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Side-stream membrane-based NH_3 extraction to improve the anaerobic digestion of poultry manure

Fanny Rivera [a,c], Joseph Akpan [a,b], Pedro Prádanos [a,c], Antonio Hernández [a,c], Laura Palacio [a,c], Raúl Muñoz [a,b,*]

[a] Institute of Sustainable Processes, University of Valladolid, 47011 Valladolid, Spain
[b] Department of Chemical Engineering and Environmental Technology, University of Valladolid, 47011 Valladolid, Spain
[c] Department of Applied Physics, Science Faculty, University of Valladolid, 47011 Valladolid, Spain

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ABSTRACT

The influence of membrane-based ammonia extraction on poultry manure (PM) wastewater treatment was assessed in a 3 L continuous stirred tank reactor (CSTR). The anaerobic digester operated for 91 days at a hydraulic retention time of 15 days and 37 °C. The flat sheet polytetrafluoroethylene (PTFE) membrane module was interconnected to the CSTR and operated at a recirculation flow rate of 0.25 L min^{-1}. The membrane-based ammonia extraction mediated a decrease of total ammonia nitrogen of 64.5 % and of total nitrogen of 53.4 %, which induced an increase in the methane yields from 360 ± 70 up to 574 ± 5 N mL CH_4 g VS fed^{-1}. Similarly, chemical oxygen demand (COD) and volatile solids (VS) removal efficiencies increased from 59 % ± 2 % and 57 % ± 3 % up to 79.1 % ± 0.8 % and 65.8 % ± 0.2 %, respectively. This work targeted the enhancement of the performance of full-scale anaerobic digestion plants via reduction of NH_3 concentration with a membrane-based extraction unit.

1. Introduction

Poultry manure (PM) contains high concentrations of phosphorus, potassium, nitrogen and organic matter, which makes it a valuable feedstock for resource recovery. Typically, poultry manure is used in agriculture as an organic fertilizer. However, the direct application of PM on soil can cause several environmental problems like odour pollution, eutrophication, propagation of pathogens and emissions of greenhouse gases [1]. At the same time, the volume of PM production from farms is rising consistently as a result of the increasing demand of chicken products [2]. It is a common PM management practice to anaerobically digest PM, with the concomitant production of biogas [3]. In this context, Monogaran et al. concluded that among the promising methods of PM treatment, anaerobic digestion (AD) shows more holistic benefits in terms of management cost and environmental impacts [4].

PM exhibits a high content of biodegradable organic matter than can be converted into biogas [5,6]. In a nutshell, AD relies on the cooperation between various groups of bacteria and archaea capable of symbiotically conducting the four steps involved: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [7]. Anaerobic archaea are the most vulnerable to environmental changes and the presence of inhibitors like ammonia, since they grow at lower rates than the bacterial communities involved in AD [8]. The optimal production of biogas from PM depends in general, of the inhibition of the methanogenesis phase. Indeed, the anaerobic digestion of PM may build up toxic intermediates such volatile fatty acids (VFAs), which accumulate as a result of organic overload or ammonia inhibition [9–11]. In this context, ammonia's toxic effects on methanogens ultimately cause the digester to produce less biogas. Thus, TAN extraction from the anaerobic broth of PM digesters could partially mitigate this inhibition, boost biogas production and promote nutrients recovery [12]. Researchers have studied a wide variety of ammonia removal/recovery techniques, involving physical processes (stripping, adsorption, ion exchange, etc.), chemical processes (chemical precipitation, oxidation, and electro-kinetic processes [13–15]) and other microbial processes (nitrification-denitrification, anammox [16]). Nowadays, multiple technologies such adsorption, membrane separation, ion exchange and ammonia stripping have been proposed for NH_3 recovery from digestates [17–20]. Of them, membrane-based NH_3 extraction has shown promising results in terms of NH_3 removal efficiency, limited use of chemical reagents, and energy demand. Chan and

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[*] Corresponding author at: Institute of Sustainable Processes, University of Valladolid, Dr. Mergelina s/n., 47011 Valladolid, Spain.
E-mail address: mutora@iq.uva.es (R. Muñoz).

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coworkers compared the performance of various technologies for ammonia removal and recovery from economic, environmental, technical, readiness level and scale-up perspectives [21].

Several studies based on AD processes treating manure and interconnected to membranes modules have recently investigated the potential of gas permeable membranes for total ammonia nitrogen (TAN) removal from domestic wastewaters, livestock manure and anaerobic broths [22–24]. For this purpose, hydrophobic, microporous, tubular, flat sheet and hollow fiber membranes are typically tested to reduce the concentration or recover NH_3 from wastewaters, assisted by an acidic solution circulating on the other side of the membrane to favor NH_3 extraction. In this context, the acidic reservoir is recirculated on one side of the membrane so that the ammonia gas dissolved in the wastewater passes by gradient force [25]. Therefore, NH_3 is retained in the acidic reservoir as ammonium ion. Side-stream NH_3 extraction with membranes has been tested during the anaerobic digestion of swine manure. Since there is less research on the anaerobic treatment of PM, therefore this approach has been tested. In this context, an effective NH_3 extraction maximizing biogas production will be beneficial for the large-scale implementation of anaerobic PM digestion processes.

In this work, the performance of a CSTR equipped with a membrane-based ammonia extraction system was investigated during the anaerobic treatment of diluted PM. The influence of NH_3 extraction on methane productivity and organic matter removal was systematically assessed for 91 days.

