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Evaluate Synergies of Using Hydrothermal Liquefaction and Anerobic Digestion Treatment Technologies for Wastewater Resource Recovery Facilities (CRADA 516 Final Report)

December 2024

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Pacific Northwest National Laboratory

Xavi Fonoll, John Norton
Great Lakes Water Authority

U.S. DEPARTMENT OF ENERGY

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Richland, Washington 99354

Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: November 2024

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions, to be provided to PNNL Information Release who will forward to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research. **PNNL acknowledges that the CRADA parties have been involved in the preparation of the report or reviewed the report.**

Parties to the Agreement:

Great Lakes Water Authority (GLWA)
Pacific Northwest National Laboratory (PNNL)

CRADA number: 516

CRADA Title: Evaluate synergies of using Hydrothermal Liquefaction and Anerobic Digestion treatment technologies for wastewater resources recovery facilities

Responsible Technical Contact at DOE Lab(PNNL): Andrew Schmidt

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John Norton

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Sponsoring DOE Program Office(s):

BioEnergy Technology Office

Joint Work Statement Funding Table showing DOE funding commitment:

	Funding Amounts			
CRADA Parties	**DOE Funding**	**Funds-In**	***In-kind**	**Total**
Great Lakes Water Authority	None	None	$465,750	$475,750
DOE Funding to PNNL	$275,000	N/A	N/A	$275,000
Total of all Contributions	$275,000	None	$465,750	$740,750

Provide a list of publications, conference papers, or other public releases of results, developed under this CRADA:

Cronin, Dylan, et al. "Comparative study on the continuous flow hydrothermal liquefaction of various wet-waste feedstock types." *ACS Sustainable Chemistry & Engineering* 10.3 (2021): 1256-1266.

Snowden-Swan, Lesley J., et al. *Wet waste hydrothermal liquefaction and biocrude upgrading to hydrocarbon fuels: 2021 state of technology*. No. PNNL-32731. Pacific Northwest National Lab.(PNNL), Richland, WA (United States), 2022.

Fonoll et al. “Using a Recirculating Anaerobic Dynamic Membrane Bioreactor to treat hydrothermal liquefaction aqueous by-product”. Submitted to Frontiers in Chemical Engineering.

X. Fonoll*, A. Schmidt, A. Busch, M. Thorson, J. Norton. Using a Recirculating Anaerobic Dynamic Membrane Bioreactor to Treat Hydrothermal Liquefaction Aqueous By-Product: Reactor Performance and Microbial Community. 18th IWA World Conference on Anaerobic Digestion (AD-18). June 2028.

X. Fonoll*, A. Schmidt, A. Busch, M. Thorson, J. Norton. Great Lakes Water Authority research efforts on hydrothermal liquefaction to recover energy from sludge. MWEA biosolids conference. March 2023.

X. Fonoll*, A. Schmidt, A. Busch, M. Thorson, J. Norton. Using A Novel Anaerobic Technology to Treat Hydrothermal Liquefaction Aqueous By-product. 17th IWA World Conference on Anaerobic Digestion (AD-17). June 2022.

X. Fonoll*, A. Schmidt, A. Busch, M. Thorson, J. Norton. Reducing the Toxicity in Hydrothermal Liquefaction aqueous phase using a New Anaerobic Digestion Bioreactor to maximize resource recovery from sludge. Residuals and Biosolids Conference. May 2022.

X. Fonoll*, A. Schmidt, A. Busch, M. Thorson, J. Norton. Using A Novel Anaerobic Technology to Treat Hydrothermal Liquefaction Aqueous By-product. IWA LET 2022. March 2022.

X. Fonoll*, A. Schmidt, A. Busch, M. Thorson, J. Norton. Energy recovery from sludge through production of biocrude and methane using hydrothermal liquefaction and a novel anaerobic digestion bioreactor. European Biosolids & Bioresources Conference. November 2021.

X. Fonoll. Next Generation Biosolids. Eckenfelder Lecture Series 2024. Denton (TX), USA, November 2024.

X. Fonoll. Using A New Anaerobic Digestion Configuration to Treat Hydrothermal Liquefaction Aqueous By-product. IEA Bioenergy Task 36: Treating and valorizing the aqueous phase from hydrothermal liquefaction (HTL). Online presentation (2024).

