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Innovative ammonia recovery and biogas enhancement via direct contact membrane distillation in thermophilic anaerobic digestion of mixed sludge

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ABSTRACT

The effect of membrane distillation (MD) on both NH_3 recovery and anaerobic digestion during the treatment of urban wastewater mixed sludge was studied in a 3 L thermophilic continuous stirred tank reactor combined with a membrane-based module for extraction. A hydraulic retention time of 20 days was used to operate the thermophilic anaerobic digester at 55 °C, while the flat sheet PTFE membrane module was continuously operated at 0.25 L min^{-1} of liquid recirculation rates. MD was able to progressively reduce the total ammoniacal nitrogen (TAN) concentration from 0.4 ± 0.2 to 0.1 ± 0.1 g TAN L^{-1} after 40 operating days. The CH_4 yield increased by 3-fold as a result of NH_3 extraction. Similarly, chemical oxygen demand and volatile solids removal efficiencies increased by 1.8-fold and 1.4-fold, respectively. Interestingly, the reduction in TAN concentration led to a complete assimilation of acetic and propionic acid.

1. Introduction

As the world's population keeps increasing, the generation of organic waste is correspondingly rising. Among these wastes, sewage sludge stands out as a major source in cities, comprising the semi-solid residual material produced during the treatment of domestic wastewater in cities and industries [1]. In this context, anaerobic digestion (AD) holds significant potential to contribute to bioenergy production from waste biomass, aligning with the principles of a circular economy [2]. Thermophilic anaerobic digestion (TAD) has been identified as a solution to the limitations typically encountered in conventional mesophilic anaerobic processes. The main limitations are that mesophilic digestion has a lower methane production efficiency, which limits the energy recovery potential and also has slower degradation rates which might requires larger reactor volumes [3]. Nevertheless, TAD supports faster kinetics, increased renewable energy production, and an environmental pollution reduction [4]. Indeed, TAD requires shorter retention times and smaller reaction volumes than mesophilic anaerobic digestion, achieves a higher yield of biogas with lower H_2S concentrations, and a greater reduction in volatile solids (VS) [5]. However, TAD has a limited potential to reduce the levels of phosphorus and nitrogen from wastewater and easily cause inhibition under elevated concentrations of ammonia and elevated pH levels [6]. Indeed, total ammoniacal nitrogen (TAN) concentrations in the range of 1700 to 14,000 mg N L^{-1} can lead to a 50 % reduction in methane production during TAD. Correspondingly, it has been reported that ammonia nitrogen concentrations exceeding 400 mg N L^{-1} induce inhibitory effects on the microbiology of AD processes [7].

Ammonia (NH_3) is an integral part of the nitrogen cycle, crucial for life, and is produced during organic matter decomposition in AD. NH_3 is highly water-soluble, forming ammonium hydroxide (NH_4OH) in aqueous solutions. It is the second most produced synthetic chemical globally, with over 90 % of its consumption derived from a catalytic process that combines nitrogen and hydrogen [8]. Despite its importance, uncontrolled NH_3 emissions can significantly harm ecosystems and human health [9]. NH_3 emissions are crucial in the formation of small particulates ($PM_{2.5}$), which contributes to air pollution, and play a key role in nitrous oxide (N_2O) atmospheric formation, a greenhouse effect gas with a high potential for global warming. N_2O also contributes to air pollution, which has been linked to respiratory problems and an increased likelihood of cancer. This dual impact on the climate and human health underscores the environmental risks associated with

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ammonia emissions [10]. Nearly 90 % of global ammonia emissions are generated by agricultural activities, such as the application of ammonia-based fertilizers and the uncontrolled management of animal manure [11]. Under the European Directive 2016/2284, NH_3 emissions must be reduced by up to 3 % during the period from 2020 to 2029 (relative to 2005 levels), while from 2030 onward, the required reduction target 16 % [12]. In this context, the effective recovery of NH_3 from wastewater can substantially reduce consumption of energy for the produced and removed nitrogen, thus the reliance on synthetic methods for nitrogen fixation. Additionally, the production costs may be compensated the recovered by-products economic value [13].

Over the past few decades, multiple techniques have been investigated for ammonia recovery from wastewater. These methods include biological treatments, electrochemical approaches, adsorption, ion exchange, chemical precipitation, and air-steam stripping [14]. Biological treatment faces limitations due to the toxic effects of free ammonia on microorganisms, which inhibit activity of microbes [15]. Furthermore, most research on biological technologies has aimed on ammonia removal as N_2 rather than the recovery of nitrogen [16]. Electrochemical methods for NH_3 recovery demand a constant high-power source and substantial electricity consumption, making them impractical for large-scale applications [17]. Adsorption-based recovery, issues such as selective adsorbent regeneration and adsorption pose significant threats [14]. Chemical precipitation, which recovers ammonia as magnesium ammonium phosphate, requires large quantities of phosphorus and magnesium reagents, leading to high operating expenses [18]. Additionally, the magnesium ammonium phosphate complex composition hinders purification or its direct use as a slow-release fertilizer [19]. Stripping methods often result in ammonia gas spillage, causing secondary environmental pollution. Moreover, maintaining and repairing large equipment like stripping towers is demanding [20]. Consequently, engineering of unconventional processes is essential to achieve efficient and sustainable ammonia recovery from wastewater.