2. Materials and methods

2.1. Poultry manure and inoculum

Fresh PM was collected from a poultry farm (Zaragoza, Spain), diluted 1:4 with tap water, sieved by 20–0.99 mm and then stored at 4 °C. Every two weeks new diluted PM batches of 2 L were prepared. The average composition of the diluted PM was: pH 7.4 ± 0.1, 30 ± 4 g COD/L, 0.7 ± 0.1 g TAN L^{-1}, 3.3 ± 0.2 g TKN L^{-1}, 32 ± 1 g TS/L, 22 ± 1 g VS/L, 10 ± 1 g TOC/L, 1 ± 2 g IC/L, 5 ± 2 g acetic/L, 12 ± 3 g propionic/L, 0.1 ± 0.7 g isobutyric/L, 0.5 ± 0.2 g butyric/L, 0.7 ± 1.1 g Cl^-/L, 0.2 ± 2.0 g PO_4^{-3}/L and 0.2 ± 1.0 g SO_4^{-2}/L. The inoculum used was obtained from an anaerobic mesophilic pilot plant treating diluted PM located in Zaragoza, Spain which generates biogas exclusively from diluted PM in a single stage. The composition of the inoculum was: pH 8.3 ± 0.3, 3 ± 4 g COD/L, 0.7 ± 1.1 g TAN L^{-1}, 3 ± 2 g TKN L^{-1}, 8 ± 2 g TS/L, 3.3 ± 0.1 g VS/L, 3.1 ± 0.1 g TOC/L, 2 ± 3 g IC/L, 5 ± 1 g acetic/L, 9 ± 4 g propionic/L, 0.01 ± 0.10 g butyric/L, 0.2 ± 0.1 g isovaleric/L, 1.4 ± 0.1 g valeric/L, 1 ± 1 g Cl^-/L. No measurable amounts of isobutyric acid were detected.

2.2. Experimental set-up

A schematic representation of the experimental set-up, which consisted of a 3000 mL CSTR magnetically stirred (Agimatic-HS, Selecta®, Spain) at 120 rpm and 37 °C, is shown in Fig. 1. The culture broth was tangentially recirculated with a peristaltic pump (Watson Marlow 520, Spirax-Sarco Engineering plc, United Kingdom) at 0.25 L min^{-1} over the active layer of a hydrophobic flat sheet rectangular membrane holder (area of 44 cm^2), with neither spacers nor gaps. The flow inside the membrane holder operated under parallel cross-flow. A hydrophobic gas permeable membrane was herein used to extract NH_3. Details of the membrane used are given in Table 1. The use of a microporous and hydrophobic membrane favors the passage of gas, since it has a high permeability to gas flows at low pressure. The passage of NH_3 through the membrane will be by diffusion, with NH_3 being capture by the acid solution that recirculates on the other since of the membrane. According to previous assays, Rivera and coworkers concluded that these were the most suitable operation conditions to carry out NH_3 extraction from anaerobic broths [26]. The extracted ammonia was captured in a 1 M sulfuric acid solution, which was also tangentially recirculated at 0.25 L min^{-1} over the support layer of the membrane with a peristaltic pump

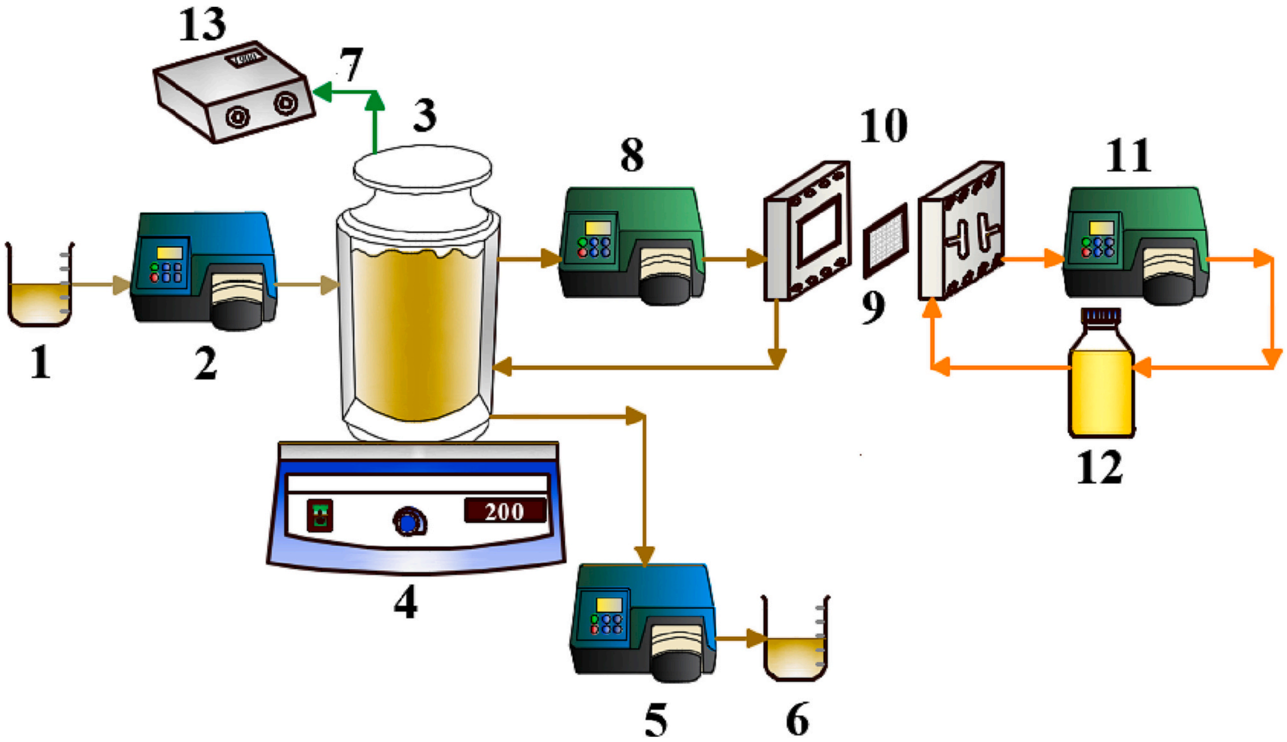

Fig. 1. Schematic diagram of the lab scale CSTR coupled with a membraned-based ammonia extraction system. Influent (1), influent pump (2), CSTR (3), magnetic stirrer (4), effluent pump (5), effluent (6), biogas (7), cultivation broth recirculation pump (8), membrane (9), membrane holder (10), acid recirculation pump (11), acid reservoir (12) and biogas pulse counter (13).

Table 1
Detailed description of the membrane used in this research.