X. Fonoll. Using A Novel Anaerobic Technology to Treat Hydrothermal Liquefaction Aqueous By-product. Hydrothermal Liquefaction in Metro Vancouver workshop. Vancouver, Canada, June 2022.

Provide a detailed list of all subject inventions, to include patent applications, copyrights, and trademarks:

None

Executive Summary of CRADA Work

The research focuses on utilizing a new anaerobic digestion (AD) configuration to treat the aqueous by-product generated by hydrothermal liquefaction (HTL) of sewage sludge. This report found that for Anaerobic Digestion for HTL By-product, Anaerobic biofilms can degrade some HTL wastewater contaminants, but co-digestion is essential to address nutrient deficiencies and optimize performance. Without AD, toxicity of HTL aqueous streams may limit broader adoption in wastewater treatment plants (WWTPs). Great Lakes Water Authority (GLWA) used an innovative reactor design, involving a dynamic membrane anaerobic bioreactor to promote biofilm growth, improving contaminant degradation. The tree-like structure inside the reactor supports biofilm development with recirculation enhancing microbial activity. Overall, a 70% chemical oxygen demand (COD) removal was achieved, although nutrient supplementation is required for stability. The reactor achieved a diverse microbial community, including methanogens and bacteria capable of degrading phenols and aromatics.

Summary of Research Results

1. Introduction

Municipal wastewater treatment generates substantial amounts of sludge, presenting both a disposal challenge and an opportunity for resource recovery. Traditional methods of sludge management, such as land application or incineration, have limitations due to environmental concerns and regulatory constraints. Hydrothermal liquefaction (HTL) has emerged as a promising technology to convert wet biomass like sewage sludge into valuable biofuels and bioproducts without the need for extensive dewatering. HTL processes sludge under high temperature and pressure in the presence of water, producing biocrude oil, gas, solids, and an aqueous byproduct (HTL-AB).

While HTL effectively transforms sludge into energy-rich products, the resultant HTL-AB contains a complex mixture of organic compounds, including nitrogenous substances like pyrrolidine and pyrazine. These compounds can be toxic to microbial communities and pose a challenge for downstream treatment processes. Traditional wastewater treatment systems often require significant dilution of HTL-AB to mitigate toxicity before biological treatment, which is impractical for large-scale implementation due to increased volume and associated costs.

Developing efficient methods to treat HTL-AB without excessive dilution is crucial to advancing HTL as a viable sludge management and resource recovery option. Anaerobic digestion presents a potential solution by converting organic contaminants in HTL-AB into methane-rich biogas, thus providing a pathway for energy recovery. However, standard anaerobic digesters may not effectively process HTL-AB due to its inhibitory compounds and nutrient imbalances.

The Recirculating Anaerobic Dynamic Membrane Bioreactor (R-AnDMBR) is a novel treatment system designed to enhance anaerobic biodegradation of complex waste streams. By promoting biofilm formation on a dynamic membrane, the R-AnDMBR increases microbial retention and resilience against toxic compounds. The system recirculates the feedstock through the biofilm-coated membrane, allowing prolonged contact between microbes and contaminants, which can enhance degradation efficiency.

This study explores the application of the R-AnDMBR for treating HTL-AB generated from municipal wastewater sludge. The primary objectives are to assess the system's efficiency in reducing chemical oxygen demand (COD) and toxic compounds without extensive dilution, to evaluate methane production for energy recovery, and to identify operational challenges such as nutrient limitations. By addressing these objectives, the research aims to contribute to the development of sustainable and integrated sludge management strategies that maximize resource recovery at wastewater treatment facilities.

2. Results

Substrate and Inoculum Preparation

A mixture of primary and secondary sludge was collected from the Great Lakes Water Authority (GLWA) Water Resource Recovery Facility (WRRF) in Detroit, USA and transported under refrigeration to the Pacific Northwest National Laboratory (PNNL). Upon arrival, the sludge was stored at 4°C until processing. The collected sewage sludge was subjected to continuous-flow hydrothermal liquefaction (HTL) at PNNL. The HTL system operated under subcritical water conditions at a temperature of 350°C and a pressure of 2900 psi. The sludge was processed as a 15.5% (wt/wt) slurry at a flow rate of 12 L/h, resulting in a liquid hourly space velocity of 4 L L^{-1} h^{-1}, corresponding to a residence time of 15 minutes. The biocrude oil produced was separated by gravity from the aqueous phase without the use of solvents. The aqueous byproduct (HTL-AB) generated from this process was collected and shipped to GLWA for subsequent treatment in the R-AnDMBR. Other conditions, including lower temperature HTL were also tested with the HTL-AB being provided to GLWA.