Membrane distillation (MD) is an emerging technique for NH_3 recovery, serving as a hybrid process that integrates the benefits of membrane separation and thermal evaporation in one unit [21]. MD derives from its similarity to conventional distillation, as the process relies on energy to supply the latent vaporization heat, enabling separation under the equilibrium of vapor-liquid conditions [22]. MD operation is induced by a partial pressure gradient created by the difference in temperature maintained on the microporous membrane's sides [23]. Separation occurs because the membrane material is hydrophobic, meaning its surface resists being wetted by liquid water up to a certain threshold known as the entry pressure of liquid. This threshold is set by the properties of both the membrane and the solution, enabling only water vapor to flow through the pores of the membrane [24]. To overcome the issue of membrane wetting, a growing body of research has demonstrated that enhancing membrane hydrophobicity is an effective approach to improve wetting resistance. The wettability of a membrane is primarily influenced by its surface roughness and surface energy. Consequently, most membranes used in MD are fabricated from polymers with inherently low surface energy [25,26]. Among the different configurations of MD, Direct Contact Membrane Distillation (DCMD) is the most well-known for NH_3 recovery considering ammonia is both a valuable resource and a pollutant [27]. DCMD entails close contact between the warm feed and the cold permeate across a hydrophobic microporous membrane. This setup establishes a gradient of vapor pressure, allowing low vapor pressure liquids, such as water, to selectively pass through to the permeate side which is colder and also the transport of NH_3 by processing anaerobic effluents [28]. Testing membranes for ammonia extraction in situ can improve AD by continuously eliminating ammonia from the system, reducing its inhibitory impact on microbial activity [29].

As NH_3 accumulation presents a major challenge to the efficiency of TAD, there is an increasing need for effective in situ NH_3 recovery strategies to enhance process stability and methane production. In this study, the operation of a continuous stirred tank reactor (CSTR) combined with a DCMD module, operating under a temperature gradient of 20 °C, was evaluated during the TAD of mixed sludge. The novelty lies in evaluating the continuous performance of this hybrid system over 103 days, emphasizing on TAN removal, organic matter degradation, and enhanced CH_4 productivity yields.

2. Materials and methods

2.1. Substrate and inocula

The anaerobic mixed sludge (AMS) was collected in Valladolid (Spain) from the municipal Wastewater Treatment Plant (WWTP) and maintained at 4 °C until use, with a storage duration not exceeding 30 days. The thermophilic inoculum was collected from the full-scale digester system of the selectively collected organic urban waste of San Sebastian (Spain), which was mixed with a mesophilic anaerobic inoculum from a digester of Valladolid WWTP. The main physicochemical parameters are described in Table 1.

2.2. Experimental set-up

A 3 L CSTR in a temperature- controlled room (maintained at 35–37 °C) with magnetic stirring set at 180 rpm, (Fig. 1) (Fig. S1). To tangentially recirculate the anaerobic culture broth from the thermophilic CSTR (55 °C), a peristaltic pump (Watson Marlow 520, Spirax-Sarco Engineering plc, United Kingdom) at 0.25 L min^{-1} of flowrate was used across the active layer of a hydrophobic PTFE membrane in a rectangular cell of 44 cm^2 (Millipore, Ireland), as described by [30]. The captured NH_3 was collected in a 0.5 M H_2SO_4 solution, which was tangentially recirculated at 0.25 L min^{-1} using a peristaltic pump (Watson Marlow 520, Spirax-Sarco Engineering plc, United Kingdom) through the membrane's support layer. To achieve a hydraulic retention time (HRT) of 20 days, the 3 L CSTR, 0.15 L of fresh AMS was daily fed, and an equivalent volume of anaerobic cultivation broth was simultaneously withdrawn with a peristaltic pump (Watson–Marlow Sci-Q 323 Spirax–Sarco Engineering plc, United Kingdom). To carry out the distillation process and TAD, a water bath (Lauda CS 12-D, Gemini Lab Sustainable Equipment, The Netherlands) was used to keep the CSTR's anaerobic culture broth at 55 °C, thus creating a temperature gradient of 20 °C. The experimental setup and key operational parameters were selected based on preliminary tests conducted prior to this study. These tests were performed to ensure system stability and optimal performance under selected conditions. While the detailed results of these preliminary experiments are not included in this manuscript, they served as the basis for the design and parameters selection used herein.

2.3. Effect of membrane distillation on NH_3 extraction and AD operation

For 103 days, the experimental set-up was run under two operational conditions. The CSTR was inoculated with thermophilic and mesophilic inocula (0.25 L and 1 L, respectively). During stage 1, the CSTR was

Table 1
Composition of substrate and inocula.

