the isoelectric point of the membrane is at pH 2.9, the membrane is negatively charged. The higher orthophosphate rejection could therefore be explained by the negative charge of the ion being repulsed by the membrane, while the positively charged ammonia ion faces no such repulsion. Additionally, the dynamic hydrated radius of orthophosphate is larger than that of ammonia (0.3 nm and 0.1 nm, respectively) (Kirillov and Collins, 2002).

Another possible explanation for the high TAN rejection is the use of MgCl₂ as a draw solution: Hu et al. attributed this to the Donnan equilibrium (Hu et al., 2017): Reverse salt diffusion of Cl⁻ ions exceeds that of Mg²⁺ ions (Table 2). This causes a charge imbalance and is prompting anions to diffuse from the feed solution to the draw solution in order to restore the charge equilibrium and leads to an accumulation of NH₄⁻ in the feed.

### Characterisation of FO fouling layer

Organic fouling was analysed by comparing ATR-FTIR spectra of the clean and fouled active layers of the membranes (Figure 4). The spectrum of the clean active layer shows characteristic bands of polyamide at 1658 and 1578 cm⁻¹, which can be associated with amide I (C

O stretching) and amide II (N

H) respectively (Hey et al., 2016; Melián-Martel et al., 2012), whereas the bands at 1486 cm⁻¹ (CH₃

C stretching), 1322 cm⁻¹ (CH₃

SO₂

C symmetric stretching), 1298 cm⁻¹ (S

O stretching), 1242 cm⁻¹ (C

O

C stretching), 1151 cm⁻¹ (C

SO₂

C symmetric stretching), as well as 1106 cm⁻¹ and 872 cm⁻¹ (skeletal aliphatic C

H rocking) can be ascribed to the porous PES support layer, because the penetration depth samples both active and support layer (Singh et al., 2006).
The distinct peaks of the clean membrane attenuated probably due to the presence of organic and/or biological fouling deposits on the membrane surface. All fouled membranes except the one exposed to potato starch wastewater sample exhibit a broad, distinctive peak at 3241–3290 cm⁻¹, which can be attributed to OH stretching of hydroxyl groups or NH stretching of amide A (Xu et al., 2016; Zarebska et al., 2014). The broadness of this peak suggests presence of polysaccharides, i.e. –CH and –OH groups.

Furthermore, there are smaller C H stretching vibrations, indicating the presence of proteins in the fouling layer (Bell et al., 2016; Hashim et al., 2010). Controversially, Bell and colleagues attributed a peak at 1625 cm⁻¹ to a C C stretch of aromatics (Bell et al., 2017). In principle, aromatic groups in manure-based effluents could stem from lignin breakdown of lignocellulosic materials in the animals feed. However, the BA medium based effluents contain no lignin-based material, thus the band is likely to be associated with amide I.

The small peak at 1429–1432 cm⁻¹ can be attributed to amide II (N H stretch), while another small peak at 981–1022 cm⁻¹ due to C O stretching corresponds to polysaccharides or polysaccharide-like substances (Chang et al., 2011; Melián-Martel et al., 2012; Provenzano et al., 2014).

ATP concentrations are often used as a tool in membrane autopsy as an indicator of biofouling and to assess the cellular viability of the biomass. After 24 h of FO experiment duration, there was a visible biofilm formation on the feed side of the membrane, while no sign of fouling was visible on the draw side. The ATP concentrations of the extracted foulants are shown in Table 4. Some attempts have been made to link ATP concentrations to total cell numbers (Hammes et al., 2010; van der Wielen and van der Kooij, 2010). However as the amount of ATP per cell may vary (Liu et al., 2013), the reliability of these methods is still debated and therefore, the results will be presented as microbial ATP concentrations.

