Bioresource Technology 362 (2022) 127829

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Enhancement of swine manure anaerobic digestion using membrane-based NH_3 extraction

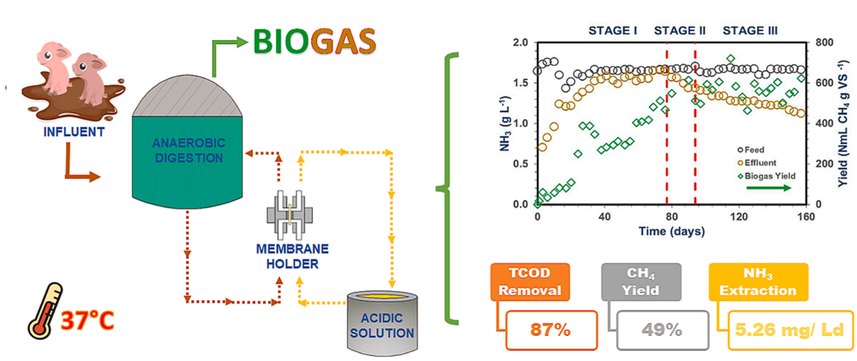
Fanny Rivera [a,b], Luis Villareal [a], Pedro Prádanos [a,b], Antonio Hernández [a,b], Laura Palacio [a,b], Raúl Muñoz [a,c,*]

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

HIGHLIGHTS

- NH_3 extraction from piggery wastewater was enhanced by increasing pH values.
- Suspended solid concentration did not affect NH_3 extraction from piggery wastewater in batch tests.
- CH_4 yields increased by 49% under continuous NH_3 extraction in the digester.
- COD and vS removal efficiencies increased by 87% and 48%, respectively.
- VFAs were completely removed from the anaerobic broth during NH_3 extraction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Ammonia recovery
Anaerobic digestion
Biogas production
CSTR bioreactor
Flat sheet membranes

ABSTRACT

The influence of suspended solids and pH in anaerobically digested piggery wastewater on membrane-based NH_3 extraction was evaluated in batch tests. The increase in pH in the anaerobic broth from 8 to 9 resulted in an increase in NH_3 removal efficiencies from 15.8 % ± 0.1 % to 20.9 % ± 0.4 % regardless of the suspended solids. The influence of membrane based NH_3 extraction on piggery wastewater treatment was also assessed in a CSTR interconnected with PTFE membrane modules. The decrease in TKN concentrations mediated by membrane operation induced an increase in CH_4 yield from 380.4 ± 84.9 up to 566.1 ± 7.8 NmLCH$_4$ g VS fed^{-1}. Likewise, COD and VS removal efficiencies significantly increased from 33.0 % ± 2.0 % and 25.7 % ± 2.3 % up to 61.8 % ± 1.3 % and 37.9 % ± 1.8 %, respectively. Interestingly, the decrease in NH_3 concentration entailed a complete assimilation of VFA.

1. Introduction

Today, there is an urgent need to substitute fossil fuels by renewable energy vectors in order to mitigate climate change and to protect the environment (Kang et al., 2020). In this context, while the main source of bioenergy in Earth is lignocellulosic biomass (Guldhe et al., 2017),

* 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).

https://doi.org/10.1016/j.biortech.2022.127829
Received 13 July 2022; Received in revised form 17 August 2022; Accepted 21 August 2022
Available online 27 August 2022

biogas from the anaerobic digestion of animal manure, industrial or urban solid waste, sewage sludge, energy crops or wastewaters, etc., has recently attracted an increasing attention due to its versatility and high energy content (Kunatsa and Xia, 2022; Ye et al., 2021).

Anaerobic digestion is based on the microbial hydrolysis and bioconversion of biodegradable organic matter in the absence of oxygen into biogas, which is primarily composed of methane and carbon dioxide (Reyes et al., 2015). Biogas is a renewable gas energy vector used to generate heat and electricity, which can replace (prior upgrading) natural gas in the gas networks and fossil fuels in transportation (Andriani et al., 2014). Biogas composition is determined by the oxidation–reduction state of the organic matter in the biodegradable substrate and the type of anaerobic digestion (AD) process (Jonsson et al., 1997). The hydrolysis of organic matter and the further ammonification of organic nitrogen generate high ammonia concentrations in the digestates, which entail a detrimental impact on water bodies (eutrophication and nitrate pollution) and air quality (NH_3 emissions) (Yenigün and Demirel, 2013). Indeed, NH_3 emissions can cause cancer, pulmonary diseases and are considered atmospheric precursors of N_2O, which is a powerful greenhouse gas (Temkin et al., 2019). Indeed, the European Directive 2016/2284 will enforce reductions in NH_3 emissions up to 3 % between 2020 and 2029 and up to 16 % from 2030 onwards (European Parliament and Council, 2016). In addition, concentrations higher than 0.4 g NH_3-N L^{-1} can inhibit methane production during anaerobic digestion, which represents a technical limitation during the anaerobic digestion of livestock manure (Procházka et al., 2012; Sung and Liu, 2003). Methanogens are the most sensitive microorganisms exposed to NH_3 toxicity (Chen et al., 2008). For instance, total ammoniacal nitrogen concentrations of 1.7 – 14 g L^{-1} cause a 50 % reduction in methane production during anaerobic digestion (Angelidaki and Ahring, 1994; Chen et al., 2008; Hendriksen and Ahring, 1991; Sung and Liu, 2003).