Main parameters	Anaerobic Sludge	Thermophilic Inoculum	Mesophilic Inoculum
pH	6.4 ± 0.1	8.5 ± 0.1	7.7 ± 0.1
Chemical Oxygen Demand (COD g L^{-1})	41.9 ± 4.7	71.2 ± 4.5	20.0 ± 3.7
Ammonia (NH_3 g L^{-1})	0.1 ± 0.1	1.9 ± 0.1	0.3 ± 0.1
Total Kjeldahl Nitrogen (TKN g L^{-1})	3.6 ± 0.1	3.6 ± 1.6	3.3 ± 1.1
Total Solids (TS g L^{-1})	37.6 ± 0.8	204.9 ± 3.8	19.9 ± 0.9
Volatile Solids (VS g L^{-1})	28.9 ± 0.1	114.2 ± 1.1	12.0 ± 0.4

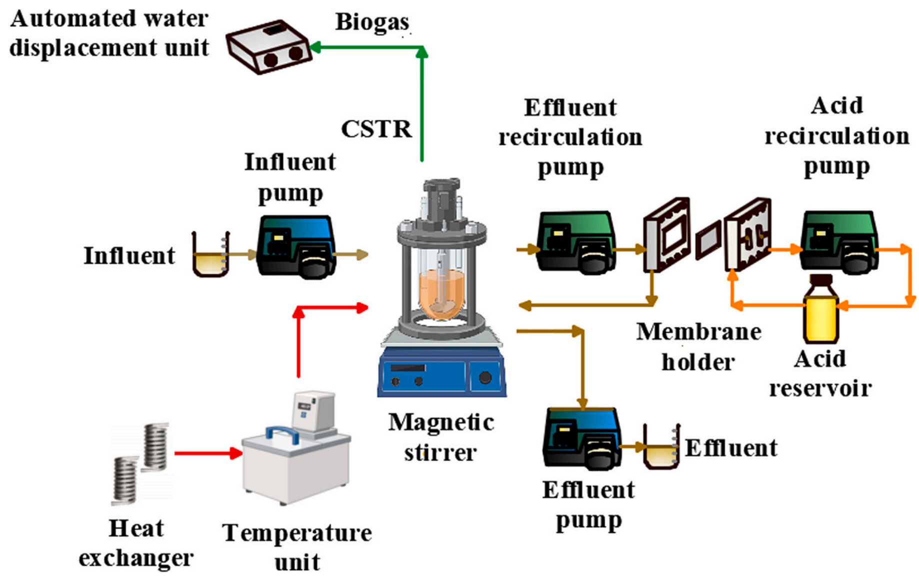

Fig. 1. Schematic representation of the experimental anaerobic CSTR combined with a membrane-based NH_3 extraction devoted to distillation.

operated for 63 days at a HRT of 20 days without membrane-based NH_3 extraction. During stage 2, 40 days of continuous operation were required to operate a 44 cm^2 PTFE flat sheet membrane module (rectangular cell) combined to the CSTR through the 0.25 L min^{-1} anaerobic broth recirculation. A H_2SO_4 solution of 0.5 M was used to capture dissolved NH_3 through a distillation process, which was mediated by a temperature gradient of 20 °C. In this process, the anaerobic culture broth was kept at 55 °C, however the H_2SO_4 solution was kept at 35 °C. The pH remained stable throughout the operation of the CSTR, with no significant increase detected. Consequently, no external pH adjustment was necessary during the experimental period. The hydrophobic PTFE membrane was replaced weekly to ensure the effectiveness of the NH_3 extraction, which was hindered by the gradual membrane fouling. To monitor pH, temperature, TAN, TKN, total nitrogen (TN), COD, TS, VS, total organic and inorganic carbon (TOC, IC), and volatile fatty acids (VFAs) of the CSTR, 150 mL of liquid samples were collected twice a week from both the influent AMS and the effluent. Biogas composition and production were also monitored daily.

2.4. Analytical methods

By using Nessler method, dissolved total ammoniacal nitrogen was determined with absorbance measured at 425 nm on a SPECTROstar Nano Absorbance Reader spectrophotometer (BMG LABTECH, Germany). pH and temperature were monitored using a Basic 20 pH meter equipped with a 50 14 T electrode (Crison Instruments, S.A., Spain). TN concentrations were measured using a Shimadzu TOC-VCSH analyzer (Shimadzu, Japan) with a chemiluminescence module of TNM-1. COD, TKN, TS, and VS concentrations were determined based on the Standard Methods for the Examination of Water and Wastewater [31]. Concentrations of VFAs were quantified using an Agilent 7820 A GC-FID (Agilent Technologies, USA) assembled with a G4513A autosampler and a TEKNOKROMA NF29370-F packed column (2 m × 1/8″ × 2.1 mm) (Teknokroma, Spain). To determine the composition of biogas (CO_2, H_2S, O_2, N_2, and CH_4) a 100 μL gas-tight syringe (Hamilton, 1710 SL SYR, United States) was used in a gas chromatograph equipped with a thermal conductivity detector (GC-TCD) (Varian CP-3800, United States). The GC-TCD system was equipped with a CP-Molsieve 5 A (15 m × 0.53 mm × 15 μm) and CP-PoraBOND Q capillary columns (25 m × 0.53 mm × 10 μm). Ultra-pure helium at a flow rate of 0.013 L min^{-1} was used as the carrier gas.

3. Results and discussion

3.1. Effect of the MD process of TAD on nitrogen removal

During the AD process of wastewater and solid organic waste, NH_3 is a significant inhibitor of methanogenic archaea. The AD is negatively impacted by the elevated TAN concentrations present in these high-strength wastewater, which can lead to the VFAs accumulation of and ultimately, cause the collapse of the anaerobic microbial consortium [32]. In this particular context, previous research reported that TAN concentrations from 1.5 to 7 g N L^{-1} can cause inhibition of the AD process [33]. Hence, reducing NH_3 concentrations in the anaerobic broth lower than inhibitory results can improve AD operation, leading to higher COD and VS removal, and consequently, higher biogas productivity [34].