<table>
<thead>
<tr>
<th></th>
<th>Total ATP [ng] ATP/cm² membrane</th>
<th>Free ATP [ng] ATP/cm² membrane</th>
<th>Microbial ATP [ng] ATP/cm² membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swine manure</td>
<td>34.30±9.56</td>
<td>1.08±1.19</td>
<td>33.22±8.37</td>
</tr>
<tr>
<td>Potato starch wastewater</td>
<td>1.40±0.34</td>
<td>0.13±0.08</td>
<td>1.46±0.15</td>
</tr>
<tr>
<td>Cattle manure (thermophilic)</td>
<td>17.18±11.56</td>
<td>0.15±0.02</td>
<td>17.03±11.54</td>
</tr>
<tr>
<td>Cattle manure (mesophilic)</td>
<td>6.54±0.75</td>
<td>0.70±0.03</td>
<td>5.84±0.72</td>
</tr>
<tr>
<td>BA medium + GTO</td>
<td>149.96±23.92</td>
<td>1.11±0.14</td>
<td>148.85±24.06</td>
</tr>
<tr>
<td>BA medium + glucose</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>BA medium + mixture</td>
<td>10.52±0.47</td>
<td>0.34±0.21</td>
<td>10.37±0.96</td>
</tr>
</tbody>
</table>
Free ATP is one to two orders of magnitude lower in comparison to total ATP, which is in agreement with previous results (van der Kooij, 1992; van der Wielen and van der Kooij, 2010). Overall, the variation of microbial ATP concentrations on the membrane surface differs significantly between the AD effluents. The highest microbial ATP concentration is found with high-lipid medium (BA medium + GTO) with 165.87 ng ATP/cm² membrane, which also had the highest methane yield, while high-protein medium (BA medium + casein) has the lowest microbial ATP concentrations with 0.77 ng ATP/cm² membrane. The differences in microbial ATP concentrations also reflect differences in the microbial viabilities in the bioreactors, which were operated at different conditions in terms of reactor type, OLR and HRT (see Supplementary data), containing different microbial communities with different amounts of ATP/cell. Furthermore, effluents were collected over a period of several weeks in order to have sufficient feed volumes, which may have affected the microbial viability as well.

The fouled and clean FO membranes were visually examined using SEM (Figure 5). The results show that, after 24 h of FO operation, the active layer of the pristine membrane (Figure 5I) is entirely covered by a deposited cake layer in all fouled samples, which as revealed by FTIR contains proteins and carbohydrates.

![Fig. 5 SEM of FO membranes active layer fouled with effluents from anaerobic digestion over a time period of 24 h (A) swine manure, (B) potato starch wastewater, (C) cattle manure (thermophilic), (D) cattle manure (mesophilic), (E) BA medium + GTO, (F) BA medium + casein, (G) BA medium + glucose, (H) BA medium + mix, (I) clean membrane (AL).](alt-text: Fig. 5)

In some cases, singular (Figure 5A, C, E, F, G) or clustered (Figure 5H) rod-shaped microbial structures can be seen incorporated in the fouling layer, suggesting that biological fouling occurred in agreement with ATP measurements. Both ICP-OES and IC analysis (Table 5) reveal the presence of Mg and Cl ions in the fouling layer. The difference between findings from SEM and ICP-OES and IC can be attributed to the fact the first method is surface sensitive, whereas the latter method analyses the foulants extract. Although Mg was already present in the effluents (see Supplementary data), the relative concentration in comparison with other divalent cations seemed to increase. This can be explained by reverse salt flux deposits on the membrane active layer surface. Divalent cations like Mg²⁺ and Ca²⁺ have been shown to promote organic fouling by forming complexes carboxylic groups of natural organic matter; thus helping to form intermolecular bridges (Mi and Elimelech, 2008).
The presence of N and P on the fouled membrane suggests biofouling and the presence of extracellular polymeric substances (EPS), which is confirmed by ATP analysis. Results from ICP-OES analysis and indicate the presence of magnesium ions on the active layer due to the reverse salt flux. The P could stem from the rejected orthophosphate in the feed accumulating on the membrane surface.

Table 5: ICP-OES and IC analysis cation concentration in foulants extracted from membrane surface in [g* kg$^{-1}$ membrane]. For ICP-OES, results of Ba, Mn and Sr are omitted due to very low concentrations. For IC, results for nitrate and bromide are not displayed, as they could not be detected in the samples.

