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Authors

Rao, Unnati
Posmanik, Roy
Hatch, Lindsay E
et al.

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Coupling hydrothermal liquefaction and membrane distillation to treat anaerobic digestate from food and dairy farm waste



Unnati Rao^a, Roy Posmanik^b, Lindsay E. Hatch^d, Jefferson W. Tester^c, Sharon L. Walker^d, Kelley C. Barsanti^d, David Jassby^{a,*}

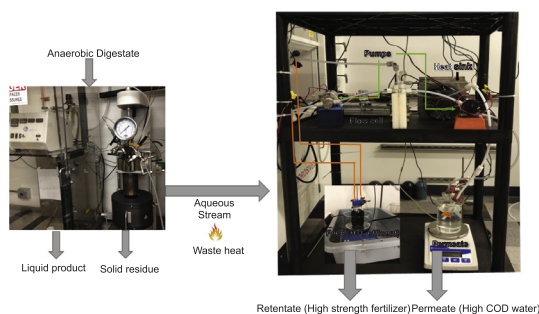
^a Department of Civil and Environmental Engineering, University of California, Los Angeles, CA, United States

^b Agricultural Research Organization (ARO), Volcani Center, Israel

^c School of Chemical and Biochemical Engineering, Cornell University, Ithaca, NY, United States

^d Department of Chemical and Environmental Engineering and College of Engineering – Center for Environmental Research and Technology, University of California, Riverside, CA, United States

GRAPHICAL ABSTRACT



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ABSTRACT

Increased demand for water, energy and food requires new ways to produce fertilizers, fuels and reusable water. Recovery of resources from wastes could lead to an additional source of energy and nutrients, and also reduce the waste to be disposed. In this work, we used hydrothermal liquefaction to produce a biocrude oil product, followed by membrane distillation of the aqueous effluents to concentrate a nutrient-rich stream that can be used as fertilizer. The motivation for this work is that residual heat from the hydrothermal liquefaction process could be utilized to drive the membrane distillation process, which would improve the efficiency and reduce the cost of the distillation process. The membrane distillation system was demonstrated to be able to recover 75% of the water. The membrane distillation retentate had very high ammonium and phosphate concentrations, making it suitable as a fertilizer. Membrane permeate contained high concentrations of volatile organics.

1. Introduction

Fertilizers have played a critical role in the development of agriculture by substantially improving crop yields, and their importance is growing as the population increases. Commercial fertilizers are

composed primarily of nitrogen, phosphorous and potassium, with several also containing some organic species (Romero et al., 2013). Fertilizer production is an energy intensive process, accounting for approximately a third of the energy consumption during US crop production (Gellings and Parmenter, 2016). The main source of

* Corresponding author.

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phosphorous is phosphate rock, which is mined in several locations around the globe (primarily in Morocco, China and South Africa (Van Kauwenbergh, 2010)). During the fertilizer manufacturing process, phosphate rock is converted to various forms of soluble orthophosphates (Rehm, 1997). However, natural phosphate rock deposits are dwindling, which could have dramatic impacts on global agricultural yields (Gilbert, 2009). Nitrogen in fertilizers is generated through the Haber-Bosch process, where atmospheric nitrogen is converted to ammonia in a process that requires hydrogen which is usually generated from steam reforming of methane (Sutton et al., 2011). Given the high energy costs, and dwindling precursor materials, an attractive alternative to current fertilizer production methods is the recovery of nitrogen and phosphorous species from various waste streams (Ren and Umble, 2016). Various resource-recovery methods have been explored, with many investigations reporting the extraction and recovery of nitrogen and phosphorous from waste such as municipal and industrial wastewater, manure lagoons, and landfill leachate (Abdel-Raouf et al., 2012; Xie et al., 2014).

Due to its high reliance on dairy as a food source, the United States has a large number of dairy farms; a 2014 USDA report states that there were over 9.2 million milking cows, with this number growing steadily (James and Macdonald, 2014). Each cow produces 20–30 tons of liquid manure every year, which translates into the production of 180–200 million cubic meters of manure per year. Liquid manure is rich in organic carbon, and nutrients such as nitrogen, phosphorous and potassium (Eghball and Power, 1999). A common treatment strategy for this waste is anaerobic digestion, which converts approximately 50% of the biomass into biogas that is used as a source of heat and electricity (De Meester et al., 2012). Liquid effluent from anaerobic digestion (known as digestate) contains large amounts of organics and nutrients. Traditionally, anaerobic digestate is disposed of in landfills or sent to a wastewater treatment plant (Arnon et al., 2008; Inoue et al., 2002). In addition to wasting valuable resources, this practice can result in soil and groundwater pollution, due to leaching (Hombach et al., 2003). Digestate may also be directly applied to agricultural land as fertilizer. Direct spreading of digestate on land is not recommended during winter, however, as excess precipitation can cause it to run off the land and contaminate local water sources. This need for seasonal application results in large storage requirements (Tambone et al., 2010). Further, since dairies tend to be clustered, this leads to the clustering of biogas plants and the oversupply of digestate in certain regions (Al Seadi et al., 2013). Thus, the digestate either needs to be transported to remote agricultural land that is nutrient deficient, or processed in a different way. Since digestate is 95% water, the transportation of this liquid product is economically and logistically complicated. Many biogas plants separate the solid and liquid fractions of digestate and then use the solid fraction as fertilizer, with the liquid fraction requiring further treatment (Al Seadi et al., 2013). This practice leaves two concentrated streams containing organic carbon and nutrients. However, crops do not require such large amounts of organic carbon to be provided through soil. Thus, a better utilization of the carbonaceous fraction found in digestate would be to valorize this carbon into a useful form of fuel, and in addition, recover the nutrients in a concentrated form that can be readily transported. One way to achieve both these goals along with producing a stream of treatable water is by the integration of two energy efficient processes; hydrothermal liquefaction (HTL) and membrane distillation (MD). A brief description of both these processes follows.