Continuous anaerobic process of AMS resulted in stabilized condition characterized by an anaerobic broth with a pH of 8.03 ± 0.04 and TN, TAN, and TKN and concentrations of 3.3 ± 0.1 gTN L^{-1}, 0.4 ± 0.1 gTAN L^{-1}, and 2.8 ± 0.1 gTKN L^{-1} respectively, during stage 1 without the MD ammonia extraction connected (Fig. 2). In stage 2, the operation of the MD ammonia extraction system resulted in an anaerobic effluent with reduced pH levels of 7.98 ± 0.08 and steady state concentrations of TN, TAN, and TKN of 1.4 ± 0.1 gTN L^{-1}, 0.08 ± 0.01 gTAN L^{-1}, and 1.2 ± 0.2 gTKN L^{-1}, respectively. This entails TAN, TKN and TN removals of 76 %, 58 %, and 58 %, respectively. Interestingly, the substantially higher TN and TKN removal rates compared to the elimination of TAN under stable conditions in stage 2 suggested that MD ammonia extraction in the anaerobic CSTR enhanced organic nitrogen ammonification in the anaerobic broth. This continuous NH_3 removal mitigates free ammonia inhibition of sensitive methanogenic populations and supports stable digestion performance. As shown in Fig. 2, the operation of the MD system resulted in a significant reduction in TAN concentrations, which contributed to the alleviation of NH_3 inhibition and enhanced the overall stability of the TAD process. This apparent increase in TAN, TKN, and TN concentrations in the effluent compared to the influent during stage 1 can be attributed to the ammonification of organic nitrogen compounds under anaerobic conditions. During anaerobic digestion, complex organic nitrogen sources such as proteins are hydrolyzed and subsequently mineralized by microbial activity, leading to the formation of TAN, and the subsequent increase in the soluble TN concentration. This process results in elevated dissolved nitrogen concentrations in the effluent, even in the absence of an external nitrogen input. Such

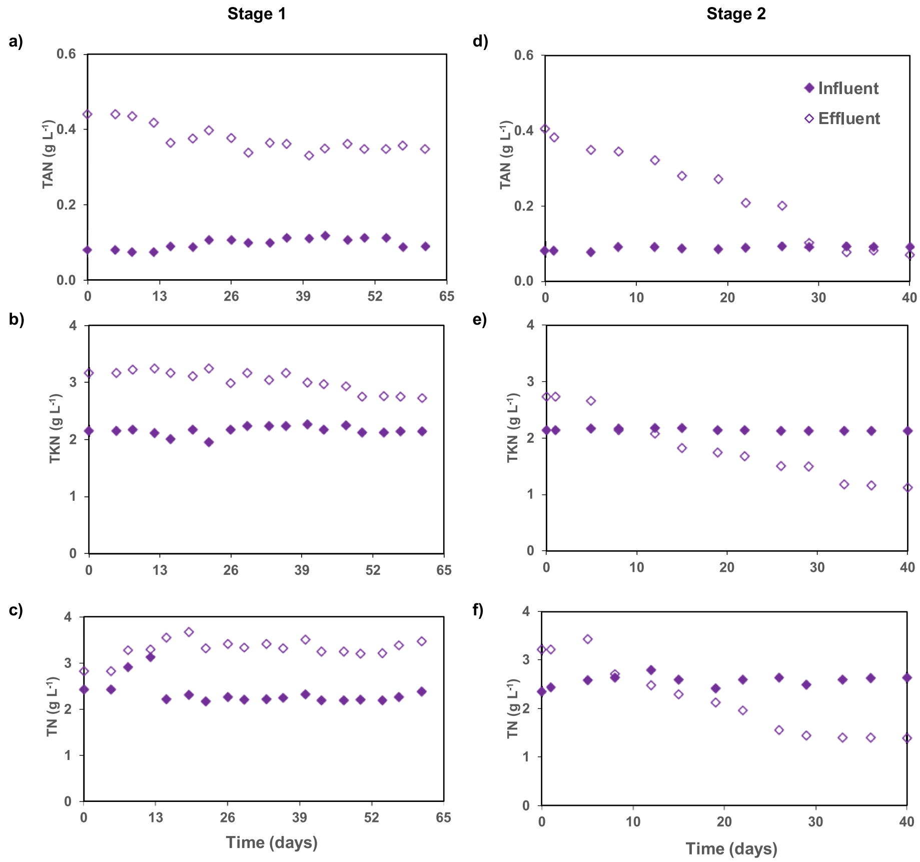

Fig. 2. Time course of the TAN (a,d), TKN (b,e), and TN (c,f) concentrations in the influent AMS and anaerobic effluent along stages I and II at a HRT of 20 days.

behavior is well-documented in anaerobic systems lacking nitrogen removal mechanisms and is consistent with previous findings [35]. In addition, process operation at 55 °C entails significant water evaporations, which entails a pre-concentration of TKN in the effluent. A comparison between the TAD operation in stage 1 and the integrated MD-TAD system in stage 2 highlights the benefits of MD incorporation. During stage 1, TAN accumulation was associated with limited methane production, whereas operation with MD distillation in stage 2 achieved 76 % TAN reduction and a 3-fold increase in CH_4 yield. These findings demonstrate that coupling MD with AD enables effective nitrogen management, enhances microbial stability, and substantially improves overall process efficiency, offering a novel strategy for advancing TAD. MD represents a suitable technique for NH_3 extraction in TAD, being compatible with thermophilic digestion temperatures (55–65 °C) and benefiting from the inherent temperature gradients of this configuration. Within this system, the unionized NH_3 is absorbed in the acid reservoir, which passes through the support layer of the membrane. NH_4^+ ions are generated in the acid reservoir by mixing with free protons, thereby achieving across the membrane a maximum NH_3 concentration gradient [36]. In this sense, Zhu and coworkers (2024) reported a 86.8 % removal of ammonium using a PTFE 0.22 μm flat sheet membrane combined to a synthetic NH_4Cl reservoir for a hybrid ultrasonic stripping-membrane distillation at 80 °C and pH 8.2 [37].