Nowadays, multiple technologies are applied in order to reduce NH_3 concentrations from wastewaters. The implementation of NH_3 stripping or denitrification-nitrification processes entail high operational costs (Licon Bernal et al., 2016) and a severe impact to the environment. Therefore, the development of cost-efficient and sustainable technologies for NH_3 recovery from wastewater is mandatory in the current quest for creation of circular bioeconomy concepts. In this context, membrane-based NH_3 extraction from wastewaters represents a feasible technology for ammonia recovery over conventional methods (Brennan et al., 2020). An effective ammonia recovery can be achieved via membrane contactors as a result of their high surface area, selective NH_3 extraction and low consumption of energy (Mahmud et al., 2000; Yeon et al., 2003). NH_3 extraction from wastewater is based on NH_3 gas transfer between the wastewater and an acid solution separated by a hydrophobic membrane. The type and area of the membrane, which determines both the pores available and contact surface for NH_3 mass transfer, and the type of acid driving NH_3 diffusion, rank among the most important operational parameters of this technology (Guo et al., 2019; Hasanoĝlu et al., 2010; Rivera et al., 2022). Hollow fiber contactors are likely the most promising alternative for ammonia recovery in anaerobic broths. This configuration exhibits higher contact area per volume of membrane, allows a broad range of pHs, and exhibit a high resistance to chemicals and high temperatures, mechanical stability and hydrophobicity (Darestani et al., 2017; Eykens et al., 2016). Different chemical fertilizers such as ammonium sulfate, ammonium phosphate and ammonium nitrate can be produced depending on the type of acid used (Darestani et al., 2017). Despite this technology has been successfully tested to extract NH_3 from the effluent of anaerobic digesters, its direct implementation into an anaerobic digester to support in-situ ammonia recovery and enhance the anaerobic digestion process has never been tested.

This work investigated the potential of hydrophobic flat sheet membranes to in-situ and ex-situ extract NH_3 from the anaerobic broth of piggery wastewater digestion. Batch tests were initially conducted ex-situ to study the influence of the concentration of suspended solids and pH on NH_3 extraction from anaerobically digested piggery wastewater using circular and rectangular configurations of Polytetrafluoroethylene PTFE hydrophobic membranes. The influence of in-situ NH_3 extraction from the culture broth of a continuous anaerobic digester treating piggery wastewater on the performance of anaerobic digestion was also investigated using the above cited membrane configurations.

2. Materials and methods

2.1. Piggery wastewater and anaerobic sludge

Fresh piggery wastewater, previously centrifuged in an industrial decanter, was obtained from a nearby farm (Segovia, Spain) and stored at 4 °C for periods no longer than 45 days. Piggery wastewater exhibited a constant composition throughout the entire experiment: 54.90 ± 4.14 g COD/L, 1.62 ± 0.05 g NH_3/L, 5.51 ± 1.31 g TKN/L, 31.51 ± 2.92 g TS/L, 21.74 ± 2.23g VS/L and pH 7.54 ± 0.07. The anaerobic inoculum was obtained from the full-scale digester of Valladolid wastewater treatment plant (WWTP) (Valladolid, Spain). The inoculum composition was as follows: 4.14 g COD/L, 0.33 g NH_3/L, 1.62 g TKN/L, 13.00 g TS/L, 7.83 g VS/L and pH 7.90.

2.2. Experimental Set-up

The first experimental set-up, composed of a continuous recirculation of anaerobically digested pig slurry (obtained from the second experimental set-up) using a peristaltic pump (Watson Marlow 520, USA) over the active layer of a PTFE hydrophobic membrane in two tailor made membrane holders, was used to investigate the influence of suspended solids and pH in the digested pig slurry on NH3 extraction. A similar peristaltic pump was used to recirculate a 1 M sulfuric acid solution on the support layer of the membrane. Both solutions were maintained in 0.3 L enclosed Erlenmeyer bottles kept in a thermostatic bath (HAAKE type E12, Thermo Fisher Scientific, Waltham, MA, USA) at 35 °C. The PTFE membrane was purchased from Millipore (Ireland) and exhibited a pore size of 0.22 μm, a nominal thickness of 170 μm, a contact angle of 150°and a porosity of 70 %. This membrane was selected based on its effective performance during NH_3 recovery from sewage sludge digestates (Rivera et al., 2022).

The second experimental set-up was composed of a continuous stirred tank reactor (CSTR) with a working volume of 3L and magnetically stirred at 200 rpm in a thermostatic room (37 °C) (Fig. 1). The anaerobic cultivation broth present in the CSTR was tangentially recirculated at 0.25 L min^{-1} using a peristaltic pump (Watson Marlow 520, Spirax-Sarco Engineering plc, Cheltenham, UK) over the active layer of a hydrophobic PTFE membrane casted on a circular (8.55 m^2) or rectangular (44.

m^2) membrane holder (Silva et al., 2011). Ammonia was recovered in a 1 M sulfuric acid aqueous solution recirculated on the support layer of the membrane at 0.25 L min^{-1}. Fresh piggery wastewater and anaerobic digestate were daily fed and withdrawn using peristaltic pumps (Watson–Marlow Sci-Q 323, Spirax–Sarco Engineering plc, Cheltenham, UK).