Recirculating Anaerobic Dynamic Membrane Bioreactor Setup

The R-AnDMBR system consisted of a 7 L cylindrical bioreactor with a working volume of 5 L. It has a mesh pore size of 25 microns and was fed with a raw COD of 75gCOD/L, a feedstock concentration of 2-10gCOD/L, an organic loading rate of 0.2-2.1 gCOD/L_R/day and an HRT of 5-10 days (Table 1). The inoculum was sludge coming from digester treating food waste and sludge. Figure 1 provides a schematic of the reactor. The design of the RAnDMBr involves a tree-like structure submerged in the bioreactor which branches were surrounded by a stainless-steel mesh of 25 µm pore size. The goal of the tree-like structure if to build a high surface area biofilm to enhance the degradation of HTL-aq. The branches in the tree-like structure provided a very high surface area (19.79 m^2 $m_{reactor}^{-3}$) in the system where the biofilm (dynamic membrane) was developed. Contrary to common dynamic membrane bioreactors, the reactor bulk liquid was not permeated continuously through the dynamic membrane. To generate a biofilm on the branches of the tree-like structure and promote advective substrate transport, the bulk liquid was recirculated through the meshes. Therefore, the R-AnDMBR would work under cycles of recirculation and permeation (Figure 2). For a period of time of tR, the system would recirculate the bulk liquid through the stainless steel meshes and for a period of time tP the system would perform permeation. Permeation would take place by activating a three-way valve that would switch the direction of the fluid from recirculation to permeation (Figure S1B). Because the dynamic membrane permeability would not be constant, the time of recirculation and permeation varied during the study to keep the reactor at the desired HRT (5 or 10 days depending on the experiment stage, see Table 1). To determine how often the bulk liquid was recirculated through the dynamic membrane, the recirculation ratio was calculated by dividing the recirculation flow rate by the effluent flow rate. The R-AnDMBR operated under different organic loading rates by diluting the HTL-aq with DI water. The operating conditions of this study can be seen in Table 1.

Table 1 Reactor operating parameters

Time period (days)	0-25	26-75	76-115	116-166	167-359	360-473	474-521	522-600
OLR ($g\ COD\ L_R^{-1}\ day^{-1}$)	0.5 ± 0.2	0.2 ± 0.0	0.4 ± 0.2	0.9 ± 0.1	0.5 ± 0.2	1.1 ± 0.4	1.5 ± 0.2	2.1 ± 0.3
HRT (days)	6.7 ± 2.1	11.5 ± 2.8	10.7 ± 1.6	10.3 ± 0.9	10.9 ± 2.0	5.6 ± 2.3	6.5 ± 0.6	6.0 ± 1.7
Dilution factor for HTL-AB	30.0	30.0	15.0	7.5	15.0	9.0	7.5	5.6
Feedstock ($g\ COD\ L^{-1}$)	2.4 ± 0.2	2.4 ± 0.2	4.7 ± 1.1	8.6 ± 1.7	5.0 ± 0.4	6.0 ± 1.6	9.4 ± 1.3	12.5 ± 0.8
Recirculation ratio ($L\ L_R^{-1}$)*	20.0	3.8-20.0	3.8	3.8-5.5	5.5	1.5	1.5	1.5

*The recycle ratio shows maximum and minimums used during the specific period (see figure 2)