HTL is an attractive technology for the production of energy products and bio-based chemicals from high-water-content biomass (Angenent et al., 2017). The main advantage of HTL is the use of water as the reaction media. This is in contrast to conventional dry thermochemical processes (i.e., pyrolysis or gasification) where water has to be removed prior to the process (Peterson et al., 2008). Therefore, HTL offers opportunities for valorization of wet-waste streams, such as food waste and manure (Yin et al., 2010). HTL typically takes place over a

range of temperature (280–380 °C), pressure (7–30 MPa) and reaction time (10–60 min) conditions (Peterson et al., 2008). These conditions allow the production of bio-crude oil (liquid) and hydro-char (solid) products along with some biogas, all with higher heating values than the raw feedstock (Biller et al., 2013). HTL has been tested with a variety of biomass feedstocks, particularly in regard to the bio-crude oil and hydro-char products (Biller et al., 2015; Posmaniket et al., 2017a; Qian et al., 2017). In addition, the HTL process also produces a significant amount of an aqueous-phase product, traditionally considered a waste. One possibility of valorizing the HTL aqueous effluents is by considering it as a secondary feedstock for bioenergy production via anaerobic digestion and gasification processes (Elliott et al., 2015; Posmaniket et al., 2017b; Van Doren et al., 2017). Since the HTL aqueous effluents have resulted from a thermochemical process, they are sterile and hot, and therefore may be a feasible feed for MD processes. In this configuration, the residual heat present in the HTL aqueous effluent is used to drive the MD process, which uses thermal energy to separate volatiles (water, volatile organics) from non-volatiles (nutrients) (Alkhudhiri et al., 2012).

MD is a membrane-based water treatment method that uses a vapor-pressure gradient across a hydrophobic membrane as the driving force for the transport of water vapor (and other volatiles) across the membrane, while preventing liquid water (which contains the contaminants) from passing through the membrane (Alkhudhiri et al., 2012; Lawson and Lloyd, 1996). In MD, the vapor-pressure gradient is induced by a temperature gradient between the feed stream and the permeate stream, which are separated by the membrane itself. Because the process blocks liquid water from passing through the membrane, and because the driving force is not a pressure differential, MD is typically used for treating highly contaminated waste streams with low concentrations of volatile species (Curcio and Drioli, 2005). Membrane distillation faces several challenges such as membrane fouling, wetting, high energy requirements and the inability to separate volatile compounds (Curcio and Drioli, 2005). Fouling occurs when organic and inorganic materials in the feed deposit on the membrane surface, partially or completely blocking the passage of water vapor, which causes a decrease in the permeate flux (Dudchenko et al., 2014). Because MD relies on the prevention of liquid water from passing through the membrane, it is essential that the membrane is not wetted (i.e., allow the passage of liquid water through the pores) (García-Payo et al., 2000). Thus, operating conditions in the MD module have to be maintained such that transmembrane pressure does not exceed the liquid-entry pressure, defined as the minimum transmembrane pressure causing the water in the feed to enter the membrane pores (Goh et al., 2013). However, membrane wetting can also occur as a result of the deposition and accumulation of organic and inorganic species within the membrane's pores (Franken et al., 1987). For example, amphiphilic organic molecules can sorb onto the hydrophobic pores of the membranes, which creates a hydrophilic surface that can be readily accessed by contaminated liquid water (Franken et al., 1987). Once the membrane is wetted and contaminated liquid water passes into the permeate, the performance of the membrane rapidly plummets (Goh et al., 2013). Since the MD process relies on a thermal driving force, the process is considered highly energy intensive due to water's high heat capacity (Lawson and Lloyd, 1996). Thus, for MD to be economically feasible, it needs to be applied to either high-salinity brines or a waste (i.e., free) heat source needs to be available (Alkhudhiri et al., 2012).

Here, we report on the performance of an integrated energy-efficient process, which aims to convert the organic carbon contained in anaerobic digestate into bio-crude oil, while concentrating nutrients to produce a high-strength fertilizer and generating a stream of water that can be readily disposed. The integrated approach described in this paper is based on a two-step process, where first the digestate is processed using hydrothermal liquefaction (HTL) to produce valuable hydrocarbons (energy), and then the aqueous effluent from the HTL process is treated using membrane distillation (MD) produce two

streams: (1) a concentrate nutrient stream (nitrogen and phosphorous) that can be used as high quality fertilizer, and (2) a stream of water devoid of organic matter and nutrients (ideally). In this paper, we focus on the performance of the MD part of the system. Heated HTL aqueous effluent is used as a feed stream for MD, with vapor from the feed passing through a hydrophobic membrane, while nutrients and organic carbon are retained on the feed side. This MD process produces two distinct streams: a retentate stream rich in organics and nutrients, and a permeate stream of water containing any residual volatile organic compounds (VOCs) found in the HTL aqueous effluent. MD performance was followed in terms of flux and wetting, while all system streams (feed, permeate and retentate) were extensively characterized in terms of water quality characteristics, with a particular emphasis on the concentration and speciation of nutrients and carbon. HTL effluent derived from food waste and dairy manure was used as the feed for the MD process, and we investigated how these two feedstocks impact membrane performance and the water quality of feed and two membrane product streams. Because the aqueous HTL product streams contain large amounts of volatile organic compounds (VOCs), we expect a fraction of the VOCs present in the feed to pass through to the permeate (Posmaniket et al., 2017b). To characterize the VOCs within each stream, volatiles were collected and then analyzed by two-dimensional gas chromatography with detection by time-of-flight mass spectrometry (GC × GC-TOFMS system). While the motivation for this work is the potential use of residual waste heat from the HTL process to drive MD, in this work, we did not use residual heat, instead using traditional heating methods to provide the driving force for separation.