Membrane	Material	Pore size (μm)	Nominal thickness (μm)	Contact angle (θ)	Porosity (%)	Wettability	Manufacturer
PTFE 0.22	PTFE	0.22	175	150	70	Hydrophobic	Millipore

(Watson Marlow 520, Spirax-Sarco Engineering plc, United Kingdom). Culture broth and sulfuric acid solution were recirculated continuously on the membrane. Sulfuric acid recirculation is essential due to the reaction of ammonia with the acid contained in the permeate side of the hydrophobic membrane. A commercial fertilizer such as ammonium sulfate (Eq. 1) is generated during membrane-based ammonia recovery when using H_2SO_4, which boosts NH_3 diffusion [27]. According to previous studies sulfuric acid is more effective than phosphoric acid and nitric acid for NH_3 recovery [28]. pH (Fig. S-I) and temperature (35–37 °C controlled temperature room) were monitored daily. The system was fed daily with 200 mL of diluted poultry manure and 200 mL of cultivation broth were also daily withdrawn, which entailed a hydraulic retention time (HRT) of 15 days.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)2SO_4 \quad (1)$$

2.3. Influence of membrane-based TAN extraction on AD performance

The experiment was carried out for 91 days under 2 operational stages, without and with membrane-based ammonia extraction system, considering that steady conditions were reached at the end of each stage. The anaerobic CSTR was inoculated with 3000 mL of fresh PM inoculum. Stage I (S-I) was operated for 45 days at a HRT of 15 days without membrane-based ammonia extraction. Stage II (S-II) involved continuous operation for 46 days under membrane-based ammonia extraction. The PTFE membrane was replaced every 3 weeks to prevent deterioration and fouling, which ultimately hinder NH_3 permeation and induce H_2SO_4 intrusion into the CSTR. The lifetime of the membrane was selected according to preliminary experiments carried out with the same experimental set-up [23]. The Daily biogas samples were drawn to determine the composition of the biogas generated from PM degradation. The volume of biogas daily produced was also broth recorded throughout a custom-made pulse counter. Twice a week, 100 mL liquid samples of diluted PM and effluent of the CSTR were drawn to analyze temperature, pH and the concentration of TAN, total and volatile solids (TS, VS), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total nitrogen (TN), total carbon and inorganic carbon (TOC, IC), volatile fatty acids (VFAs) and anions (NO_3^-, NO_2^-, and PO_4^{-3}). Fouling on the membrane used was assessed using atomic force microscopy (AFM) by comparison with new membranes.

2.4. Analytical methods

2.4.1. Digestate samples

Ammoniacal nitrogen was measured using the Nessler's method at a wavelength of 425 nm in a SPECTROstar Nano spectrophotometer (BMG LABTECH, Germany). Concentrations of TS, VS, COD and TKN were examined according to Standard Methods for the analysis of water and wastewater [12]. The determination of TKN and COD concentrations involved a preliminary digestion (Selecta Digestion Bloc, Bloc-Digest Macro 12) followed by distillation (Buchi distiller, Kjelflex K-360) and titration, respectively. pH and temperature were monitored using a Basic 20 pH meter with a 5014 T electrode (Crison Instruments, S.A., Spain). The concentrations of TOC, IC and TN were measured in a Shimadzu TOC-VCSH analyzer (Shimadzu, Japan) equipped with a TNM-1 chemiluminescence module. NO_3^-, NO_2^-, and PO_4^{-3} concentrations were analyzed by high-performance liquid chromatography-ion conductivity (HPLC-IC) (Waters, USA) 515 HPLC pump coupled to a Waters 432 conductivity detector using a Waters IC-Pak Anion HC column (15 cm × 0.46 cm) [29]. VFAs concentrations were determined in an Agilent 7820A GC-FID (Agilent Technologies, USA) equipped with a G4513A autosampler and a TEKNOKROMA NF29370-F packed column (2 m × 1/8″ × 2.1 mm) (Teknokroma, Spain) [25]. Pretreatment of the sample for VFAs analysis consisted in a centrifugation of 10 min at 7000 rpm. Then it was filtered by 0.45 μm, afterwards diluted 1:40 and filtered again by 0.22 μm. The sample was acidified with 20 μL for every mL of sample with sulfuric acid. The standard used for the calibration curve was VFA from Sigma Aldrich (Merck, Germany).

2.4.2. Biogas samples

Carbon dioxide, hydrogen sulfide, oxygen, nitrogen and methane concentrations were determined using a gas-tight syringe (Hamilton, 1710 SL SYR, 100 μL, United States) in a gas chromatograph with thermal conductivity detection (Varian CP-3800, United States). The GC-TCD was equipped with a CP-Pora BOND Q capillary column (25 m × 0.53 mm × 10 μm) and a CP-Molsieve 5A capillary column (15 m × 0.53 mm × 15 μm). The gas carrier was Helium (ultra-pure at 13 mL min^{-1}).

2.5. Membrane characterization techniques

PTFE microporous membrane is well known for its use in many other membrane processes; its structural characteristics are reported in literature [26,30]. For this study, the characterization by AFM was added to illustrate the low fouling suffered by the membrane in this particular application. AFM provides information of the membrane's roughness and depositions on its surface. Surface morphology was analyzed by using AFM. Images were obtained with a Nanoscope IIIA microscope using Tapping mode (Digital Instruments, Veeco Metrology Group, USA). Images were analyzed using the NanoScope Software Version 5.30 (Veeco Metrology Inc., Santa Barbara, CA, USA).

2.6. Mass balance calculation

The global mass balance calculation for Nitrogen and Carbon were calculated based on the average concentrations of all their chemical species at the input (PWW) and output (effluent).

Nitrogen mass balance:

$$TKN_{PWW}\, Q_{PWW} = TKN_{EFF}\, Q_{EFF} + N_2 \quad (2)$$

Carbon mass balance:

$$C_{PWW}\, Q_{PWW} = C_{EFF}\, Q_{EFF} + CO_2 + CH_4 \quad (3)$$

where TKN, NH_3 and TC (g L^{-1}) stand for the concentrations in the influent (PWW) and effluent (EFF). Q_{PWW} stands for the influent PWW flowrate (L d^{-1}) and Q_{EFF} for the effluent flowrate (L d^{-1}). N_2, CO_2 and CH_4 were calculated according to the total value of (mol d^{-1}) from each gas with had compositions in (%).

All data is reported as means ± SD, n = 4 (in steady state).

3. Results and discussion

3.1. Influence of membrane-based TAN extraction on AD performance

Ammonia is one of the major inhibitors of methanogenic archaea during the AD process of chicken manure. AD of livestock wastewaters is affected by the high TAN concentrations of these high-strength wastewaters, which can cause accumulation of VFAs and ultimately induce the malfunction of the entire AD system [5,31,32]. In this context, Chen et al. reported that inhibitory TAN concentrations of 1400–14,000 mg L^{-1} can reduce biogas production by up to 50 % [33].