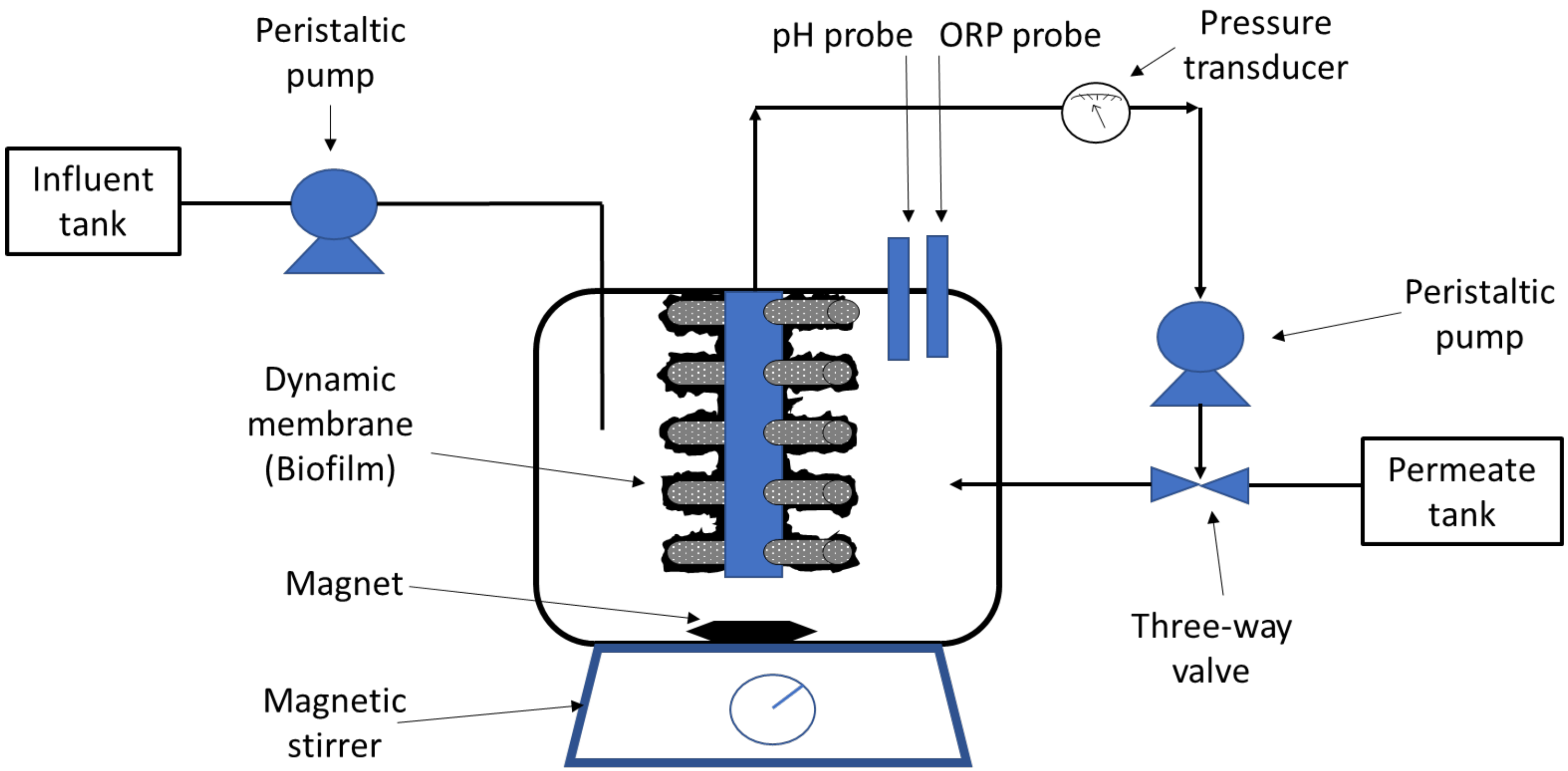

Figure 1. Schematic representation of the experimental apparatus

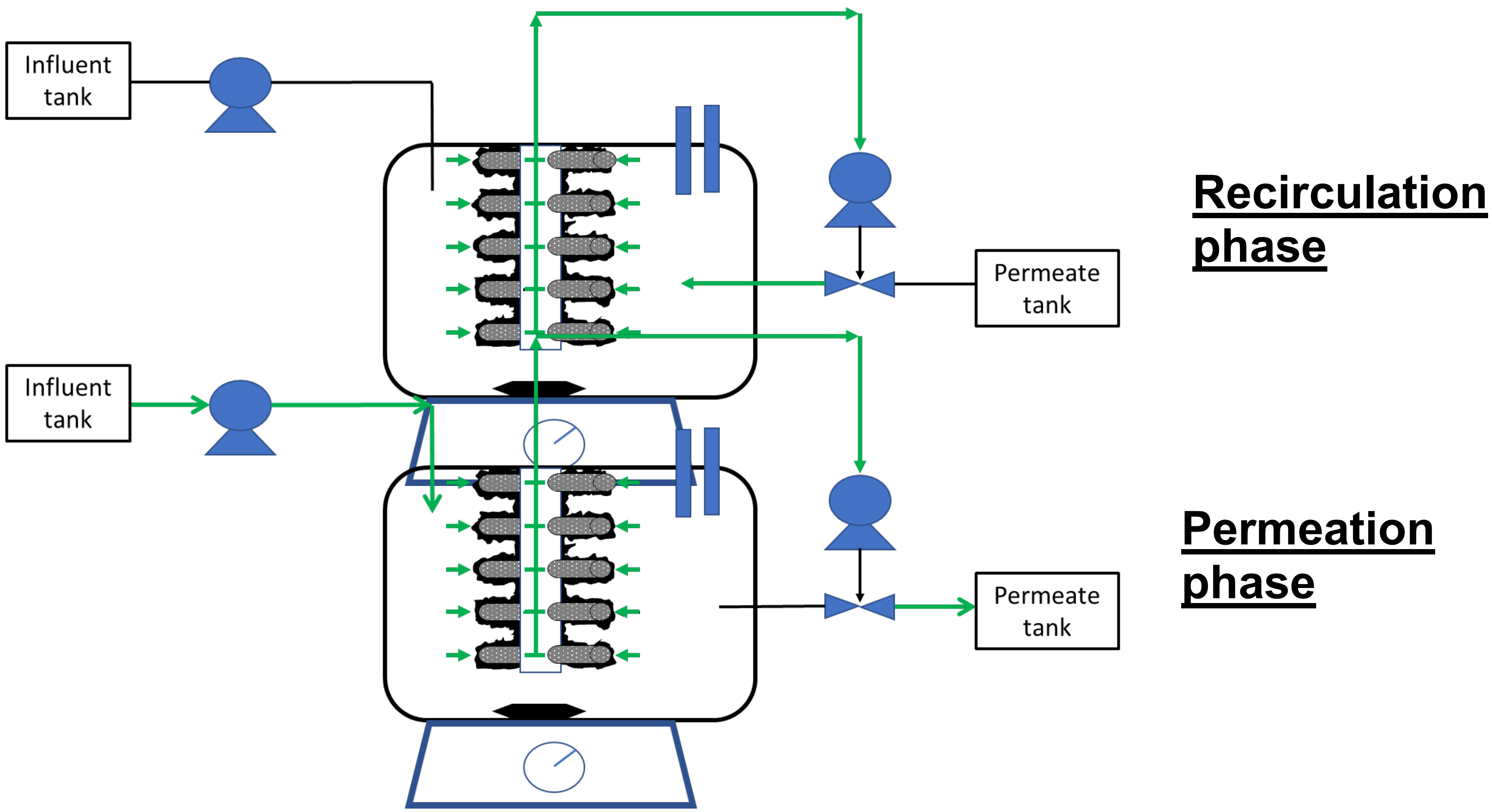

Figure 2. Schematic representation of the R-AnDMBR cyclic operational strategy.

The operating parameters and performance during the 600-day R-AnDMBR test are presented in Figure 3.