2. Materials and methods

2.1. Hydrothermal liquefaction and phase separation

The HTL batch reactor used in this study has been previously described in detail (Posmaniket et al., 2017a). Briefly, a 500 mL stainless steel vessel (Model 4575 Parr Instruments Co., Moline, IL) was loaded with 200 mL of biomass and water mixture. Carbohydrate-rich food waste (herein referred to as 'food waste') and anaerobically digested cattle manure (herein referred to as 'manure') were used as biomass feedstocks. Food waste was collected from Cornell University dining halls (Ithaca, NY) and characterized in the lab (fruits 15 wt%, vegetables, 47 wt%, grains and breads, 38 wt%). Digested cattle manure was taken from an anaerobic digester located on a dairy farm (Sunnyside farm, Scipio Center, NY). The food waste and manure had average solids contents of 10 and 8 wt%, respectively. The initial solids concentrations loaded to the reactor for all experiments were 5 wt% for food waste and 4 wt% for manure, using Milli-Q water as reaction medium. Some pretreatment was required to ensure that the feed was well mixed and with relatively small particle sizes. After loading the feed mixture, the HTL reactor was closed and the system was purged with nitrogen and pressurized to an initial pressure of 2.5 MPa. The reaction mixture was stirred (100 rpm) using a magnetic agitator. The temperature was set to 300 °C and the reaction time was set to 60 min. The reaction period started when the temperature reached 80 °C, followed by a heating ramp (from 80 to 300 °C) of approximately 20 min and was completed after an additional 40 min of heating at 300 °C, when the product was collected.

The liquid product from the reactor was collected through a tube-in-tube heat exchanger connected to the reactor's outlet to rapidly quench the liquid effluent and to avoid the cooling ramp. After collecting the liquid product, the heater was turned off and the reactor was cooled down, following cleaning and removal of any solid residue. Phase separation was conducted using a multi-stage procedure: 1) gravimetric filtration using a Whatman #1 filter paper to separate the solids; 2) separation of the polar and non-polar liquids using solid-phase extraction (SPE) tubes (Sigma Aldrich, St. Louis, MO); and 3) filtration of the aqueous phase via 0.45 µm membrane filter.

Based on standard HTL operating temperatures, the amount of energy that can be obtained from cooling the heated HTL effluent with a reaction temperature of 300 °C is 1229.1 KJ/kg. This energy can be recovered using heat exchangers and fed back to heat this stream before it enters the MD system. Assuming 50% efficiency in heat recovery (a conservative measure) and a water heat capacity of 4,180 J/(kg × °K), the feed could be heated by nearly 150 °K, which is more than sufficient (and in fact, is too hot for MD).

2.2. Membrane distillation system design and procedure

A flat sheet flow cell setup was used in this study, where the flow cell was made out of nylon 66 (McMaster-Carr). Channel dimensions were 8 cm × 5 cm, with a channel height of 4 mm. The feed and permeate channels were identical. Teflon tubing was used for all process streams. In our setup, the feed was heated by an external source because HTL was carried out at a different location (Cornell University, Ithaca, NY). The feed reservoir was immersed in a bath of silicon oil and heated using an immersion heater. A proportional-integral-derivative (PID) controller maintained the feed inlet temperature at a steady value. Gear pumps (Cole Palmer) were used on the feed and permeate side. A hydrophobic polypropylene membrane (3M; with a pore diameter of 0.59 µm and a thickness: 110 µm) was used for separation. The weight of the permeate tank was continuously measured using a precision balance (Scientific Industries). The system was designed using open-source hardware (Arduino) and open-source software (Python) (Slade and Jassby, 2016).

A 300 mL glass jar was used as the feed reservoir. Three holes were drilled through the cap to allow for the inlet, outlet and temperature probe, with 250 mL of HTL effluent measured into the jar. After the sample reached the desired temperature (60 °C), the pumps were started with flow rates of 1 L/min, resulting in a crossflow velocity of 8 cm/s. The feed solution was continuously passed through the flow cell and allowed to concentrate and reduce in volume, as vapor from the feed passed into the permeate stream through the membrane. A 2-L glass bottle was used as the permeate reservoir with two holes drilled through its cap for inlet and outlet. The reservoir was initially filled with 600 mL of deionized water (DIW). This was flowed through the permeate side of the flow cell, collecting vapor from the feed side, causing the permeate reservoir to increase in volume. The permeate stream was cooled using two miniature fan cooled heat sinks (McMaster-Carr) to maintain permeate side temperature at 21 °C. The experiment was continued for approximately 2.5 h, until the feed volume reached 62 mL, corresponding to 75% water recovery, and the permeate volume reached 788 mL. 10 mL of permeate was extracted in 30 min intervals to monitor the conductivity and chemical oxygen demand (COD) of the liquid. A new membrane was used for each experimental run.

2.3. Fouling experimental procedure

Fouling was evaluated by monitoring changes in membrane flux, which was measured by continuously recording the weight of the permeate tank. MD runs were conducted using consistent hydrodynamic conditions, temperature gradients, and membrane materials to ensure that only the feed content impacted membrane fouling (Schofield et al., 1990). Scanning electron microscope (SEM) images and X-ray photoelectron spectroscopy (XPS) analyses were carried out to perform membrane autopsies of the fouled membranes.