Within this context, the molar fluxes of TAN across the PTFE membrane under stabled conditions in stage 2 accounted for 0.06 mol TAN m^{-2} h^{-1}. Previous studies reported a molar flux of 0.05 mol TAN m^{-2} h^{-1} with a similar experimental set-up (membrane contactor) [34]. Likewise, a more recent investigation on membrane-based NH_3 extraction without MD reported a molar flux of 0.07 mol TAN m^{-2} h^{-1} using poultry manure as substrate [38]. The TAN flux across the membrane is determined by parameters such as temperature, pH of the anaerobic broth, and the type of membrane, which affects ammonia's partial pressure. The reduced operation of the membrane-based extraction process studied in this work could be attributed to the gradual fouling, which eventually hinders the ammonia permeation throughout the membrane, as similarly demonstrated in previous work under comparable conditions [39]. In those studies, fouling was confirmed through atomic force microscopy and flux decline analyses. The rapid fouling of the membrane was evident from the brief acidification of the anaerobic broth due to its replacement. For biotechnological applications, membrane fouling, caused by the accumulation of microorganisms or organic and inorganic materials on the membrane surface, is a critical challenge. This buildup leads to pore obstruction and partial reduction in membrane's hydrophobicity, ultimately lowering its capacity to extract NH_3 [40]. However, membrane performance can be restored to optimal levels through the use of both physical and chemical cleaning methods [41].

3.2. Effect of membrane distillation on organic matter removal during thermal anaerobic digestion

Under steady state conditions without TAN extraction via MD (stage 1), the removal efficiencies of COD and VS accounted for 44 % ± 2 % and 48 % ± 1 %, respectively (Fig. 3). The operation of the MD process with a temperature gradient of 20 °C improved the removal efficiencies of COD and VS by a factor of 1.6 and 1.4, respectively. Consequently, COD and VS removal rates of 71 % ± 4 % and 66 % ± 1 %, respectively, were achieved in stage 2. The enhancement in COD and VS removal was presumably driven by a reduction in the anaerobic broth's NH_3 concentration which boosts the microbial biodegradation efficiency and alleviates inhibition. Sung and coworkers (2003) reported a decline in COD removal efficiency when increasing TAN concentrations, indicating methanogens inhibition even in an acclimated community in a CSTR working with synthetic wastewater at 55 °C and 7 days of HRT. The

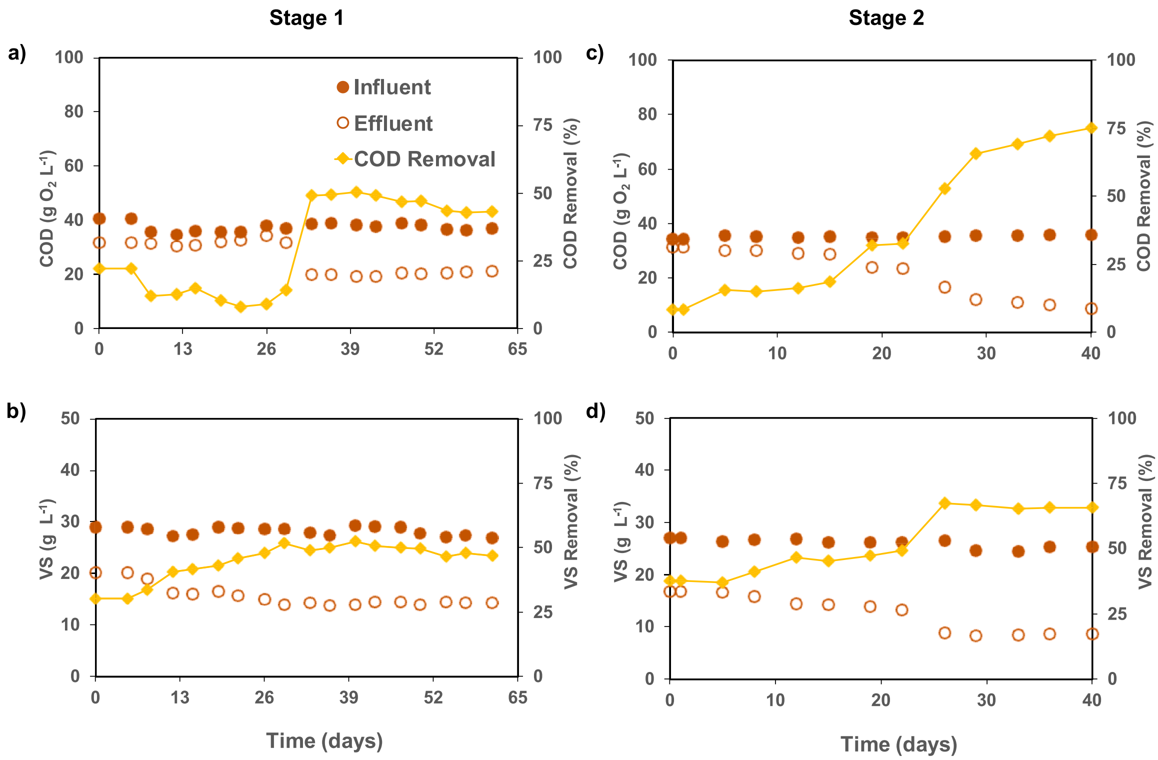

Fig. 3. Time course of the concentrations of COD (a,c) and VS (b,d) in the influent AMS and anaerobic effluent, and their removals.