<table>
<thead>
<tr>
<th></th>
<th>Concentration [g* kg$^{-1}$ membrane]</th>
<th>Swine manure</th>
<th>Potato starch wastewater</th>
<th>Cattle manure (thermophilic)</th>
<th>Cattle manure (mesophilic)</th>
<th>BA medium + GTO</th>
<th>BA medium + glucose</th>
<th>BA medium + mixture</th>
<th>BA medium + casein</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>3.93±2.62</td>
<td>1.25±1.08</td>
<td>4.26±0.06</td>
<td>4.22±1.76</td>
<td>2.84±0.86</td>
<td>4.84±2.11</td>
<td>2.07±0.34</td>
<td>2.08±1.21</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.76±0.53</td>
<td>0.18±0.13</td>
<td>0.45±0.02</td>
<td>0.44±0.24</td>
<td>0.84±0.13</td>
<td>0.60±0.19</td>
<td>0.35±0.04</td>
<td>0.32±0.05</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>2.97±3.07</td>
<td>13.62±0.52</td>
<td>3.51±0.98</td>
<td>2.82±1.51</td>
<td>3.92±1.72</td>
<td>4.87±1.93</td>
<td>3.35±2.14</td>
<td>1.17±0.62</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>19.75±20.44</td>
<td>34.11±2.59</td>
<td>12.82±4.94</td>
<td>9.3±5.23</td>
<td>36.04±10.32</td>
<td>28.89±8.37</td>
<td>33.54±14.34</td>
<td>32.52±5.85</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1.16±1.20</td>
<td>1.69±0.18</td>
<td>1.43±0.36</td>
<td>1.17±0.56</td>
<td>1.75±1.15</td>
<td>2.87±1.28</td>
<td>2.18±1.69</td>
<td>1.89±1.56</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>25.10±27.72</td>
<td>32.83±13.58</td>
<td>15.83±6.19</td>
<td>11.46±8.83</td>
<td>59.11±16.41</td>
<td>32.40±11.11</td>
<td>33.13±11.39</td>
<td>43.12±23.09</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>2.59±2.63</td>
<td>2.91±0.87</td>
<td>0.62±0.08</td>
<td>0.56±0.06</td>
<td>1.05±0.63</td>
<td>2.12±1.66</td>
<td>1.71±1.30</td>
<td>2.75±2.08</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.29±0.19</td>
<td>0.18±0.04</td>
<td>0.24±0.04</td>
<td>0.22±0.16</td>
<td>0.30±0.06</td>
<td>0.30±0.11</td>
<td>0.18±0.03</td>
<td>0.12±0.06</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>2.38±1.57</td>
<td>0.16±0.10</td>
<td>0.13±0.03</td>
<td>0.10±0.09</td>
<td>0.16±0.04</td>
<td>0.16±0.07</td>
<td>0.11±0.01</td>
<td>0.07±0.04</td>
<td></td>
</tr>
</tbody>
</table>

SEM-EDS was used to analyse the overall elemental composition of the fouling layer (Table 6). Asides from C, N and O, the main elements in the fouling layers are Mg, P and Ca. These results are in agreement with the results from ICP-OES analysis and indicate the presence of magnesium ions on the active layer due to the reverse salt flux. The P could stem from the rejected orthophosphate in the feed accumulating on the membrane surface. The presence of N and P on the fouled membrane suggests biofouling and the presence of extracellular polymeric substances (EPS), which is confirmed by ATP analysis.

Table 6: Representative SEM-EDS results of FO membranes fouled with effluents from anaerobic digestion in weight %.