The continuous anaerobic treatment of diluted PM resulted in steady state TAN, TKN and TN concentrations of 0.8 ± 0.1 g TAN L^{-1}, 3.0 ± 0.1 g TKN L^{-1} and 3.4 ± 0.1 g TN L^{-1}, respectively, during stage I in the absence of membrane-based ammonia extraction (Fig. 2). The operation of the membrane-based extraction system in stage II resulted in a decrease in the steady state concentrations of TAN, TKN and TN of 0.3 ± 0.1 g TAN L^{-1}, 1.6 ± 0.1 g TKN L^{-1} and 1.7 ± 0.16 g TN L^{-1}, respectively. In this system, the acid reservoir receives the un-ionized ammonia, which permeates through the membrane's support layer. In the acid reservoir, NH_4^+ ions are formed by merging with free protons, which supports a maximum ammonia concentration gradient throughout the membrane [22,25]. Bayrakdar et al. observed a gradual decrease in TAN concentration to 2 g L^{-1} by operating a leach-bed anaerobic digester treating PM coupled with a membrane-based ammonia extraction unit [34]. According to the mass balance, 0.30 g TAN day^{-1} should be recovered from the acid reservoir (Fig. S3). Previous studies using a similar experimental set-up, with swine manure as a substrate, achieved a decrease in TAN concentration of 1.2 g L^{-1} [23]. In this context, TAN molar fluxes across the PTFE membrane under steady state in stage II accounted for 0.01 mol TAN m^{-2} h^{-1}. This molar flux is lower than that obtained in a similar experimental set-up using swine manure as substrate (0.05 mol TAN m^{-2} h^{-1}), which can be explained by the lower TAN concentration gradient encountered in the diluted PM [23]. Similarly, TAN molar fluxes of 0.07 mol TAN m^{-2} h^{-1} were recorded during membrane-based NH_3 extraction in a dry digester treating PM [35]. NH_3 flux through the membrane is affected by pH, temperature and membrane type, which influence the partial pressure of ammonia. The low performance of the membrane-based extraction system herein evaluated might be also caused by the gradual membrane fouling, which ultimately hinders ammonia permeation through the membrane. If the only parameter determining gaseous compound extraction from the anaerobic broth was pore size, CH_4, CO_2 and H_2S would diffuse through the 0.22 μm membrane. However, considering that poultry wastewater with a pH of 8.2 is polar, and CO_2, and CH_4 are nonpolar (NH_3 is polar) it is unexpected that these could be retained in the cultivation broth. Moreover, since the CSTR is operated at 35 °C, the aqueous solubility of gases is low, thus minimizing CH_4, CO_2 and H_2S diffusion.

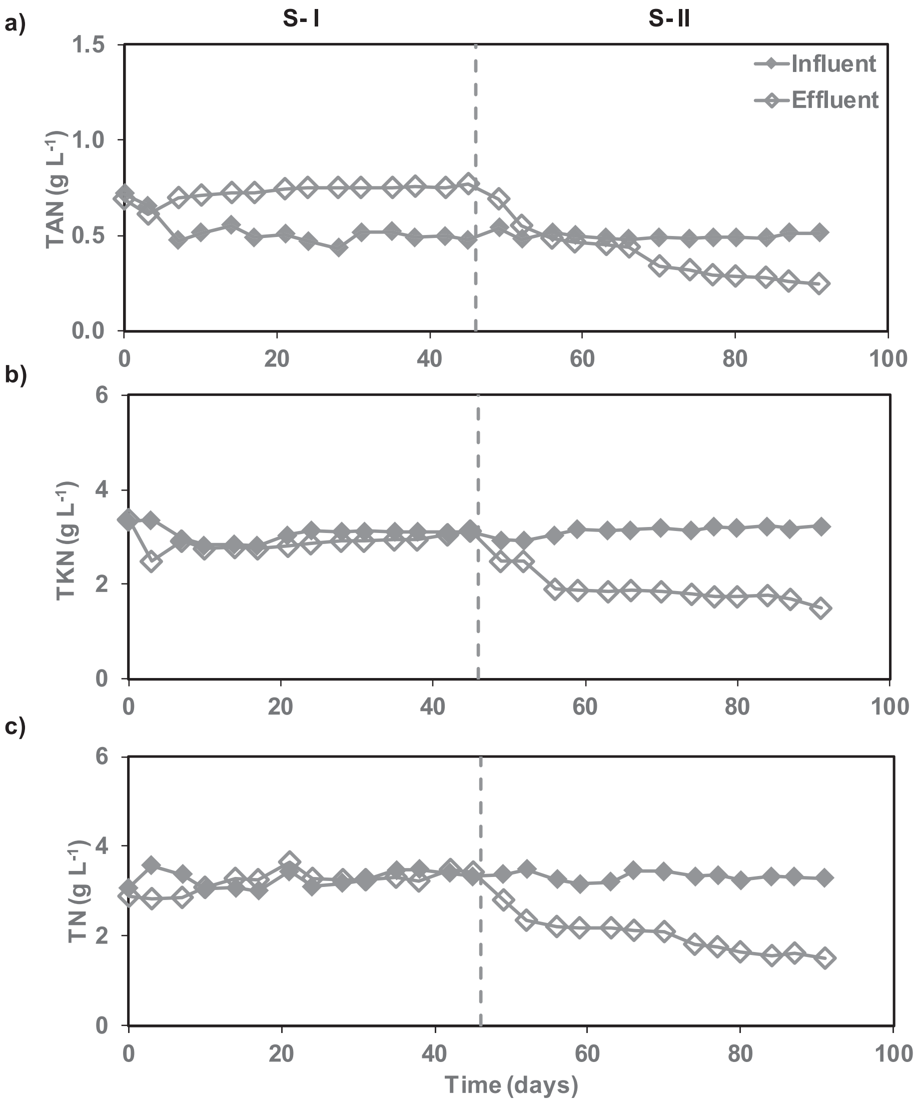

Fig. 2. Time course of the TAN (a), TKN (b) and TN (c) concentrations in the influent and anaerobic effluent during stage I (no NH_3 extraction) and stage II (membrane-based NH_3 extraction).