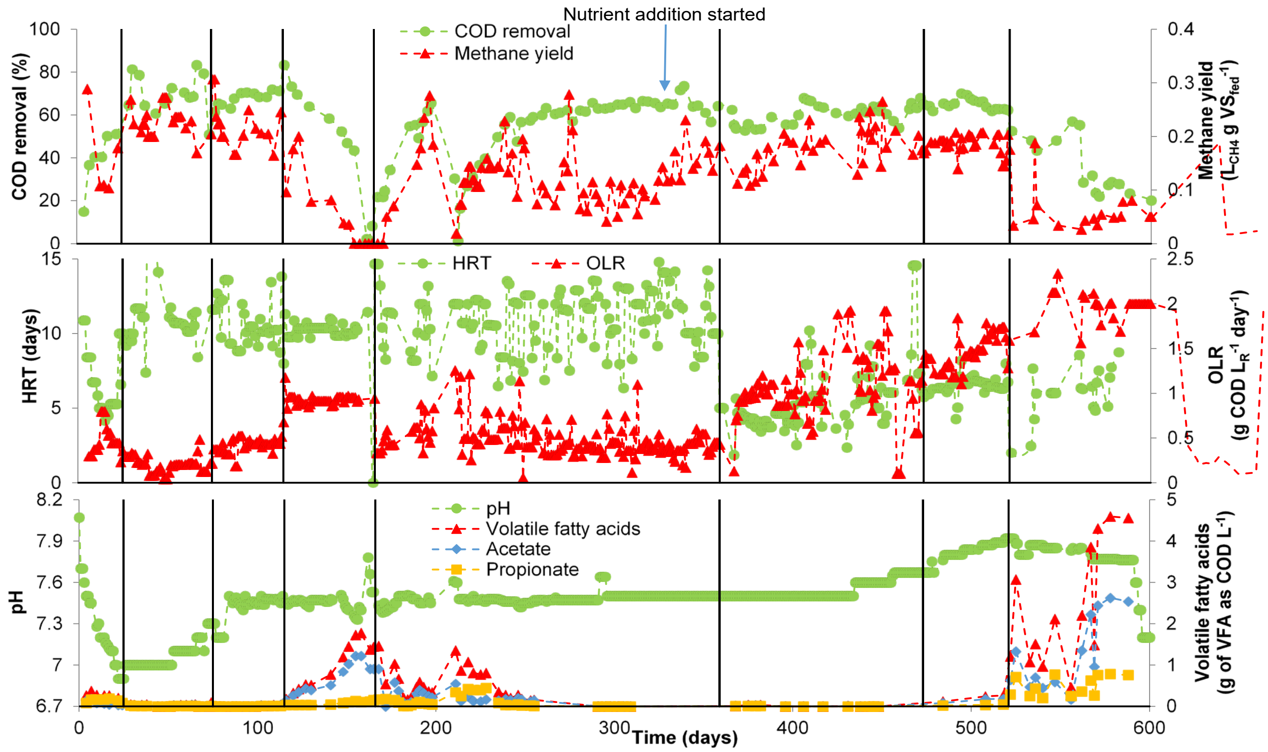

Figure 3. Chemical oxygen demand (COD) removal and methane yield (A), hydraulic retention time (HRT) and organic loading rate (OLR) (B), and pH and volatile fatty acids (VFA) accumulation (C). The vertical line indicates changes made to the OLR.

In the reactor, we achieved 70% COD reduction but at low organic loading rates as shown in Figure 3. COD reduction fell off when the organic loading was increased to 1.0 gCOD L_R^{-1} day^{-1} One of the reasons the R-AnDMBR could not work at an OLR higher than 0.5 g COD L_R^{-1} day^{-1} could be the low nutrients concentration in the substrate (Table 2). As seen in Figure 3 the COD:P of the substrate and the digester content was not in the ideal range for anaerobic digestion (400-17) (Thaveesri et al., 1995; Janke et al., 2017). In this study, the HTL-aq was provided by PNNL and their HTL system has a settling separation vessel to enhance the separation of inorganics from the biocrude/HTL-aq mixture. The settling vessel promotes the separation of phosphates from the HTL-aq, producing a hydrochar rich in P that can use as fertilizer and an HTL-aq with very low concentration of P for bioprocesses (Elliott et al., 2016). To avoid inhibition in the system due to the lack of P and trace metals, on day 332 we started to mix the feedstock with a solution rich in nutrients (details about the nutrient stock solution can be found in Table 3).

Table 2 Nutrient composition of the HTL aqueous phase

	Concentration (ppm)		
Compound	HTL Aqueous phase	Reactor day 248	Reactor day 260
N	630 ± 15	642 ± 49	
P	1.2 ± 0.4	5.6 ± 0.1	
S	11	9	6
Na	8	6	8
Ca	62.2	9.4	10.9
K	22	24	24
Mg	3	3	3
Fe	1.8	5.8	3.6
Ni	< 1.6	< 1.6	< 1.6
Co	< 0.2	< 0.2	< 0.2
Zn	< 0.6	< 0.6	< 0.6
Mo	< 0.3	< 0.3	< 0.3
W	< 1	< 1	< 1
Cu	0.15	0.3	0.3
Mn	< 0.3	< 0.3	< 0.3