increase in TAN concentrations from 0.4 g L^{-1} up to 4.9 and 5.8 g L^{-1} led to reductions in CH_4 production rates by approximately 39 % and 64 %, respectively, in comparison to the initial phase of operation [6]. Similarly, Rivera and coworkers (2022b) observed an improvement in COD and VS removal efficiencies from 33 % to 62 % and from 26 % to 38 %, respectively, mediated by NH_3 membrane-based extraction in a similar experimental configuration digesting swine manure [34]. Previous studies have reported typical VS removals ranging from 60 % to 70 % in TAD systems, with reductions improving under thermophilic conditions. MD supports improved performance by addressing key limitations of conventional TAD systems [35]. Winter (1997) reported a comparison of the wet organic fraction fermentation of household waste in laboratory-scale reactors under mesophilic and thermophilic conditions. They concluded that, with thermophilic operation, microbial flora could tolerate at least twice the amount of free ammonia in comparison to mesophilic flora, with threshold values of 0.2 g N-NH_3 L^{-1} and 0.7 g N-NH_3 L^{-1}, respectively, at a COD loading of 9.6 g L^{-1} day^{-1}. Under these conditions, degradation of 63 % and 67 % of the COD was achieved

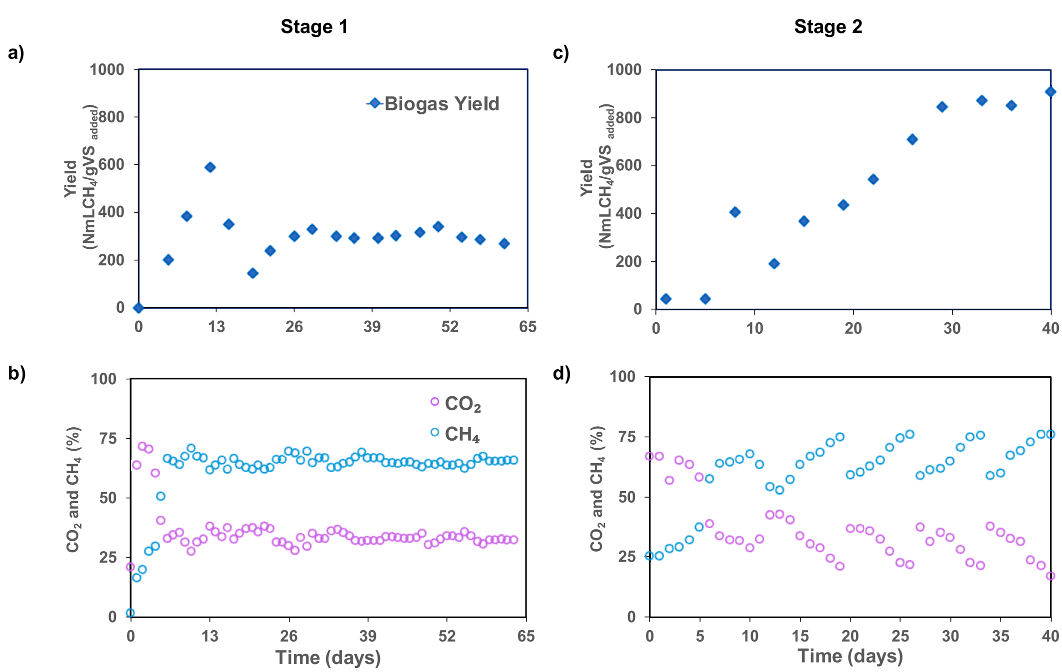

Fig. 4. Time course of the biogas yield (a,c) and concentrations of CO_2 and CH_4 (b,d) in the biogas generated.

at 37 °C and 55 °C, respectively, with an associated reduction in VS of 64 % and 65 % [42]. Resch and coworkers (2011) found that the reduction from 7.5 to 4.0 g kg $^{-1}$ of TKN led to a 55 % increase in COD removal, which was attributed to improved VFAs assimilation [43]. Nevertheless, TAN extraction must be closely monitored, as methanogenesis is inhibited when ammonia concentrations decrease from 0.1 to 0.01 g NH_4^+-N L^{-1} at C:N ratios ranging from 59 to 210 [43]. The comparison with existing studies underscores the innovative contribution of MD in enhancing organic matter removal and improving the overall efficiency of TAD.