2.3. Influence of suspended solids and pH on NH_3 recovery from digested pig slurry

Four test series were carried out using the effluent from the 3L anaerobic digester treating piggery wastewater under mesophilic conditions. Two membrane holders with areas of 8.55 cm^2 (Montalvillo et al., 2014) and 44 cm^2 were used to investigate the influence of pH (8.2 ± 0.32 and 9.0 ± 0.05) and suspended solid concentration (raw digested pig slurry and digested pig slurry centrifuged at 10000 rpm for 10 min in a Thermo Scientific Sorvall TM Legend TM RT Plus centrifuge). The experiments were performed in duplicate at 35 °C using a 1 M solution of H_2SO_4. The recirculation rates of the digested pig slurries and H_2SO_4

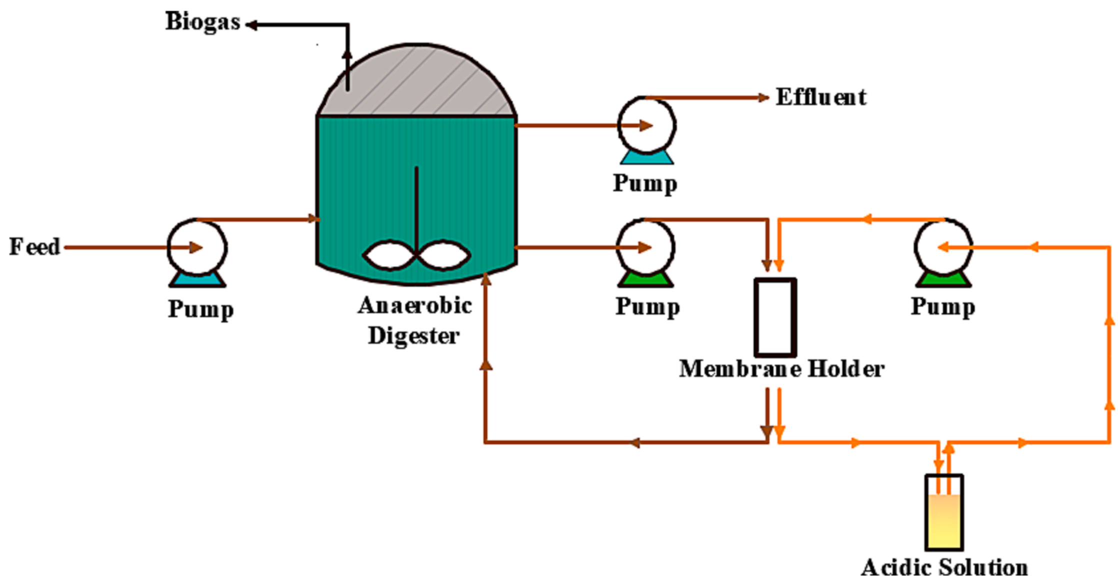


Fig. 1. Schematic representation of the CSTR anaerobic digester coupled with an external membrane-based NH_3 extraction unit.

solutions were set at 0.25 L min^{-1} and the experiments lasted for 120 min. Samples (2 mL) for the determination of NH_3 concentrations were taken every 30 min.

2.4. *Influence of membrane-based NH_3 extraction on the continuous anaerobic treatment of piggery wastewater*

The experimental set-up was operated for 157 days under 3 different operational conditions. The bioreactor was inoculated with 2.5L of anaerobic inoculum, 0.5L of raw piggery wastewater and supplemented with 5 g $NaHCO_3$ L^{-1}. Stage I was operated for 76 days with an average time spent by the substrate in the anaerobical digestor, hydraulic retention time (HRT), of 20 days without NH_3 extraction. Stage II involved the interconnection of the circular membrane holder at 0.25 L min^{-1} with 1 M H_2SO_4 for 17 days. Stage III involved the interconnection of the rectangular membrane holder at 0.25 L min^{-1} with 1 M H_2SO_4 for 64 days. The membrane was replaced weekly to maintain optimal NH_3 extraction performance. Samples (150 mL) of the raw piggery wastewater and the effluent of the anaerobic bioreactor were drawn twice a week to analyze the concentration of total ammoniacal nitrogen, total chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total nitrogen (TN), total and volatile solids (TS, VS), total organic and inorganic carbon (TOC, IC) and volatile fatty acids (VFA), and temperature and pH. The volume and composition of the biogas daily produced were also recorded.

2.5. *Analytical methods*

Samples of biogas were taken using a gas-tight syringe (Hamilton, 1710 SL SYR, 100 μL, California, USA) for determining the concentration of CO_2, CH_4, H_2S, O_2 and N_2 using a gas chromatograph (Varian CP-3800, Palo Alto, CA, USA) coupled with a detector and equipped with a CP-Molsieve 5 A (15 m × 0.53 mm × 15 μm) and a CP-Pora BOND Q (25 m × 0.53 mm × 15 μm) columns (García et al., 2019). The values of pH and temperature were monitored using a Basic 20 pH meter with a 50 14 T electrode (Crison Instruments, S.A., Barcelona, Spain) in the liquids of both sides of the membrane. Ammoniacal nitrogen was measured using the Nessler analytical method in a SPECTROstar Nano Absorbance Reader spectrophotometer at 425 nm (BMG LABTECH, Germany). The determination of COD, TKN, TS and vS was carried out according to Standard Methods for examination of water and wastewater (APHA, 2005). TN, TOC and IC were measured in a Shimadzu TOC- VCSH analyzer (Shimadzu, Kioto, Japan) equipped with a TNM-1 module. Volatile Fatty Acids (VFA) analysis was performed in an Agilent 7820A GC-FID (Agilent Technologies, Santa Clara, USA) equipped with a G4513A autosampler and a TEKNOKROMA NF29370-F packed column (2 m × 1/8″ × 2.1 mm) (Teknokroma, Barcelona, Spain) (López et al., 2018).