2.4. Membrane wetting evaluation

The conductivity and COD of the permeate were measured every 30 min. To determine whether membrane wetting occurred as a result of the treatment of the HTL effluent, the feed solution was switched to a 1 M NaCl solution, and the permeate conductivity was monitored for

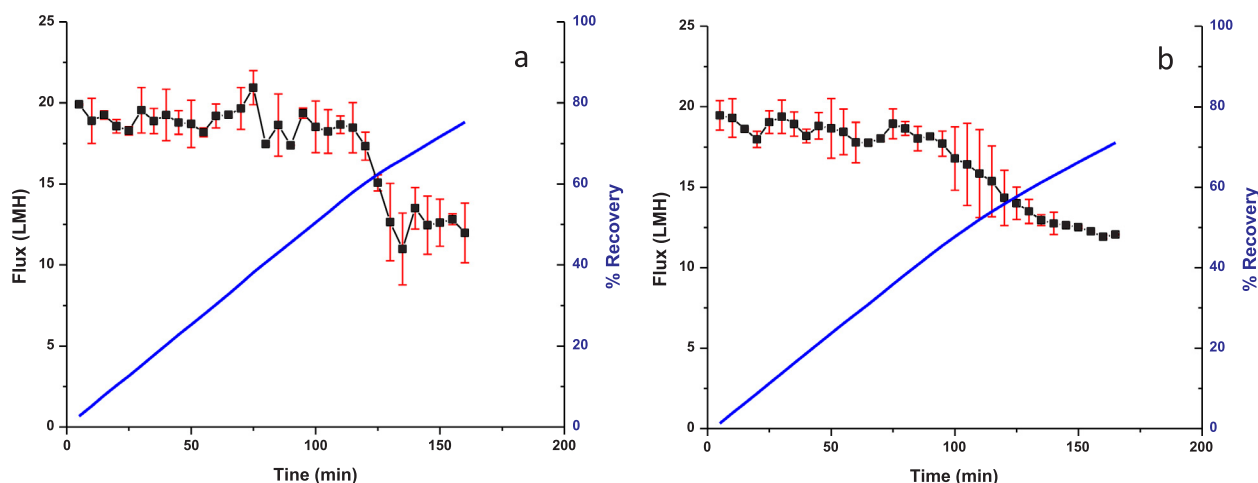


Fig. 1. Membrane flux (in black) and water recovery (in blue) of MD system treating HTL effluents derived from (a) food waste, and (b) manure. Values represent the average two replicates \pm 95% confidence intervals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

30 min, with measurements taken every 5 min. It was expected that if membrane wetting did occur, Na^+ and Cl^- ions would pass through the membrane, which would dramatically increase the conductivity of the permeate.

2.5. Volatiles analysis

To characterize the VOCs within each sample stream (feed, permeate and retentate), a custom-built purge-and-trap apparatus was used (Supplementary Material). N_2 gas was bubbled through 1 mL of sample in a round bottom flask for 30 min at a flow rate of 14 mL/min. An additional dry purge flow of 36 mL/min was mixed with the purge flow to reduce the humidity of the gas sample. The purged VOCs were trapped on a dual-bed sorbent tube containing Tenax TA and Carbograph 1 (Camsco, Houston, TX). Background samples were collected to eliminate any compounds present in the setup. Each sample was collected and run in duplicate. However, one sample of manure-retentate was lost due to technical difficulties during analysis. Flasks were cleaned thoroughly with DIW and methanol and then baked at $\sim 140^\circ\text{C}$ between sample collections. The sorbent-tube samples were thermally desorbed at 300°C using a TurboMatrix 650 automated thermal desorber (ATD, Perkin Elmer, Waltham, MA). Internal standards (1,2-dichlorobenzene- d_4 and 1-bromo-4-fluorobenzene) were added to each tube immediately prior to analysis. A fraction (4.6%) of the desorbed material was injected into a two-dimensional gas chromatograph with detection by time-of-flight mass spectrometry (GC \times GC-TOFMS, Pegasus 4D, Leco Corp., St. Joseph, MI). The column set included a DB-VRX primary column (30 m, 0.25 mm ID, 1.4 μm film, Agilent Technologies, Santa Clara, CA) and Stabilwax secondary column (1.5 m, 0.25 mm ID, 0.5 μm film, Restek Corp., Bellefonte, PA). The primary oven was held at 40°C for 6 min, followed by a ramp at $4^\circ\text{C}/\text{min}$ to 210°C with a final hold of 5 min. The secondary oven temperature was offset $+15^\circ\text{C}$ relative to the primary oven and the modulator temperature was $+20^\circ\text{C}$ relative to the secondary oven. The modulation period was 5 s. The column flow rate was 1.3 mL/min with helium carrier gas. GC \times GC-TOFMS data were processed using GasPedal (Decodon GmbH, Greifswald, Germany), an image-based GC \times GC data analysis package (Schmarr and Bernhardt, 2010). Tentative compound identifications were determined, where possible, based on NIST mass spectral library matches and retention behavior. The abundance of each observed peak within a given sample was normalized by the sum of the peak abundances for the two internal standards to account for any run-to-run variability. The mean and standard deviation for each analyte were then determined for each set of

duplicate samples.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.biortech.2018.07.064>.

2.6. Nutrient analysis procedures

COD, VOCs, and different forms of nitrogen and phosphorus were measured in every stream of the process. Mass-balance calculations were performed to determine the presence and form of these nutrients in each stream. Samples were diluted with DIW to fit in the appropriate measurement ranges. Nitrate was tested using the NitraVer X Nitrogen-Nitrate Reagent Set, HR (Hach, Loveland, CO), which is capable of detecting nitrate in the range 0.2–30 mg N/L. Ammonium was measured using the HACH TNT 831 testing kit, which can measure ammonium in the range 1–12 mg N/L. HACH TNT 845 was used for testing orthophosphate and total phosphorous in the range of 6–60 mg P/L. COD was measured using the high-range COD kit from HACH which is capable of measuring in the range of 3–150 mg/L. Total nitrogen (TN) measurements were done using the Total bound Nitrogen (TNb) module of the Aurora 1030C Combustion Total Organic Carbon (TOC) analyzer.