3.2. Effect on biogas productivity

Methane yields of 538 ± 129 and 885 ± 36 N mL CH_4 g VS removed^{-1} were accomplished during stage I and II, respectively. Thus, the implementation of a membrane-based ammonia recovery system mediated a 1.6-fold increase in methane yield (Fig. 3a). This higher AD performance agrees with the enhancement in COD and VS removals observed as a result of NH_3 extraction in stage II. The yields here achieved during stage I matched the observations from other studies anaerobically treating PM under mesophilic conditions (350–400 N mL CH_4 g VS fed^{-1}) [31,36]. In addition, a recent work in an anaerobic CSTR coupled with a membrane extraction unit treating swine manure as a substrate, reported an increase in methane yields from 380.4 N mL CH_4 g VS fed^{-1} in the absence of NH_3 extraction up to 566.1 N mL fed^{-1} g VS fed^{-1} following a reduction in NH_3 concentration from 1.6 to 1.2 g L^{-1} [23]. González-García et al. compared the performance of two anaerobic reactors with and without membrane-based ammonia extraction during the treatment of swine manure and observed a 9 % increase in methane yield [37]. Moreover, Bayrakdar et al. compared two PM leach-bed reactors with and without membrane-based NH_3 extraction and observed that methane production with membrane was 2.3 folds higher than without membrane [34]. Finally, a methane yield of 300 N mL CH_4 g VS fed^{-1} was recorded during the dry AD of PM by using an ammonia diffusion membrane [35].

Biogas composition during the first week of operation averaged values of 7.3 % ± 1.0 % CO_2, 6.8 % ± 1.7 % O_2, 84.4 % ± 0.4 % N_2 and 1.5 % ± 1.1 % CH_4. No measurable amounts of H_2S were detected. During the second week of operation, biogas composition averaged 60 % ± 3 %, CO_2, 0.5 % ± 0.1 % H_2S, 0.6 % ± 0.1 % O_2, 3.3 % ± 0.7 % N_2 and 36 % ± 3 % CH_4. Under steady state, the concentration of these permanent gases remained stable during stages I and II, with concentrations of CO_2 of 28 % ± 2 % and 30 % ± 2 %, respectively (Fig. 3b). Similarly, the concentrations of CH_4 in stages I and II averaged 72 % ± 2 % and 68.8 % ± 1.1 %, respectively. The decrease in CH_4 concentration concomitant with the increase in CO_2 concentration was mediated by the rapid proton transfer from the sulfuric acid solution to the anaerobic broth, as confirmed by the decrease in pH when interconnecting the membrane module. Niu et al. reported concentrations of 60 % for CH_4 and 40 % for CO_2 in the biogas produced in a PM mesophilic CSTR operated at a HRT of 30 days with ammonia stripping [31]. Periodic increases in CO_2 concentration, concomitant with reductions in CH_4 concentration, were observed as a result of membrane replacement, which entailed a rapid acidification of the cultivation broth during the first day of membrane operation. The pH value in the influent averaged 7.5 ± 0.1 and increased to 8.2 ± 0.1 in the PM anaerobic broth in stage I. Similarly, the pH value of the anaerobic broth in stage II remained constant at 8.2 ± 0.1 (Fig. S1). The periodic membrane replacements to prevent fouling and membrane breakage entailed an improvement on both ammonia recovery from the anaerobic broth and a more intense proton transfer from the acid reservoir to the anaerobic cultivation broth. In this context, literature studies have also reported a slight decrease in the pH of the reactor broth when connecting the membrane-based extraction system [23,34]. The reduction of the methane yield in the beginning of stage II was caused by this collateral effects of membrane extraction system connection.

3.3. Effect on organic matter degradation

The initial decrease in COD removal efficiency observed was caused by the gradual feeding of COD and the limited activity of the inoculum during the initial period of stage I. Steady state COD and VS removal efficiencies during stage I reached values of 59 % ± 2 % and 57 % ± 3 %, respectively (Fig. 4a, b). Likewise, the removal efficiencies of COD during stage II accounted for 79.1 % ± 0.8 %, while VS removal efficiencies increased up to 65.8 % ± 0.2 %. This enhancement in the biodegradation of organic matter was attributed to the decrease in the

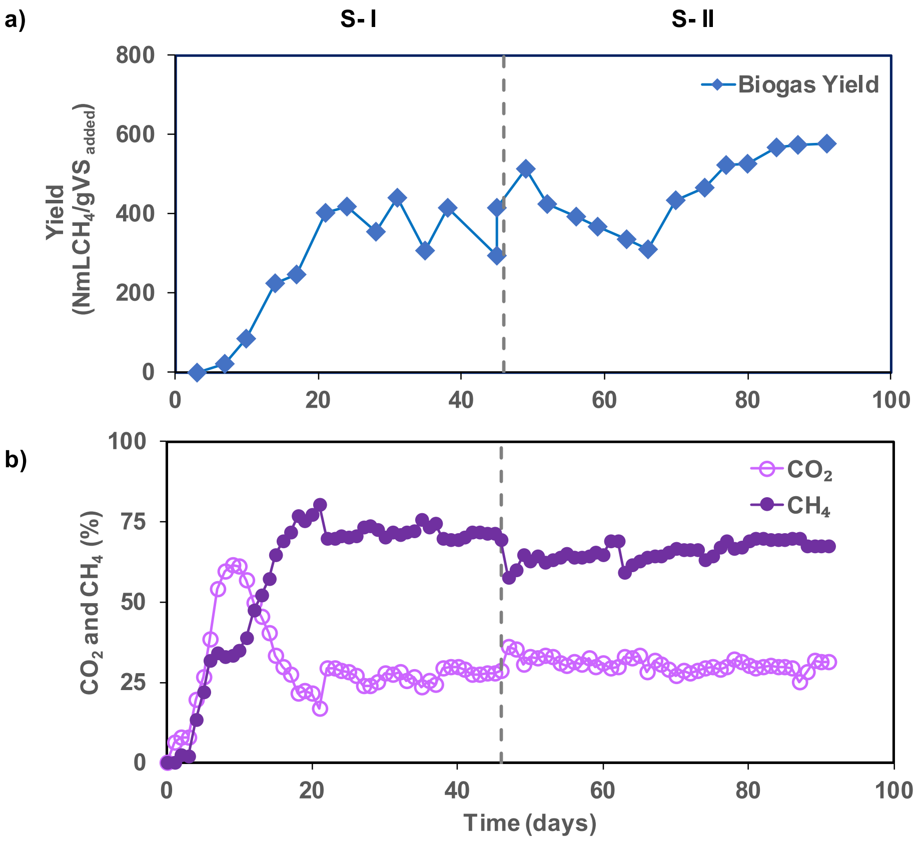

Fig. 3. Time course of the biogas yield (a) and concentrations of (b) CH_4 and CO_2 during stage I (no NH_3 extraction) and stage II (membrane-based NH_3 extraction).