3. Results and discussion

3.1. *Influence of suspended solids and pH on NH_3 recovery from digested pig slurry*

The increase in pH from 8.2 to 9 in the digestate resulted in an increase in the NH_3 extraction efficiency regardless of the area of the membrane and presence of suspended solids. Thus, an increase in the NH_3 concentration removed in 2 h from 0.20 and 0.21 g/L at pH 8.2 up to 0.28 and 0.31 g/L at pH 9 was recorded in the presence and absence of suspended solids, respectively, in the 8.55 cm^2 circular membrane module. In the 44 cm^2 rectangular membrane module, the NH_3 concentration removed in 2 h increased from 0.31 and 0.33 g/L at pH 8.2 up to 0.40 and 0.43 g/L at pH 9 in the experiments carried out with raw and centrifuged digestate, respectively. Thus, the removal efficiency of ammonia with a previous centrifugation at pH 8.2 accounted for 15.85 %, while at pH 9 this removal efficiency increased up to 20.94 %. The pH of the digestate is a key parameter during NH_3 permeation in membranes since higher pHs swift the NH_4^+/NH_3 equilibrium in the digestate towards NH_3, the chemical compound that is able to permeate through the membrane, which results in higher ammonia removal rates (Table 1). Previous works identified an optimal pH value of 9 for NH_3 recovery from real digestates along with other operational parameters of the PTFE membrane module such as a 1 M sulfuric acid concentration and recirculation flow rates of 0.25 L min^{-1} (Molinuevo-Salces et al., 2020; Rivera et al., 2022). Unfortunately, pH values higher than 9 in the anaerobic broth of digesters could negatively impact the structure and performance of the prevailing microbial anaerobic community, which would ultimately deteriorate waste treatment performance and biogas production (see supplementary material).

The circular and rectangular membrane modules were compared in terms of the influence of the flow hydrodynamics on NH_3 molar fluxes. Thus, molar fluxes of 3.15 mol m^{-2}h^{-1} and 0.85 mol m^{-2}h^{-1} were recorded using solid-free digestate at pH 9 in the 8.55 cm^2 and 44 cm^2 membrane modules, respectively. These values were in agreement with

Table 1
Operational conditions and NH_3 recovery indicators in batch extraction assays.

Test	Membrane Holder	pH	Centrifuged	H_2SO_4 (M)	Flow Rate (L min^{-1})	T (°C)	NH_3 Recovered (g L^{-1})	Flux (mol m^{-2}h^{-1})
1	Circular	8.2	x	1	0.25	35	0.20 ± 0.01	2.06
2	Circular	8.2	✓	1	0.25	35	0.21 ± 0.02	2.12
3	Circular	9.0	x	1	0.25	35	0.28 ± 0.06	2.84
4	Circular	9.0	✓	1	0.25	35	0.31 ± 0.11	3.15
5	Rectangular	8.2	x	1	0.25	35	0.31 ± 0.11	0.61
6	Rectangular	8.2	✓	1	0.25	35	0.33± 0.13	0.65
7	Rectangular	9.0	x	1	0.25	35	0.40 ± 0.14	0.80
8	Rectangular	9.0	✓	1	0.25	35	0.43 ± 0.18	0.85

the molar flux of 4.52 mol m^{-2}h^{-1} reported for synthetic anaerobic digestate at pH 10 under similar operating conditions with a circular PTFE membrane module (Rivera et al., 2022). The speed of the fluid within the circular module is 1.61 m s^{-1} with a Reynolds number of 1,640, while for the rectangular module the values were 0.10 m s^{-1} and 106 respectively. For both modules the fluid flow regime was laminar due to the low-velocity fluids. However, through the circular module the Reynolds numbers is 15 – fold higher than the rectangular and this explains the difference in the NH_3 molar flux values.

In brief, this study revealed that greater concentrations of NH_3 were recovered when increasing the membrane surface and pH, while the presence of suspended solids did not hinder ammonia extraction significantly in these short-term experiments. This latter finding represents a competitive advantage from an operational point of view (no digestate centrifugation needed), although some suspended solids would end up deposited on the membrane surface (fouling) during long-term experiments and limit NH_3 recovery.

3.2. *Influence of membrane-based NH_3 extraction on the continuous anaerobic treatment of piggery wastewater*

Since NH_3 is one of the mayor inhibitors of the anaerobic treatment of livestock wastewaters (Müller et al., 2006), the reduction of Total Ammonia Nitrogen (TAN) concentrations below inhibitory levels but above nutritional requirements is expected to enhance the performance of anaerobic digestion in terms of COD and vS removal, and ultimately of biogas productivities. In this context, (Siles et al., 2010) reported a NH_3 threshold of 0.62 g free ammonia L^{-1} during the anaerobic digestion of a synthetic solution rich in ammonia and sodium sulphate, with a decrease of 21 % in biogas production observed when the concentration of NH_3 was increased. Other authors have reported inhibitory TAN concentration ranges of 1.5 – 7.0 g N L^{-1} in anaerobic digesters (Hejnfelt and Angelidaki, 2009). The TAN inhibition threshold in anaerobic cultivation broths depends on the type and concentration of substrates, pH, temperature, microbial population structure, etc. (Chen et al., 2008). It is typically assumed that TAN concentrations above 3.0 g NH_4-N L^{-1} causes a severe inhibition of the methanogenesis of the process