3.3. Effect of membrane distillation on biogas production and VFAs concentration during thermal anaerobic digestion

Under steady state conditions without TAN extraction (stage 1), a CH_4 yield of 284.1 ± 13.3 NmLCH_4 gVS $_{fed}$ $^{-1}$ was achieved (Fig. 4a). The operation of the membrane distillation process with a temperature gradient of 20 °C improved the methane yields. Consequently, a methane yield of 876.1 ± 28.6 NmLCH_4 gVS $_{fed}$ $^{-1}$ was achieved in stage 2, which resulted in a 3-fold enhancement in methane yield mediated by ammonia extraction. The enhanced CH_4 observed in stage 2 is linked to the reduction in TAN and the associated alleviation of NH_3 inhibition on key microbial populations. High concentrations of free NH_3, typically resulting from elevated TAN and high pH, exert inhibitory effects particularly on acetoclastic methanogens, which are most sensitive to NH_3 toxicity compared to hydrogenotrophic methanogens [44]. The observed 3-fold enhancement in CH_4 yield upon NH_3 extraction is likely attributed to the alleviation of free NH_3 inhibition on sensitive methanogenic pathways. Specifically, NH_3 acetoclastic methanogens such as *Methanosaeta* spp., which are known to be inhibited at high TAN concentrations, may have recovered under the reduced NH_3 environment, leading to the reactivation acetoclastic methanogenesis. In contrast, under high NH_3 concentrations, more tolerant methanogens like *Methanosarcina* spp. tend to dominate, often relying more heavily on hydrogenotrophic pathways. Although direct microbial community analysis was not performed, these interpretations are consistent with previous studies on NH_3 inhibition in AD systems [45]. The improved VFA removal in stage 2 and the reduced TAN concentrations, suggests that the restored metabolic cooperation between syntrophs and methanogens contribute to the overall increase in system performance. Pigoli and co-workers (2021) by a recent study, conducted in a full- scale system where organic wastes were converted into nitrogen and organic fertilizers through high-solid TAD, reporting a weekly specific CH_4 production of approximately 200 ± 29 NmLCH_4 gVS $_{fed}$ $^{-1}$ [4]. Similarly, the TAD of swine manure at a HRT of 30 days in a CSTR reached a CH_4 production of 182 NmLCH_4 gVS $_{fed}$ $^{-1}$ [46]. Within the specific context of the influence of TAN extraction, González-García and coworkers (2021) recorded a 9 % improvement in methane yield mediated by membrane-based ammonia extraction unit during the operation of two CSTRs, in one batch experiment and 17 % in a semicontinuous experiment under mesophilic parameters for the treatment of swine manure from a finishing farm [47]. Additionally, Bayrakdar and coworkers (2018) compared two poultry manure leach-bed reactors with and without membrane-based NH_3 extraction and observed that CH_4 production increased by 2.3 times in the system operated with the membrane module [48].

During the first week, the biogas composition averaged values of 68 % ± 4 % CO_2, 0.8 % ± 0.5 % O_2, 9.7 % ± 8.5 % N_2, and 21 % ± 5 % CH_4. No detectable concentrations of H_2S were observed. Under stable conditions without NH_3 extraction (stage 1), the biogas composition averaged 33 % ± 1 % for CO_2, and 65 % ± 1 % for CH_4 (Fig. 4b). However, when the MD ammonia extraction unit was implemented in stage 2, the CO_2 and CH_4 concentrations were 28 % ± 6 % and 76 % ± 6 %, respectively. Within this context, CO_2 periodic increases in the biogas concentration, along with a CH_4 decrease, were obtained after the weekly membrane replacement. This change was attributed to a minimum acidification of the anaerobic broth, caused by a fast permeation of a hydrogen ion. The implementation of periodic membrane replacement was mandatory to prevent fouling, which improves TAN recovery and facilitates transfer of the protons from the sulfuric acid reservoir to the anaerobic broth. It has previously been reported that also pH variations occur in the anaerobic broth after membrane replacement [48,49]. In this setup, the membrane allows for selective transport phenomena driven by the concentration gradient and pH differential across the membrane interface. This enables protons (H^+) from the acid reservoir to diffuse toward the anaerobic broth, contributing to pH regulation and enhancing TAN recovery. The weekly replacement of the membrane was performed to ensure its operational integrity throughout the process. For large-scale applications, the implementation of appropriate cleaning protocols could extend membrane lifespan, allowing for replacement intervals of at least 2 years under thermophilic membrane distillation conditions.

Furthermore, under steady-state conditions VFAs removals in the absence of NH_3 extraction resulted in 8.7 % ± 0.9 % for acetic acid and ~ 0 % for propionic acid. On the other hand, butyric, isobutyric, valeric, and isovaleric acids were not identified in the anaerobic broth during stage 1 (Fig. 5). During stage 2, the implementation of MD ammonia extraction resulted in removal efficiencies of 100 % ± 0 % for both acetic acid and propionic acid. It was primarily attributed to the reduction of TAN concentration or other inhibitory compounds, which facilitated the microbial uptake of VFAs. In this regard, studies in the literature have shown that high TAN levels are typically associated with the VFAs accumulation [38]. The complete assimilation of VFAs observed is likely linked to the mitigation of ammonia toxicity. As ammonia inhibition is relieved, the metabolic conversion of VFAs becomes more efficient, leading to a complete VFA degradation [50]. The potential transfer of VFAs to the acid reservoir in the membrane module from the cultivation broth was ruled out in an independent set of experiments carried out under abiotic conditions [51]. The most toxic VFA is typically propionic acid, which impacts the performance of AD [52], and propionate/acetate ratios greater than 1.4 have been shown to impair AD performance [53]. The ratio propionate/acetate in this study was 0.5 during stage 1, which would entail a negligible impact on AD. At high levels, VFAs affect the microbial community due to its toxicity, which intensifies as pH decreases as a result of VFA production [54]. According to Kroeker and coworkers (1979), inhibitory levels of acetic acid can be lower than 0.01 g L^{-1} [55]. In this particular study, the undetectable concentrations of VFAs in the cultivation broth, resulting from MD ammonia extraction, repeatedly improved the AD process of AMS. These outcomes surpass the performance reported in traditional TAD systems, where CH_4 production improvements under high NH_3 concentrations are usually limited without external interventions. Thus, comparison with prior studies emphasizes the effectiveness of MD integration not only in mitigating NH_3 inhibition but also in sustaining higher biomethane productivity under thermophilic conditions [50].