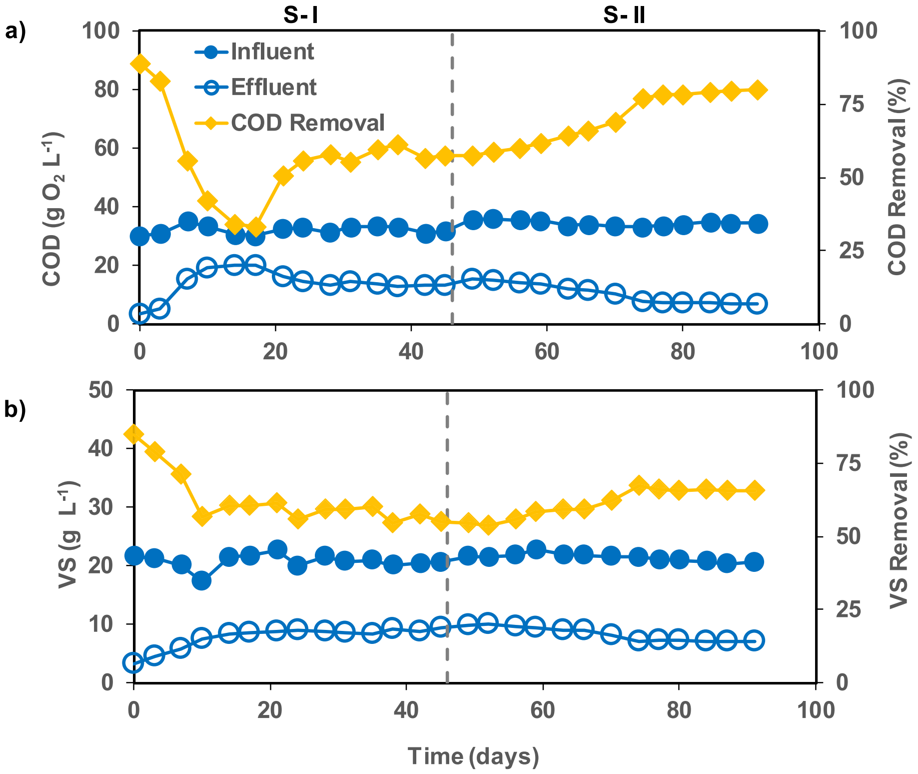

Fig. 4. Time course of the concentrations of COD (a) and VS (b) in the influent and anaerobic effluent, and their corresponding removal efficiencies during stage I (no NH_3 extraction) and stage II (membrane-based NH_3 extraction).

ammonia concentrations in the anaerobic broth caused by the operation of the membrane-based ammonia extraction process (Fig. 4b). Resch et al. observed that reducing TKN from 7.5 to 4.0 g/kg mediated an increase in COD removal by 55 % as a result of an enhanced VFAs assimilation [38]. Nevertheless, TAN concentrations below 10 mg NH_4-N L^{-1} should be avoided to support an effective methanogenesis [38,39]. Molinuevo-Salces et al. operated a semi-continuous CSTR under mesophilic conditions treating swine manure at a HRT of 5 days and

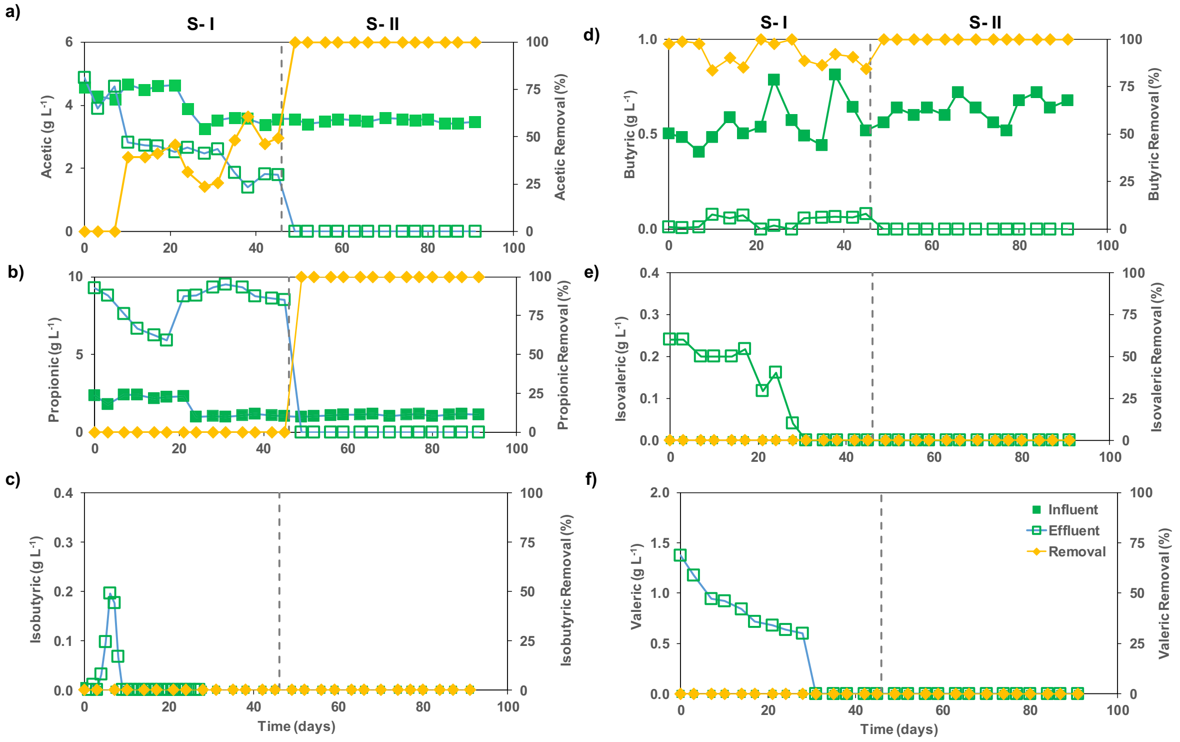

Fig. 5. Time course of the concentrations of acetic (a), propionic (b), isobutyric (c), butyric (d), isovaleric (e) and valeric (f) acids in the influent and anaerobic effluent, and their corresponding removal efficiency during stage I (no NH_3 extraction) and stage II (membrane-based NH_3 extraction).