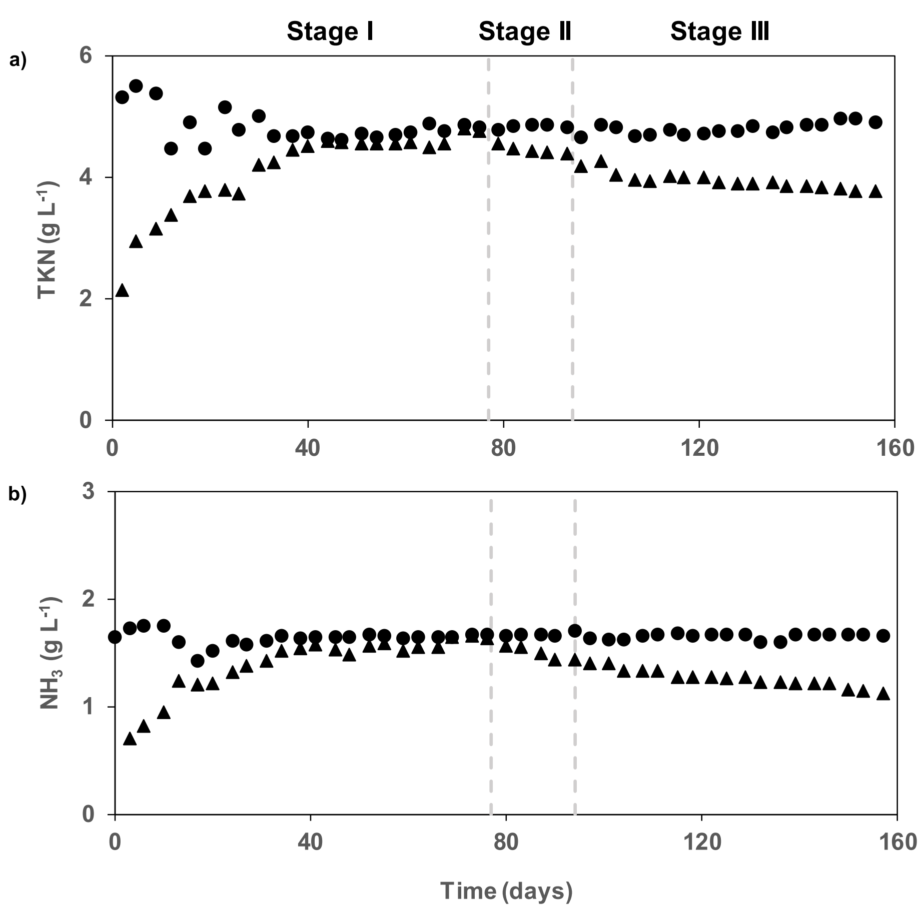


Fig. 2. Time course of the TKN (a) and NH_3 (b) concentrations in the feed (●) and anaerobic effluent (▲) during the three operational stages.

(McCarty, 1964).

Temperature and pH are one of the most important parameters governing ammonia removal since they determine the rate of ammonia mass transfer across the membrane. Indeed, a temperature increase of 30 ªC entailed an increase in ammonia mass transfer by a factor of 7.3-fold using synthetic wastewaters (Deĝermenci et al., 2012; Jiang et al., 2014).

The anaerobic treatment of centrifuged piggery wastewater resulted in steady state TKN and TN concentrations of 4.77 ± 0.04 and 4.01 ± 0.25 gN L^{-1} during stage I (Fig. 2a). The implementation of NH_3 extraction using the circular flat sheet membrane induced a decrease in TKN and TN concentrations to 4.45 ± 0.07 g N L^{-1} and 3.64 ± 0.17 gN L^{-1} by the end of stage II, and to 3.77 ± 0.01 g N L^{-1} and 3.38 ± 0.02 gN L^{-1} by the end of stage III, respectively (Fig. 2a; Fig. 3c). There was also a noticeable decrease in NH_3 concentrations from 1.58 ± 0.05g NH_3 L^{-1} at the end of stage I, to 1.50 ± 0.06 g NH_3 L^{-1} at the end of stage II and to 1.18 ± 0.05 g NH_3 L^{-1} at the end of stage III (Fig. 2b). The rates of ammonium removal in stages I, II and III accounted for 3.99 mg L^{-1} d^{-1}, 8.81 mg L^{-1} d^{-1} and 24.61 mg L^{-1} d^{-1}, respectively. In this context, the molar fluxes of NH_3 across the PTFE membrane in stages II and III averaged 0.41 mol NH_3 m^2h^{-1} at pH 8.15 ± 0.09 and 0.05 mol NH_3 m^2h^{-1} at pH 8.22 ± 0.02, respectively. These molar fluxes were much lower than those recorded in the batch tests at pH values of 8.2 ± 0.32 with raw digestate (2.06 mol NH_3 $m^{-2}h^{-1}$ and 0.61 mol NH_3 $m^{-2}h^{-1}$ for the circular and rectangular membrane modules). The lower performance of the membrane modules under long term operation could be explained by the gradual membrane fouling, which hindered NH_3 permeation through the membrane.