3. Results and discussions

3.1. Membrane distillation performance

HTL effluent (either from food waste or manure, maintained at 60°C) was used as feed for the MD system, with the MD process operating in a cross-flow configuration. In these experiments, MD permeate was not returned to the feed tank, and the feed was allowed to concentrate with time. For both feedstocks, the initial flux was approximately $20 \text{ L}/\text{m}^2 \text{ h}$ (LMH) (Fig. 1). When food-waste-derived HTL effluent was used in the MD system, the flux was relatively stable (with mild fluctuations) until water recovery reached 60% (Fig. 1a), at which point flux dropped by 40%, stabilizing at an average of 12 LMH for the duration of the experiment (until water recovery reached 75%). When manure-derived feed was treated by the MD system, membrane flux experienced a slow decline (from 19 to 17 LMH) until recovery reached approximately 40%, at which point flux dropped at a faster rate, reaching a value of 12 LMH when recovery reached 75% (Fig. 1b). The decline in membrane flux can be attributed to membrane fouling, mainly by organic compounds and minerals; biofouling is not expected to be an issue considering the high feed temperatures used in the study (60°C). Indeed, based on SEM image analysis of the fouled membranes no bacteria were observed on the fouled membrane surface.

(Supplementary Material). As the feed becomes more concentrated, due to continuing water recovery, membrane fouling becomes more pronounced; this is caused by accelerated deposition of foulants, such as organic molecules and particulate matter onto the membrane surface, which blocks the flow of water (Tang et al., 2017). Membrane autopsies of the fouled membranes were performed using SEM (a qualitative measure) and XPS (a quantitative measure). SEM images reveal a thick coating on the fouled membrane surface (Supplementary Material). For the membrane fouled with food waste-derived HTL effluent, the fouling layer appears more heterogeneous, with some crystal-like structures. The membrane fouled by manure-derived HTL effluent also shows some crystal-like structures, but far fewer (Supplementary Material). Overall, the fouling layer on both membranes appears to be largely composed of organic matter that is evenly deposited on the membrane surface; critically, no bacteria are visible on the membrane surface. This is not surprising considering the high temperatures achieved during the HTL process, which are likely to destroy any bacteria in the feed. Furthermore, the high temperature of the MD feed would discourage any bacterial attachment/growth due to microbial inactivation (Ahring et al., 2001). XPS analysis of the fouled membrane surface showed that for both feed streams the fouling layer is primarily composed of carbon (75% and 64% for the food waste and manure-derived feed, respectively) and oxygen (17% and 21% for the food waste and manure-derived feed, respectively), indicating that the fouling layer is primarily of organic nature (Supplementary Material). The membrane fouled with manure-derived HTL effluent had measureable amounts of phosphorous in the fouling layer (< 2%) and the membrane fouled with food waste-derived HTL effluent had very little calcium (0.25%) and phosphorus (0.66%). It is possible that some minor amount of calcium phosphate did form on the membrane surface, which contributed to the flux decline. However, considering the small amounts of calcium and phosphorous found, and the similarity in the flux decline behavior when treating the two feed streams, we speculate that inorganic scaling plays only a very minor (if any) role in membrane fouling under the conditions tested in our work. Although the flux declined as water recovery increased, it never dropped to levels that were unsustainably low, indicating that MD is a viable method to treat HTL effluent, likely not requiring excessively large membrane areas to compensate for very low fluxes.

3.2. Membrane wetting results

A critical aspect of MD performance is whether the membrane becomes wetted by dissolved species from the feed stream, leading to

catastrophic failure of the separation process. Membrane wetting can result in the transport of non-volatile species into the permeate stream, and defeats the purpose of the MD process, which is designed to allow the passage of volatile compounds (ideally, only water). Membrane wetting was evaluated by measuring the conductivity and COD concentrations in the permeate for both food waste and manure feed HTL effluent (Fig. 2). An increase in conductivity or COD in the permeate could be caused by membrane wetting or by volatile compounds being transferred across the membrane. Both conductivity and COD levels increased over time in the MD permeate when treating food waste-derived HTL effluent (Fig. 2a). Conductivity reached a level of 18 $\mu\text{S}/\text{cm}$ after 165 min (75% recovery), while COD concentrations reached a level of 148 ppm at the end of the experiment. For the manure-derived HTL effluent (Fig. 2b), conductivity increased linearly, with an endpoint of 63 $\mu\text{S}/\text{cm}$; COD also increased steadily, reaching 1042 ppm at the end of the experiment (160 min), at which point water recovery was 75%. Interestingly, the conductivity and COD concentrations behaved similarly, indicating that conductivity potentially increased as a result of VOCs passing through the membrane into the permeate, rather than non-volatile salt species (which would indicate membrane wetting).

Given the elevated COD and conductivity measurements in the permeate, an additional test was performed to verify whether membrane wetting did indeed occur. In this test, the feed stream was switched to a 1 M NaCl solution after the sample processing run (treating manure-derived HTL effluent) using the same membrane; this membrane was selected since the treatment of manure-derived HTL effluent exhibited a larger increase in permeate conductivity and COD concentrations. It is expected that if the membrane was indeed wetted by species in the HTL effluent, then Na^+ and Cl^- ions would readily pass through the membrane and dramatically increase the permeate conductivity. However, no increase in the conductivity of the permeate was observed over 30 min, indicating that membrane wetting did not occur (Fig. 2b, inset).

Thus, the observed increase in the conductivity of the permeate streams from HTL effluents being treated by MD can be attributed to VOCs passing through the membrane, and not to membrane wetting; some of these volatiles, such as organic acids, can contribute to the increase in conductivity. Critically, the increase in conductivity, while measurable, was very small (< 70 $\mu\text{S}/\text{cm}$) indicating that relatively few ionic species crossed the membrane. For reference, the conductivity of drinking water ranges between 50 and 500 $\mu\text{S}/\text{cm}$. These results demonstrate that MD using a polypropylene membrane is a feasible treatment method for HTL effluent, as these membranes are resistant to wetting (up to 75% water recovery in our experiments).