<table>
<thead>
<tr>
<th>Weight %</th>
<th>Swine manure</th>
<th>Potato starch wastewater</th>
<th>Cattle manure thermophilic</th>
<th>Cattle manure mesophilic</th>
<th>BA medium + GTO</th>
<th>BA medium + glucose</th>
<th>BA medium + mix</th>
<th>BA medium + casein</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>66.20</td>
<td>64.99</td>
<td>42.91</td>
<td>54.63</td>
<td>69.61</td>
<td>59.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>12.83</td>
<td>11.89</td>
<td>7.42</td>
<td>7.11</td>
<td>0.91</td>
<td>4.85</td>
<td>6.67</td>
<td>5.49</td>
</tr>
<tr>
<td>O</td>
<td>62.15</td>
<td>35.54</td>
<td>25.16</td>
<td>24.05</td>
<td>40.51</td>
<td>25.63</td>
<td>13.11</td>
<td>19.84</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>Mg</td>
<td>5.03</td>
<td>16.21</td>
<td>1.21</td>
<td>0.72</td>
<td>6.09</td>
<td>6.29</td>
<td>0.49</td>
<td>1.59</td>
</tr>
<tr>
<td>Al</td>
<td>0.69</td>
<td></td>
<td></td>
<td>0.34</td>
<td>0.09</td>
<td>0.14</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1.73</td>
<td>1.14</td>
<td></td>
<td>1.44</td>
<td>0.15</td>
<td>0.41</td>
<td>2.48</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>4.89</td>
<td>20.80</td>
<td></td>
<td>0.38</td>
<td>6.45</td>
<td>7.35</td>
<td>0.60</td>
<td>2.16</td>
</tr>
<tr>
<td>S</td>
<td>2.11</td>
<td>5.48</td>
<td></td>
<td>0.58</td>
<td>2.85</td>
<td>0.17</td>
<td>8.07</td>
<td>2.17</td>
</tr>
<tr>
<td>K</td>
<td>1.58</td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.11</td>
<td>0.09</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>5.74</td>
<td>1.98</td>
<td></td>
<td>0.32</td>
<td>0.06</td>
<td>0.56</td>
<td>0.48</td>
<td>4.56</td>
</tr>
</tbody>
</table>
The trace amounts of Cu, Al, and Zn found in the membranes fouled with synthetic effluents can be attributed to the trace element solution used in the preparation of the BA medium, while the S could stem from the thiamine and thioctic acid in the vitamin solution (Angelidaki et al., 1990).

The small amounts of gold found in some samples originate from sputter coating the samples before SEM/SEM-EDS. The SEM-EDS results are not directly comparable with IC and ICP-OES analysis, since it's possible that the foulant layer composition is inconsistent over the membrane area. The complete SEM-EDS spectra can be found in the Supplementary data.

4.4 Conclusions

This study provides an initial feasibility assessment for the treatment of various types of anaerobic digestion effluents by FO membranes, resulting in reclaimed water and methane production. Overall, the membranes showed reasonable initial \( J_o \) (4.3±5.1 LMH) and high nutrient rejection, with TAN rejection ranging from 80.8±97.0% and orthophosphate rejection from 98.7±99.8%.

Although effluent properties (TOC and viscosity) influenced \( J_o \), no clear correlation between the methane yield, fouling potential and FO performance of an effluent was found. This shows that no compromise between high methane yield and \( J_o \) has to be made, when choosing a wastewater candidate.

Specifically, swine manure and potato starch achieved the highest methane yield and highest water flux out of four tested real effluents and could therefore be suitable wastewater candidates for an FO-AnMBR for simultaneous water purification and energy production.

During FO water extraction from anaerobic digested effluents the prevailing fouling is of biological and organic origin.

Taken together, these results indicate that FO membranes are suitable to be used in an FO-AnMBR-RO application, where high nutrient rejection and low reverse flux are essential to sustain simultaneous high product water quality and stable biogas production. In order to optimize the process, further work is warranted with regards to the re-concentration of the FO draw solution, wastewater pre-treatment and membrane cleaning strategies.

Acknowledgements

This work was supported by the Innovation Fund Denmark (Innovationsfonden) under the MEMENTO project with grant number 4106-00021B. The laboratory technicians at DTU Environment are thanked for conducting the IC and ICP-OES analyses. The authors would further like to acknowledge the support from Aquaporin A/S for providing the FO membranes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.08.036.

References


Hu T., Wang X., Wang C., Li X. and Ren Y., Impacts of inorganic draw solutes on the performance of thin-film composite forward osmosis membrane in a microfiltration assisted anaerobic osmotic membrane bioreactor,


Appendix A. Supplementary data

Multimedia Component 1

Supplementary material

alt-text: Image 1

Graphical abstract
Highlights

- Biomimetic FO membranes extract water from anaerobic digestion effluents.
- The membranes achieve high ammonia and orthophosphate rejection.
- No trade-off between methane yield and water flux and fouling propensity.
- Organic fouling and biological fouling occurred on the active layer of the membrane.

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