observed an increase in the removal of COD from 58.3 % to 68.8 % when implementing a PTFE tubular gas membrane for NH_3 extraction [40]. Likewise, Rivera and co-workers reported an increase in COD and VS removal efficiencies from 33 % to 62 % and from 26 % to 38 %, respectively, mediated by the use of membranes in a similar experimental set-up using swine manure [23]. TOC and IC results are in accordance with the COD results (Fig. S2). Higher removal efficiencies were achieved with diluted PM over swine manure, which highlights the higher biodegradability of chicken manure. Fig. S3 shows the schematic representation of the mass balance performed during stage II.

3.4. *Effect on the reduction of VFAs*

The concentrations of VFAs in the anaerobic broth during stage I under steady state were 1.7 ± 0.2 g acetic L^{-1}, 8.6 ± 0.1 g propionic L^{-1}, 0.10 ± 0.01 g butyric L^{-1}. No measurable amounts were detected for isobutyric, isovaleric and valeric VFAs. Membrane-based NH_3 extraction promoted a rapid decrease in the VFAs concentrations present in the anaerobic broth (Fig. 5). Therefore, the removal efficiencies of acetic acid increased from 52 % ± 8 % up 100.0 % ± 0.1 % when the membrane module was installed. Correspondingly, butyric acid removal efficiencies increased from 89 % ± 4 % in Stage I up to 100.0 % ± 0.1 % in stage II. Propionic acid concentrations in the anaerobic broth during stage I increased from 1.1 ± 0.1 g L^{-1} in the feed to 8.6 ± 0.1 g L^{-1}, while isobutyric, isovaleric and valeric were not present. No VFAs were detected in the anaerobic broth following the implementation of the membrane-based extraction module in stage II. This phenomenon was mainly attributed to the decrease of TAN concentrations or any other inhibitory compound, and the subsequent microbial assimilation of the VFAs. In this context, literature studies have reported that high concentrations of TAN were correlated with the accumulation of VFAs [31,35,41]. The mass transfer of the VFAs from the cultivation broth to the acid reservoir was discarded in a separate set of experiments (data not shown). The low concentration of the VFAs makes more challenging to achieve a liquid contact throughout the membrane's pores. VFAs can be toxic to the microbial community at high levels, this toxicity being increased by decreasing pHs [42]. In Stage I, the ratio propionate/acetate in the cultivation broth was 5.2, while the implementation of the membrane significantly reduced this ratio to 0.0. This ratio is relevant from an operational point of view because values higher than 1.4 can deteriorate the AD process, since propionic acid is known as the most toxic VFAs [43,44]. High VFAs concentrations can lead to inhibition of the methanogenic microbial community, also causing a decrease of pH and buffer capacity [45,46]. Kroeker et al. reported that inhibitory levels can be as low as 0.01 g L^{-1} of acetic acid [47]. In this study, the undetectable concentrations of VFAs in the cultivation broth caused by ammonia extraction consistently enhanced the AD process of PM.

3.5. *Membrane morphology analysis*

Fig. 6 depicts AFM topographic images of the hydrophobic flat sheet membrane unused and used for ammonia extraction for 20 days. Fouling was clearly detected in the used membrane according to Fig. 6b. As stated by Zhang et al. the unused membrane shows a topography with higher roughness than the used membrane [48]. Rivera et al. reported that a PTFE membrane was not significantly deteriorated by the acid