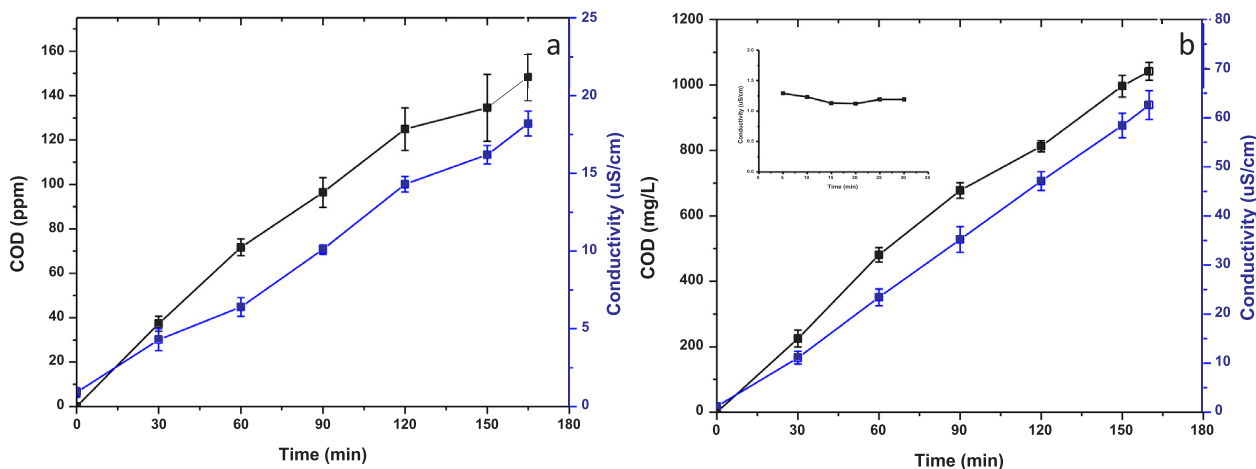


Fig. 2. COD (in black) and conductivity (in blue) of MD permeate over time when treating HTL effluent generated from (a) food waste and (b) manure. Values represent an average of two replicates \pm 95% confidence intervals. Inset: Permeate conductivity with 1 M NaCl solution used as feed, following the manure experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

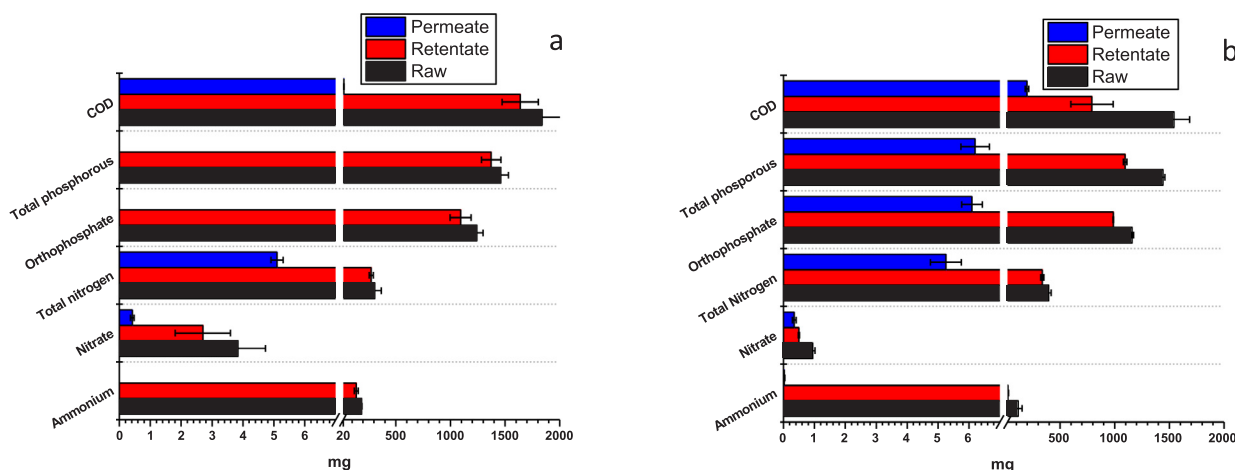


Fig. 3. Mass-balance analysis for COD, ammonia, nitrate, total phosphate, and orthophosphate in the raw, permeate and retentate streams for the food waste sample (a) and the manure sample (b). Values represent an average of two replicates \pm 95% confidence intervals.

3.3. Nutrient analysis

Detailed mass balances for COD, phosphorous (orthophosphate and total P), and nitrogen (TN, ammonium and nitrate) were carried out on the three process streams (HTL effluent, MD permeate, and MD retentate (Fig. 3). Where applicable, nutrient concentrations reported below for the permeate streams have been corrected for dilution (see Section 2.2) and therefore reflect the concentrations of the pure permeate fraction.

Large concentrations of total phosphorous were observed in the HTL effluent, with concentrations of 5900 ± 300 mg/L and 5800 ± 100 mg/L for food waste and manure HTL effluent, respectively (Fig. 3). The majority of this phosphorous was in the form of orthophosphate – 85% and 80% for food waste and manure-derived effluent, respectively. We speculate that the residual phosphorous (i.e., the difference between total phosphorous and orthophosphate) was in the form of organic phosphorous. Once HTL effluent from food waste was processed by MD, no phosphorous was detected in the permeate (Fig. 3a). However, when manure-generated HTL effluent was treated using MD, a small amount of phosphorous (32 ± 1.6 mg/L), in the form of orthophosphate, was found in the permeate stream (Fig. 3b). It is unclear how orthophosphate passed through the membrane, although a possible reason is some minor membrane wetting, which could lead to the passage of non-volatile species into the permeate. Although the membrane wetting test carried out showed that there was no bulk wetting, there were minor fluctuations in permeate conductivity. This could indicate minor membrane wetting. For both food-waste and manure-derived HTL effluent, the vast majority (100% and 99.5% for food waste and manure, respectively) of total phosphate and orthophosphate remained in the retentate stream, with final concentrations of orthophosphate being $18,000 \pm 2000$ mg/L and $15,800 \pm 50$ mg/L for food waste and manure, respectively (Fig. 3).