Membrane fouling is caused by microorganisms, organic and inorganic elements. According to extensive studies it was detected that fouling layers cause membranes to lose hydrophobicity, which also leads to reducing the period of efficiency (Xu et al., 2010; Zarebska et al.,

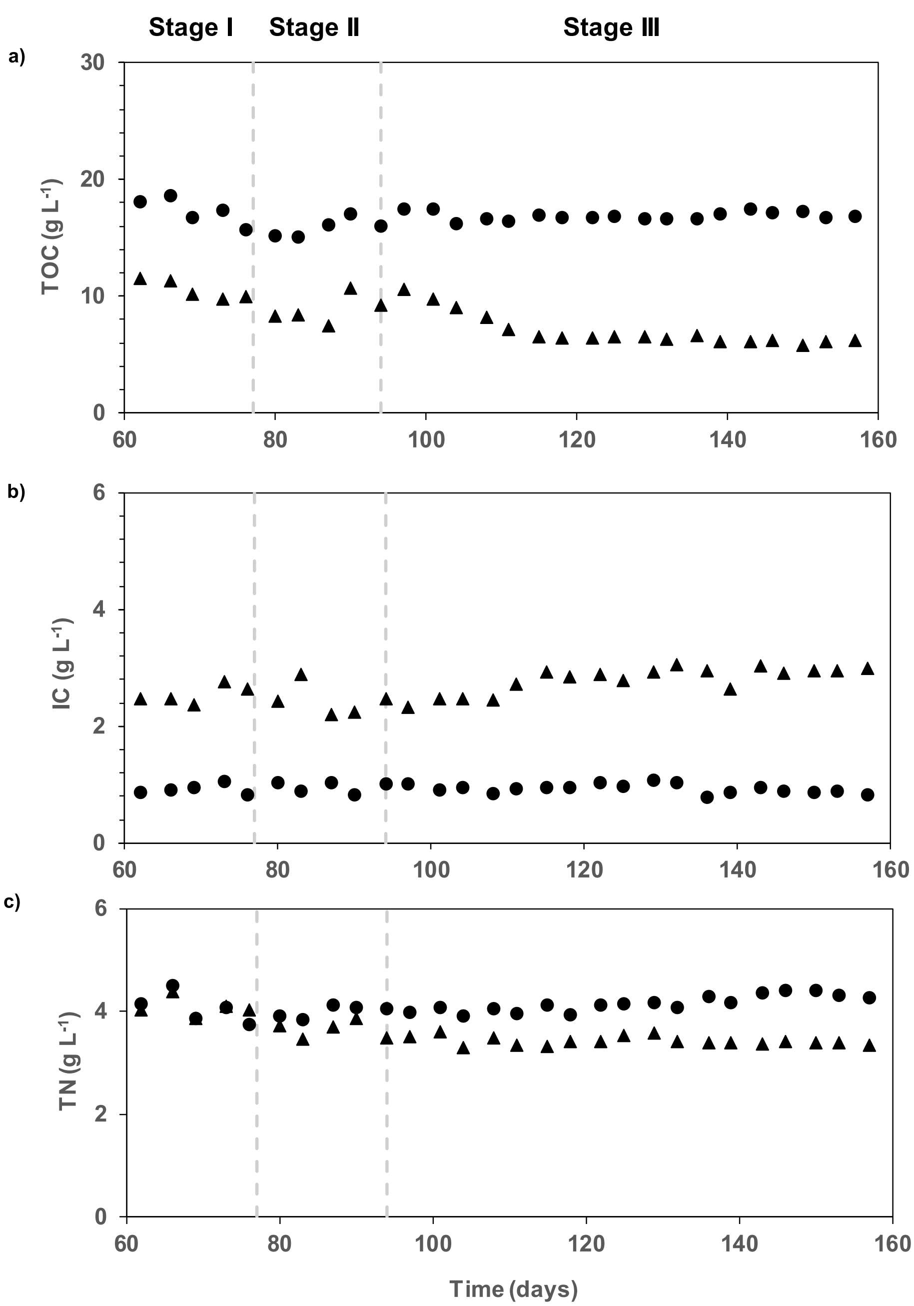


Fig. 3. Time course of the TOC, IC and TN concentrations of the feed (●) and effluent (▲) during the three operational stages.

2014). To reduce this issue, some physical and chemical cleaning methods could be applied (Darestani et al., 2017). According to (Chang et al., 2002), it is possible to achieve a complete abatement for fouling and blocking problems applying both methods and making a periodic application of chemicals.

To the best of the authors knowledge, this work represents the first study reporting in-situ NH_3 extraction using an external membrane module interconnected to a continuous anaerobic digester. This process configuration requires less maintenance, low operational costs and can support a high ammonia recovery. When the pH in the anaerobic cultivation broth was increased, NH_3 removal increased since the equilibrium is shifted towards NH3. The un-ionized NH_3 permeates through the pores to the support layer, where the acid solution is. When NH_3 reaches the acidic solution, it forms NH_4^+ ions by combining with free protons, thus maintaining the maximum NH_3 concentration gradient across the membrane (Dube et al., 2016; Garcia-González and Vanotti, 2015).

COD and vS removal efficiencies during Stage I averaged 33.05 % ± 2.01 % and 25.67 % ± 2.32 %, respectively, under steady state (Fig. 4). The removal efficiencies of COD during Stage II accounted for 42.88 % ± 2.57 %, while a significant increase up to steady state removals of 61.80 % ± 1.33 % was observed during Stage III, likely due to the reduction in NH_3 toxicity caused by the *in-situ* NH_3 extraction implemented (Fig. 4a). Similarly, vS removals during Stage II and III increased up to 26.83 % ± 3.01 % and 37.89 % ± 1.84 % as a result of the reduction in NH_3 inhibition (Fig. 4b). Other studies treating swine manure diluted with water (at an initial COD of 34.16 g/L) under mesophilic conditions in a semi-continuous CSTR operated at a HRT of 5 days reported COD removal efficiencies of 58.26 %. These authors reached COD removal efficiencies of 68.8 % when digesting swine manure pre-treated with a tubular PTFE gas membrane (Molinuevo-Salces et al., 2018). Other authors have observed that a reduction in TKN can increase COD removal by 55 %, which directly enhances the assimilation of VFA. However, methanogenesis does not take place when NH_3 concentration decreases from 0.1 g to 0.01 g NH_4-N L^{-1} (Panichnumsin et al., 2010; Resch et al., 2011).