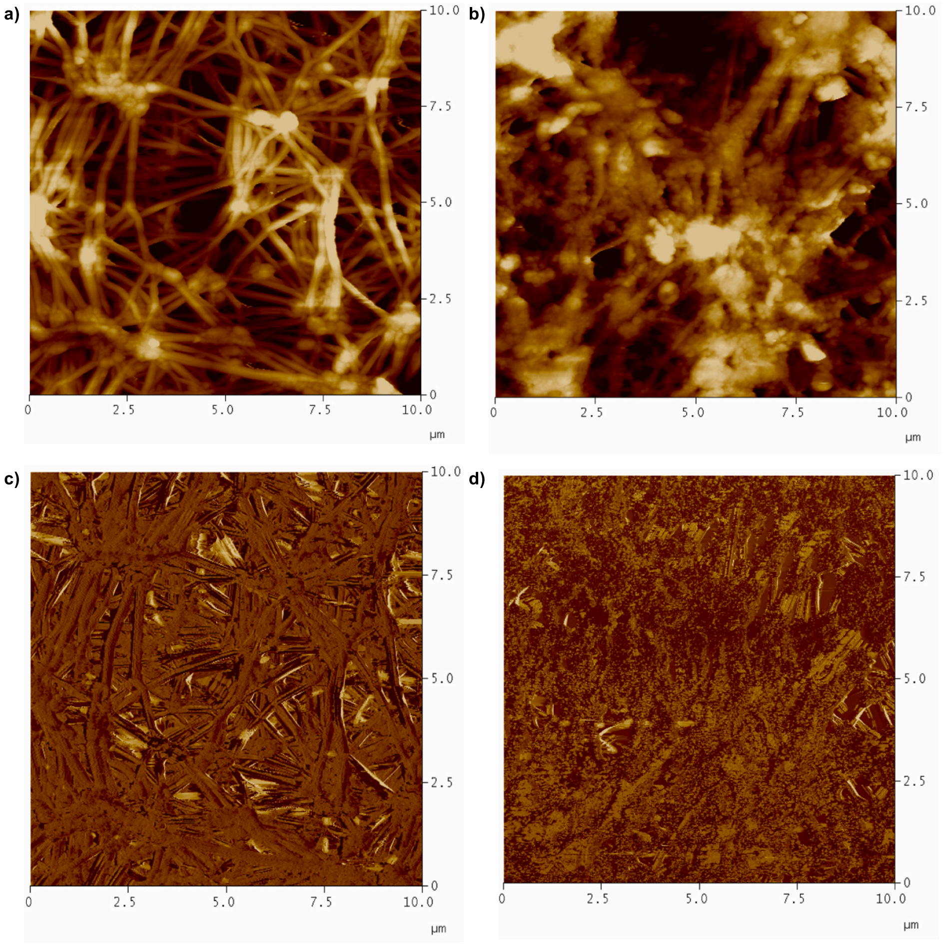

Fig. 6. AFM 2D topographic images of the unused (a) used (b) PTFE membrane. AFM Phase Imaging of the active layer of the unused (c) and used PTFE membrane (d) (scanned area 10 µm × 10 µm). Each pair of images (a–b and c–d) have the same z scale.

recirculation on the membrane surface and observed that less fouling was detected at higher velocities [26]. Phase contrast images revealed the presence of materials from the anaerobically treated PM deposited over the used membrane surface, which correspond to the deeper brown tones (Fig. 6d). Membrane fouling was likely caused by microorganisms and be both, inorganic and organic matter. Previous studies have demonstrated that fouling layers induce the loss of membrane hydrophobicity, which ultimately causes a loss of efficiency [49,50]. In this context, chemical and physical cleaning methods should be applied to mitigate the impact of fouling on membrane performance [27,51]. Flemming and coworkers reported that only few minutes are necessary for the development of irreversible attachments of cells when there is contact between wastewater and the membrane [52]. Flemming and coworkers also identified that there was an evident weakness from certain bacteria over membrane materials. Riedl and coworkers concluded that dense fouling layers are present in smooth membranes [53]. To reduce membrane fouling it is necessary to operate always below the critical flux of the plant [54]. In view of the images, fouling does not seem to be a critical problem in this process.

3.6. Economic assessment

A detailed economic evaluation of the total costs of TAN recovery from PM in an anaerobic digestion plant coupled with a membrane-based ammonia extraction system was herein conducted based on the lab scale. The values used in the techno-economic study are based on experimental results and the following assumptions: An annual production of raw PM in the farm of 1200 m^2 resulting from 13,400 chicken. The raw poultry manure contains 0.72 g TAN L^{-1}. The digester has a capacity of 150 m^3 with daily feeding of 15 m^3 d^{-1}. PM costs would not be considered because it would be produced in the farm with no transportation costs. The CAPEX (Capital Expenditures) were calculated according to the main equipment (Fig. 1), while the Total Investment Cost were calculated as 4.1 × CAPEX [55]. The OPEX (Operational Expenditures) were calculated according to the main consumables: energy, water and reagents. Maintenance costs are estimated as 3.5 % of the CAPEX. For the flatsheet membrane a 10 % of replacement per year was considered. Annual costs of equipment are calculated using a 10-year lifetime and 4 % interest [56].

For the theoretical design of the scaled-up plant, TAN recoveries of 5475 kg TAN $year^{-1}$ were estimated. A membrane surface area of 220 m^2 is needed in the scaled-up plant to achieve the target TAN recoveries. The total investment cost, considering 4 % interest and 10-year lifetime is 601,291 € (bioreactor, storage tanks, pumps, membrane module, acid tank, reagents, power and water). The annualized cost 10-year lifetime at 4 % interest is 485,036 €.

The revenues in the full scale plant would be obtained from the sales of biogas (54 ton $year^{-1}$) and ammonium sulfate (5413 kg N $year^{-1}$). The sales of biogas would account for 53,983 €. On the other hand, the corresponding fertilizer value accounts for 12,775 € (2.36 € kg^{-1} of N as ammonium sulfate [57]). A summary table of CAPEX, OPEX and revenues is shown in Table 2.

0.48 kWh kg^{-1} of recovered N was the energy consumption of this theoretical full scale plant. Molinuevo-Salces et al. reported an energy consumption of 0.68 kWh kg^{-1} recovered N in an anaerobic digester treating swine manure from a 1881 m^2 farm using tubular membranes [58]. In this context, technologies for nitrogen recovery from digestates tend to be expensive. For example, ammonia stripping can require up to 8.65 kWh kg^{-1} of recovered N [59]. Thus, membrane-based ammonia extraction represents a promising technology due to its low energy consumption.

Table 2
Summary of CAPEX, OPEX and revenues of a theoretical full scale plant.

	Description	€
1. CAPEX		
1.1	Scaled-up membrane extraction plant	**146,656.35**
2. OPEX		
2.1	Reagents (H_2SO_4)	4602.05
2.2	Power	593.44
2.3	Water	22,069.68
2.4	Maintenance	21,045.19
		48,310.36
3. Revenues		
3.1	Fertilizer sale (ammonium sulfate)	12,774.81
3.2	Biogas sale	53,982.51
		66,757.33

4. Conclusions

The performance of anaerobic digestion treatment of PM wastewater was consistently enhanced by membrane-based ammonia extraction. Continuous ammonia extraction from the reactor broth mediated NH_3 diffusion through the membrane, which resulted in a decrease in the concentrations of ammonia in the cultivation broth. This ultimately resulted in an increase of the methane yield by 60 % and a constant biogas composition. Moreover, an increase in the removal efficiencies of COD and VS up to 79 % and 66 %, respectively, was observed. Furthermore, VFAs were completely assimilated with removal efficiencies of 100 %. Additionally, membrane fouling likely caused by microorganisms, inorganic and organic matter was detected in the membrane after 20 days of operation. This work targeted the enhancement of the performance of full-scale anaerobic digestion plants via reduction of NH_3 concentration with a membrane-based extraction unit. Membrane-based ammonia extraction represented an optimal strategy to enhance the performance of full-scale anaerobic digestion plants. This novel technology can support the production of valuable products such as sustainable energy in the form of biomethane and fertilizers such as ammonium sulfate. Under full-scale operation, anaerobic plants treating livestock waste will be coupled to membrane extraction modules.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2023.103990.

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