Whereas phosphorous concentrations in the food waste and manure-derived samples were similar (1470 ± 70 mg and 1440 ± 20 mg, respectively), ammonium concentrations were significantly different (Fig. 3). Both food waste-derived HTL effluent and manure-derived HTL effluent had high ammonium concentrations (750 ± 10 mg/L and 500 ± 100 mg/L, respectively). In both cases, little to no ammonium was detected in the permeate, with non-detect levels in the food-waste-derived HTL effluent, and 1.0 ± 0.5 mg/L in the manure-derived HTL effluent. In both HTL effluents, very little nitrate was detected (< 4 mg/L), with sub-ppm levels detected in the permeate in both cases (Fig. 3). Total nitrogen concentrations in the food waste and manure HTL effluents were 1200 ± 200 mg/L and 1580 ± 92 mg/L, respectively. The difference between total nitrogen and inorganic nitrogen

(ammonium and nitrate) can be attributed to organic nitrogen; because nitrate concentrations were very low, we speculate that the same would be true for nitrite. Organic nitrogen accounted for 38% and 70% of total nitrogen for food waste and manure HTL effluent, respectively. A small amount of the total nitrogen from each effluent (27 ± 1 mg/L, and 27 ± 3 mg/L for food waste and manure, respectively) was detected in the permeate streams. Since nitrate and ammonia in the permeate from both samples was negligible, this was almost entirely organic nitrogen (see below for detailed analysis of measured nitrogen-containing volatile species).

High COD values were measured in the HTL effluent generated from both sources (7300 ± 800 mg/L and 6100 ± 600 mg/L for food waste and manure, respectively) (Fig. 3). However, when the HTL effluent from both sources was treated by MD, very different results emerged. Specifically, COD concentrations in the permeate stream generated from food-waste HTL effluent were relatively low (140 ± 10 mg/L), indicating that relatively low concentrations of VOCs were present in the HTL effluent (Fig. 3a and b). In contrast, high COD concentrations (1100 ± 80 mg/L) were measured in the permeate from manure HTL effluent, indicating the presence of large concentrations of VOCs (Fig. 3b). The differences in the MD performance can potentially be attributed to the different reaction chemistries occurring during the HTL process, which are due to the nature of two feedstocks used in this study (Posmaniket et al., 2017c). Manure is a lignocellulosic biomass, rich in cellulose, hemicellulose and lignin (Ward et al., 2008); whereas in food waste, fruits and vegetables contribute fibers composed primarily of cellulose, hemicellulose and pectin (Müller-Maatsch et al., 2016). The structural differences between cellulose, hemicellulose, lignin and pectin may explain the differing chemical pathways during the HTL process, as their primary hydrolysis products are different. Whereas cellulose and hemicellulose are hydrolyzed mainly to hexoses and pentoses, lignin forms mostly phenolic and alcoholic compounds, and pectin forms primarily galacturonic acid (Cantero et al., 2015; Müller-Maatsch et al., 2016). In addition, manure has high alkalinity, due to its high ammonia content (Chen et al., 2008), which leads to HTL reactions at high pH (9.1 ± 0.3). In contrast, food waste has low alkalinity, resulting in a lower pH of the reaction (4.0 ± 0.1) because of sugar degradation to short carboxylic acids during HTL (Posmaniket et al., 2017a). Combined, these differences lead to different components present in the HTL effluents, which could potentially impact membrane performance (e.g., fouling) and lead to the observed differences in the VOCs that pass through the membrane during the distillation process (see next section). While the US EPA has no specific guidelines for COD concentrations in drinking water, the levels measured here are too high for the water to be considered as a viable source of drinking water.

Instead, this filtered water could be sent to a wastewater treatment plant or used for an industrial process that needs a low salinity feed stream with high COD, as these compounds are easily degraded through aerobic microbial processes typically used during wastewater treatment (Fritsche and Hofrichter, 2000).

The high concentration of ammonium in the retentate stream makes this stream attractive as a concentrated fertilizer (El Diwani et al., 2007). In addition, the retentate generated from both feed streams would serve as a good source of phosphorous fertilizer; orthophosphate is the form of phosphorous most available to plants and therefore most useful as a fertilizer (De-Bashan and Bashan, 2004). Since the MD process removed 75% of the water from the HTL effluent, the cost of transporting the retentate stream would be significantly reduced.

3.4. Analysis of volatile compounds in the three process streams

High concentrations of organics were measured in the MD permeate, therefore, a detailed compositional analysis was performed on feed, retentate, and permeate samples using GC × GC-TOF-MS. A total of 103 compounds were identified in these streams (Supplementary Material), which accounted for 96% of the total normalized abundance. We limit our focus to the top 10 compounds based on the peak-normalized volume detected in the feed samples, which account for 55% and 70% of the total species in the food waste and manure HTL effluents, respectively (Fig. 4). The results from running DIW water through the MD system showed negligible volatile content; these samples were averaged along with purge-and-trap samples to determine background. The background-normalized volume was subtracted from the samples before plotting them.

Because the HTL effluent, retentate and permeate samples spanned such a wide range of concentrations, accurate quantitative measurements could not be made for these compounds; specifically, the most abundant compounds in the HTL effluent and retentate streams exceeded the linear range of the instrument and thus their relative abundances should be considered as lower limits. Fig. 4 shows the relative concentration of the top 10 compounds in each stream.