CH_4 yields of 380.4 ± 85.0, 542.2 ± 52.8 and 566.1 ± 47.8 $NmLCH_4$ g vS fed^{-1} were recorded during Stage I, II and III, respectively (Fig. 5a). These methane yields matched the observed trends in COD and vS removals along the three operational stages. In this context, (Hansen et al., 1999) reported values of 188 $mLCH_4$ g vS fed^{-1} and 65 % CH_4 content in a mesophilic CSTR bioreactor fed with fresh swine manure at 20 days of HRT. (González-García et al., 2021) compared two anaerobic reactors, with and without an internal gas permeable membrane, operating under similar conditions using swine manure as a feedstock, and reported an improvement in the anaerobic digestion process with the recovery of NH_3. Thus, an increase in the CH_4 content of biogas of up to 14 % and in the methane yield of up to 9 % higher (70 $NmLCH_4$ g vS fed^{-1}) was recorded in the digester equipped with an internal membrane module.

Biogas compositions remained stable during stages I, II and III, with concentrations of CO_2 of 20.75 % ± 1.22 %, 20.67 % ± 0.01 % and 23.24 % ± 0.29 %, respectively (Fig. 5b). CH_4 contents of 77.65 % ± 1.08 %, 77.16 % ± 2.42 % and 75.11 % ± 0.01 % were also recorded in stages I, II and III (Fig. 5c), respectively. At this point it should be highlighted that the values of the anaerobic broth pH during stages II and III varied as a result of the weekly membrane replacement, which entailed fluctuations in the CO_2 and CH_4 contents in the biogas. Indeed, the use of new membranes resulted in an improved NH_3 removal from

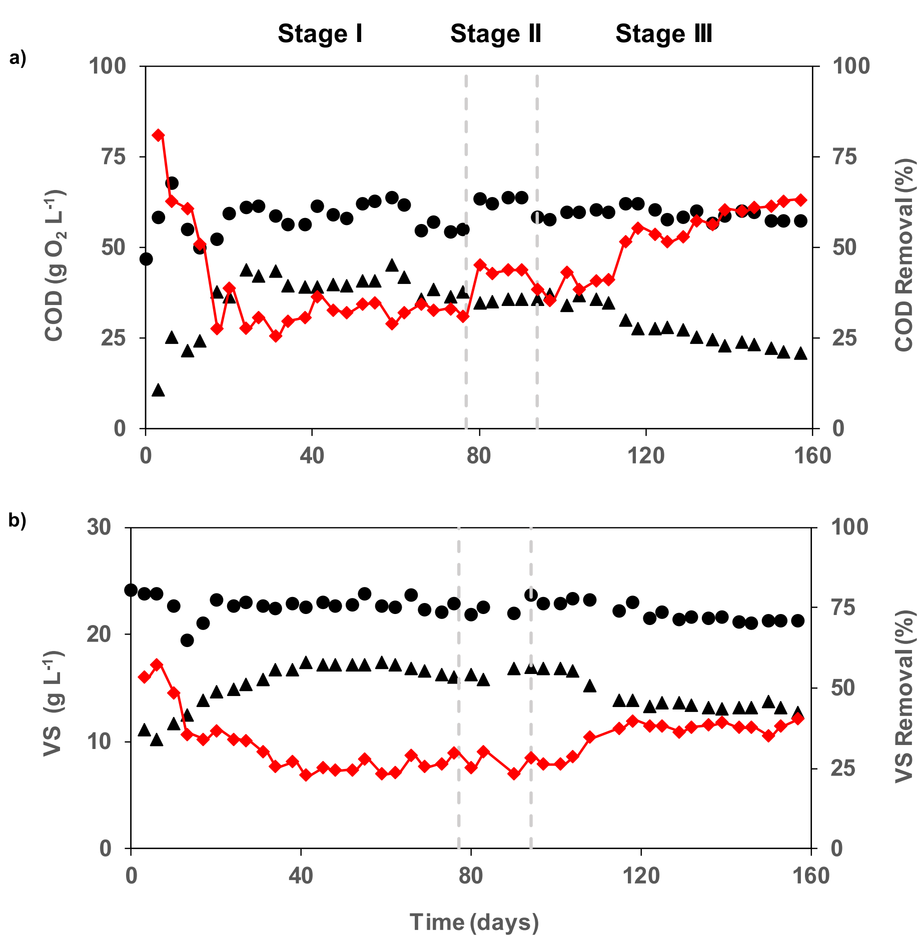


Fig. 4. Time course of the concentrations of COD (a) and vS (b) in the feed (●) and effluent (▲), and their corresponding removals (♦) during the three stages of operation.