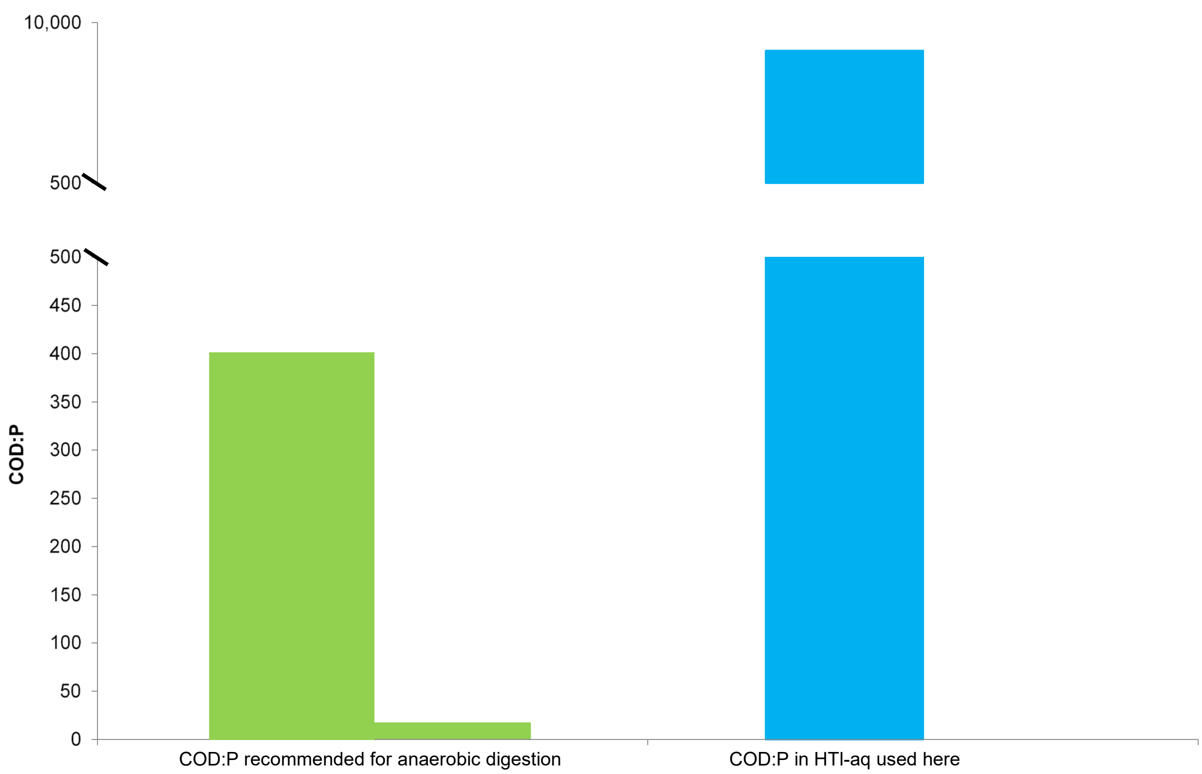

Figure 4. Ratio of Chemical oxygen demand over Phosphorous

Table 3. Description of nutrient solution used in this study

Solution A		Solution B		Solution C	
Compound	Mass or volume added to 1L distilled water	Compound	Mass or volume added to 1L distilled water	Compound	Mass or volume added to 1L distilled water
NaCl	10	$K_2HPO_4 \bullet 3H_2O$	200	$FeCl_2 \bullet 4H_2O$	2
$MgCl_2 \bullet 6H_2O$	10			H_3BO_3	0.05
$CaCl_2 \bullet 2H_2O$	5			$CuCl_2 \bullet 2H_2O$	0.038
				$MnCl_2 \bullet 4H_2O$	0.05
				$NiCl_2 \bullet 6H_2O$	0.092
				$ZnCl_2 \bullet 4H_2O$	0.05
				$(NH_4)6Mo7O_{24} \bullet 4H_2O$	0.05
				$ALCl_3$	0.05
				$CoCl_2 \bullet 6H_2O$	0.05
				Na_2SeO_3	0.1
				EDTA	
				HCl	1 ml

The final stock solution used in this study was prepared by mixing 10 ml of solution A, 2 ml of solution B and 1 ml of solution D in 987 ml of distilled water.

After adding the nutrient solution the system could operate with an OLR of 1.5 g COD Lr-1 day-1 without inhibition (dilution of 7.5)

The biofilm presented a diverse microbial community with important populations, including methanogens, aromatic and phenol compound degraders, and syntrophic bacteria as shown in Figure 5.