A major portion of the volatiles detected were aldehydes and ketones, with butanone, acetone, cyclopentanone and 2-Methyl-2-cyclopenten-1-one being the most abundant ketones detected. Some of these compounds are known to be toxic, making this process stream somewhat hazardous (Gollakota et al., 2017; Playne and Smith, 1983). Butanone was the single most abundant compound in both samples; butanone is naturally found in biomass (some fruits and vegetables) in small amounts. Butanone previously has been reported as one of the major volatiles in HTL effluent derived from algae. A significant amount of acetone was observed in both samples; it was the third most common volatile in the manure-derived HTL effluent and the ninth most common in the food-waste-derived HTL effluent. Acetone is considered to be only slightly toxic and non-carcinogenic, but it is highly volatile. Ketones are formed by various processes in the body, and the body is capable of breaking down these naturally formed ketones. Large ketone concentrations (> 240,000 mg/L) can inhibit fermentative microorganisms (Playne and Smith, 1983). Thus, MD permeate generated from HTL effluent is not anticipated to be a valuable feed stream for fermentation processes (Playne and Smith, 1983). Acetic acid methyl ester was the 9th most abundant compound observed in all the manure-derived streams, however, the amount observed in the food-derived streams was not significant. A number of aldehydes (2-Methylpropanal,

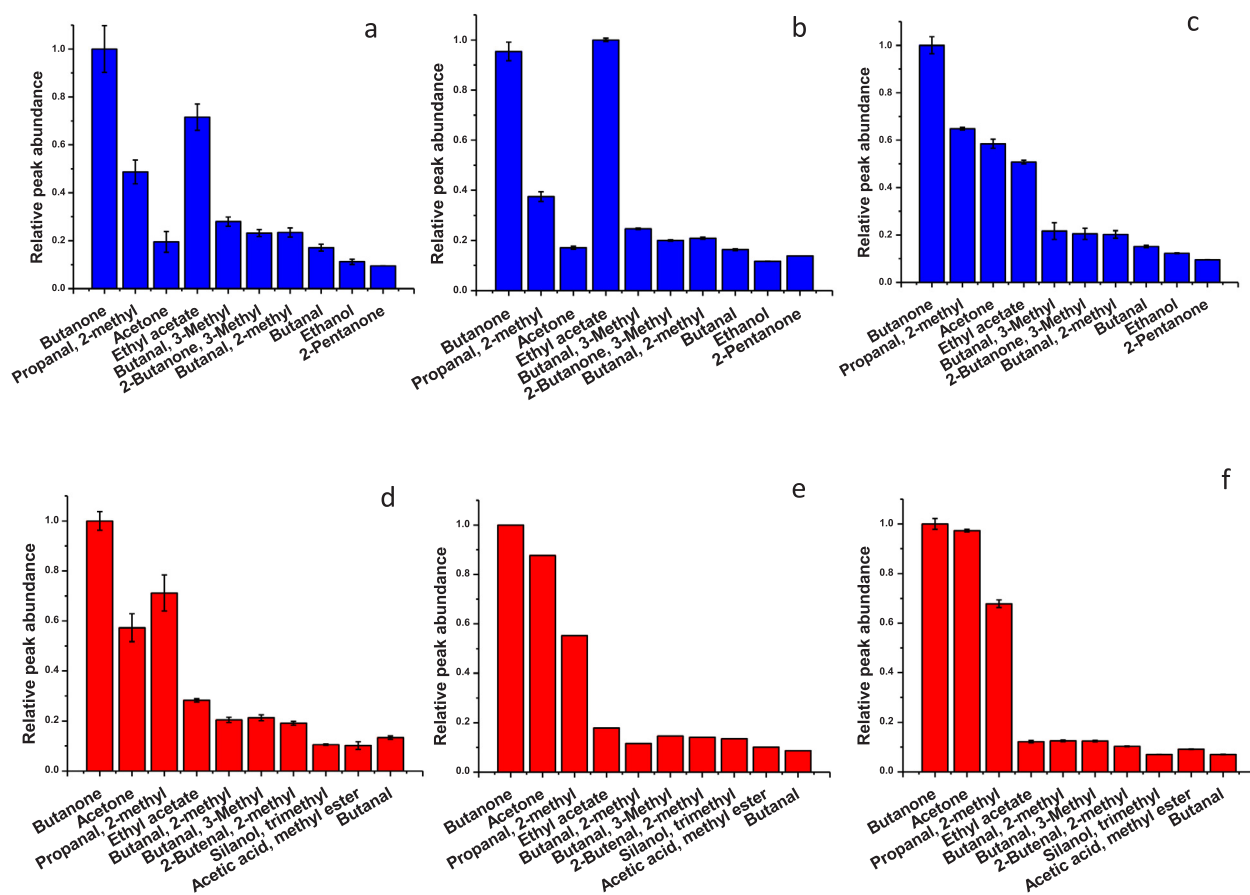


Fig. 4. Relative peak abundances for the top ten compounds based on their presence in the permeate stream in the (a) HTL effluent, (b) retentate, and (c) permeate streams of the food waste sample, and (d) HTL effluent, (e) retentate, and (f) permeate streams of the manure sample. Values represent an average of two replicates \pm 95% confidence intervals.

3-Methylbutanal, 2-Methylbutanal, 2-Methyl-2-butenal, butanal) were also detected in these samples. Aldehydes are commonly observed in the aqueous fraction resulting from HTL processing of biomass (Gollakota et al., 2017). Ethyl acetate was found in significant amounts in both samples. Pyrazine (C₄H₄N₂), a nitrogen-containing compound, was observed in the manure derived HTL effluent. It is an aromatic organic compound, found in some herbs. It can also be produced by the degradation of proteins present in the wastes during HTL. Although very little pyrazine was detected in the permeate stream of the manure sample, it is possible that it is responsible for the observed total nitrogen detected there, although the GC × GC method was not able to detect other potentially important forms of organic nitrogen such as amines.

4. Conclusions

Here we investigated the combination of HTL and MD. Aqueous HTL effluent was further treated using MD, generating liquid fertilizer containing high concentrations of nitrogen and phosphorous as the retentate stream, and high concentrations of VOCs in the permeate stream, making further treatment necessary. We demonstrated that polypropylene membranes could be effectively used up to a water recovery of 75%. While membrane fouling did occur, flux was maintained at high levels (> 10 LMH). Residual waste heat from HTL could be used to drive MD, which would dramatically reduce the cost of the MD process and increase overall process sustainability.

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