4. Conclusions

The In-situ NH_3 extraction via MD from the anaerobic broth mediated a notable enhancement in the performance of TAD of AMS. Operating with a temperature gradient of 20 °C, the MD system effectively reduced TAN concentrations in the culture broth from 0.4 to 0.1 g N L^{-1}, thereby mitigating NH_3 inhibition. This reduction is correlated with the substantial improvements in the process performance, including high removals of 66 %, 75 %, and 100 %, for VS, COD, and VFAs, respectively. Moreover, the CH_4 yield increased from 284 to 876 NmLCH_4 g VS $_{fed}$ $^{-1}$, with an increase in CH_4 content from 66 to 76 %, respectively. These findings confirm the hypothesis that continuous NH_3 recovery through MD can enhance microbial activity and bioconversion efficiency in TAD systems. The optimization of TAN removal represents a promising extension of the present study. Future work will focus on systematically investigating key operational parameters to enhance TAN

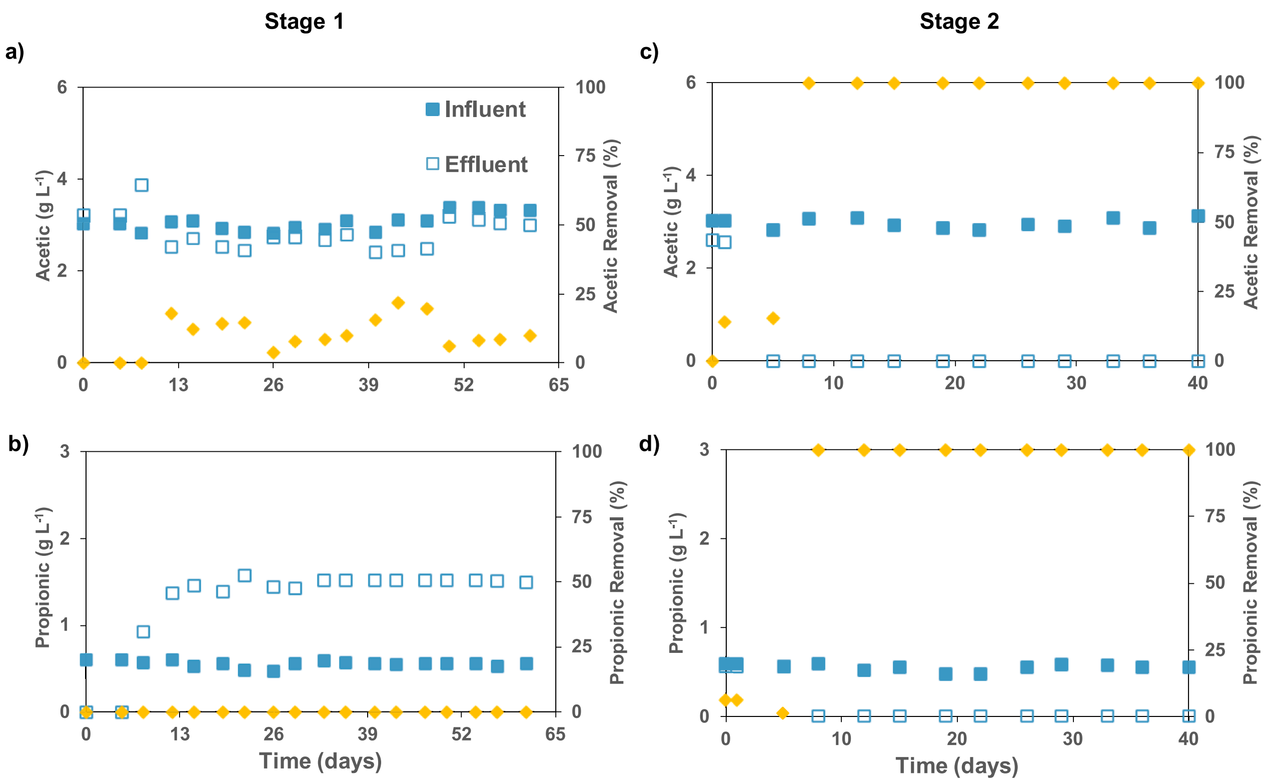

Fig. 5. Time course of the concentrations of acetic (a,c) and propionic (b,d) acids in the influent AMS and anaerobic effluent, and their removals.

recovery efficiency.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2025.108193.

CRediT authorship contribution statement

Fanny Rivera: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Luis Villarreal:** Investigation. **Pedro Prádanos:** Writing – review & editing. **Antonio Hernández:** Writing – review & editing. **Laura Palacio:** Writing – review & editing. **Raúl Muñoz:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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