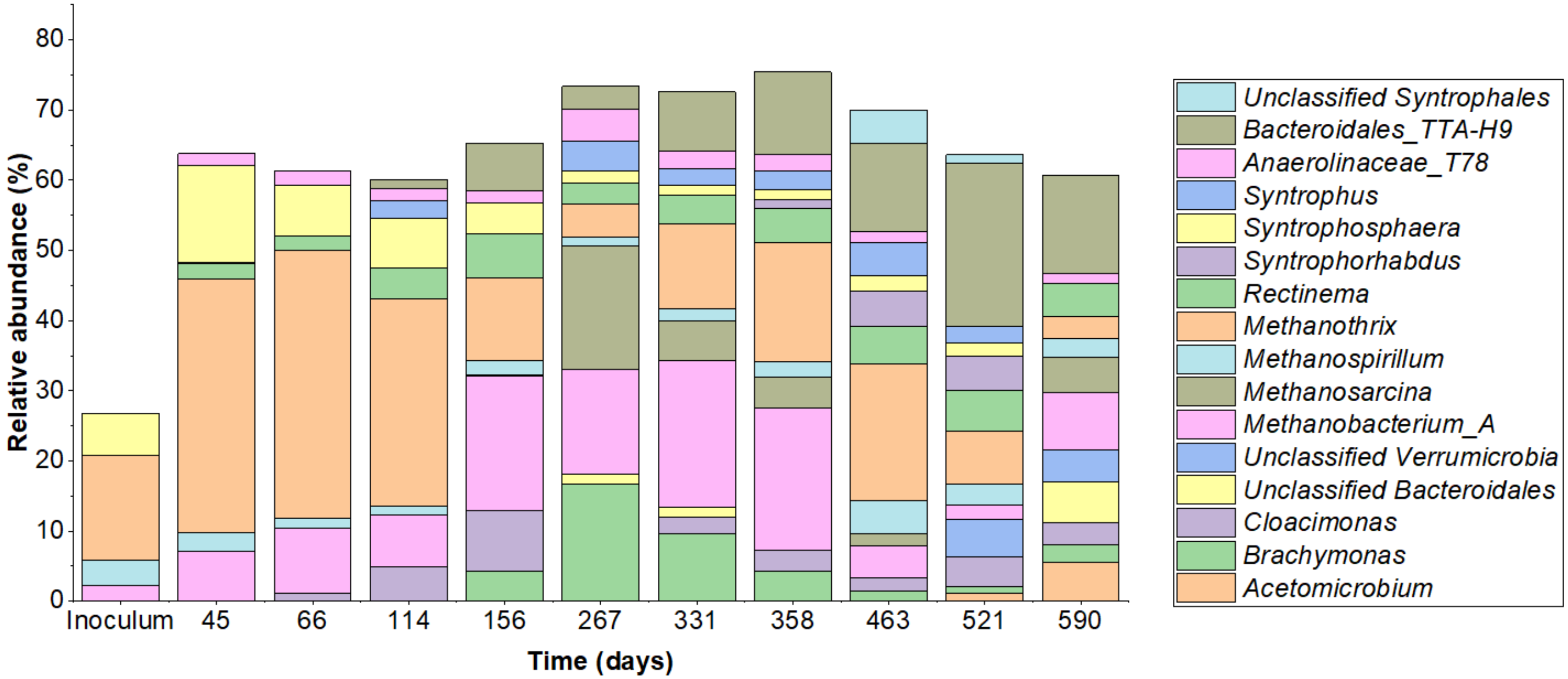

Figure 5. Relative abundance of dominant groups in the inoculum and biofilm samples collected from the recirculating anaerobic dynamic membrane bioreactor over time. Only genera present at relative activities greater than 1% in at least 6 samples or present at a relative abundance of 5% at least once are shown.

Overall, the R-AnDMBR was able to treat diluted HTL-aq (dilution factor of 7.5) and degrade 65% of the COD at 1.5 ± 0.2 g COD L_R^{-1} day^{-1} and 5.6 ± 2.3 days producing 0.19 ± 0.02 LCH4 $gCOD_{fed}^{-1}$. However, co-digestion with a substrate like sewage sludge or sludge centrate would be necessary to overcome the deficiency of P and other nutrients in HTL-aq. The system presented severe inhibition after the OLR increased to 2.0 g COD L_R^{-1} day^{-1}.

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