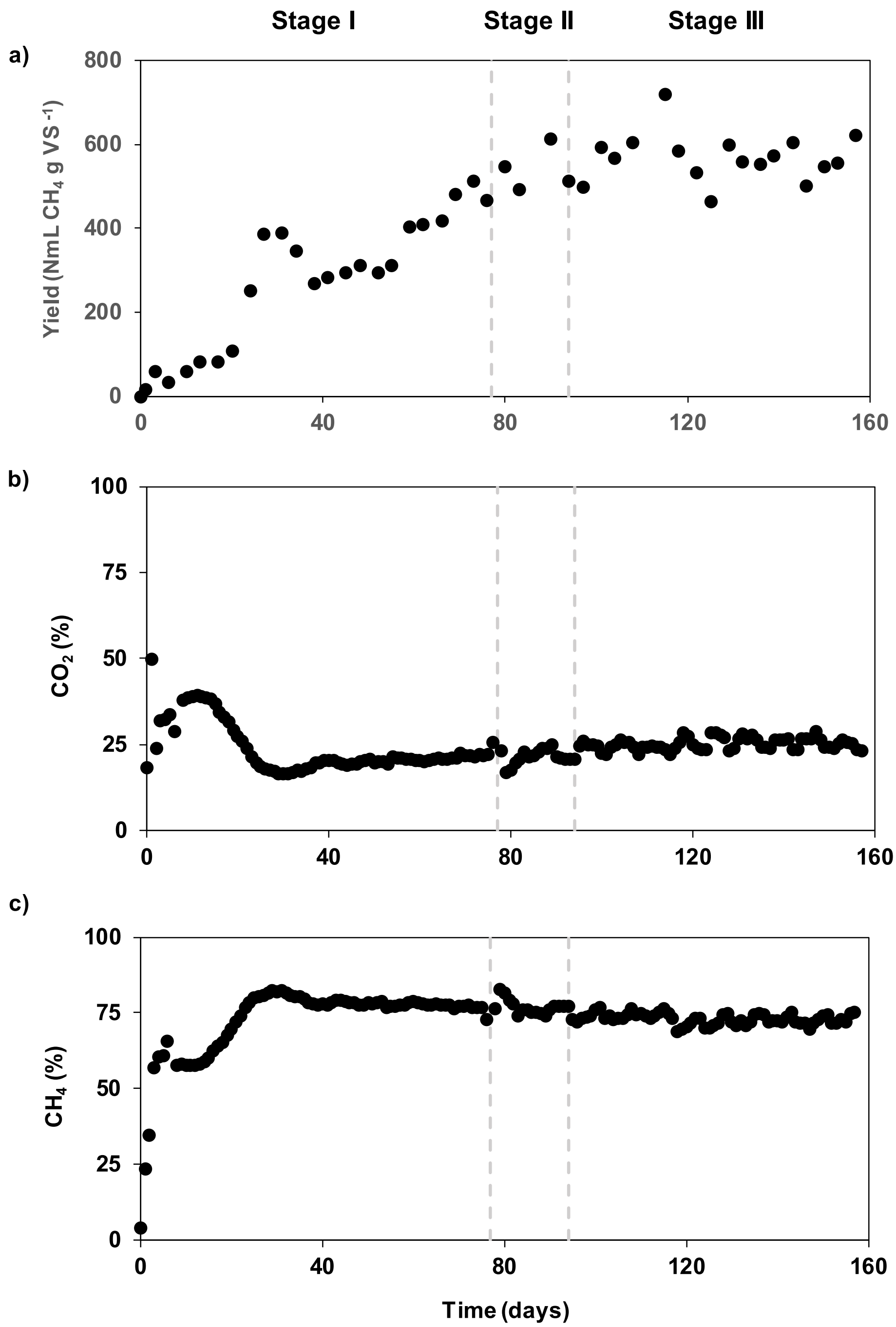


Fig. 5. Time course of biogas (a) yield and concentrations of (b) CO_2 and (c) CH_4.

the anaerobic broth, but also proton transfer from the 1 M H_2SO_4 solution to the anaerobic broth.

Finally, the VFA concentrations present in the anaerobic broth decreased significantly as a result of membrane operation. Thus, the removal efficiencies of acetic acid accounted for 72.0 % ± 8.1 %, 73.4 % ± 0.2 % and 93.7 % ± 1.9 %, respectively, during stages I, II and III. Similarly, the removals of propionic acid remained constant during stages I and II at 0 % ± 0 %, 0.5 % ± 0.8 %, respectively, but increased up to 98.6 % ± 1.9 % in stage III. A stepwise increase was also observed in isobutyric acid removals in stages I, II and II (48.3 % ± 4.8 %, 80.1 % ± 3.1 % and 100 % ± 0 %, respectively). The removals of butyric acid increased from 80.6 % ± 24.6 % in stage I up to 97.2 % ± 0.9 % and 100 % ± 0 % in stages II and III, respectively. Finally, the removals of isovaleric acid accounted for 61 % ± 31.3 %, 53.2 % ± 0.4 % and 100 % ± 0 % and those of valeric acid for 50.0 % ± 30.7 %, 78.4 % ± 3.5 % and 100 % ± 0 % in stages I, II and III (Fig. 6). These enhanced VFA removal efficiencies were likely explained by the enhancement in the anaerobic digestion process mediated by the gradual extraction of NH_3 from the anaerobic broth. At this is point it should be highlighted that a potential VFA mass transfer from the anaerobic broth to the 1 M H_2SO_4 solution was ruled out because concentrations of VFAs were low, which makes difficult to achieve a liquid contact through the pores of the membrane. The implementation of membrane-based NH_3 extraction gradually reduced the propionate/acetate ratio in the anaerobic broth, which accounted for 1.39, 1.29 and 0.81, respectively. In this context, propionate/acetate ratios > 1.4 are known to deteriorate anaerobic digestion performance (Gao et al., 2015), since propionic acid is considered the most toxic volatile fatty acid (Wang et al., 2009). Overall, high VFA

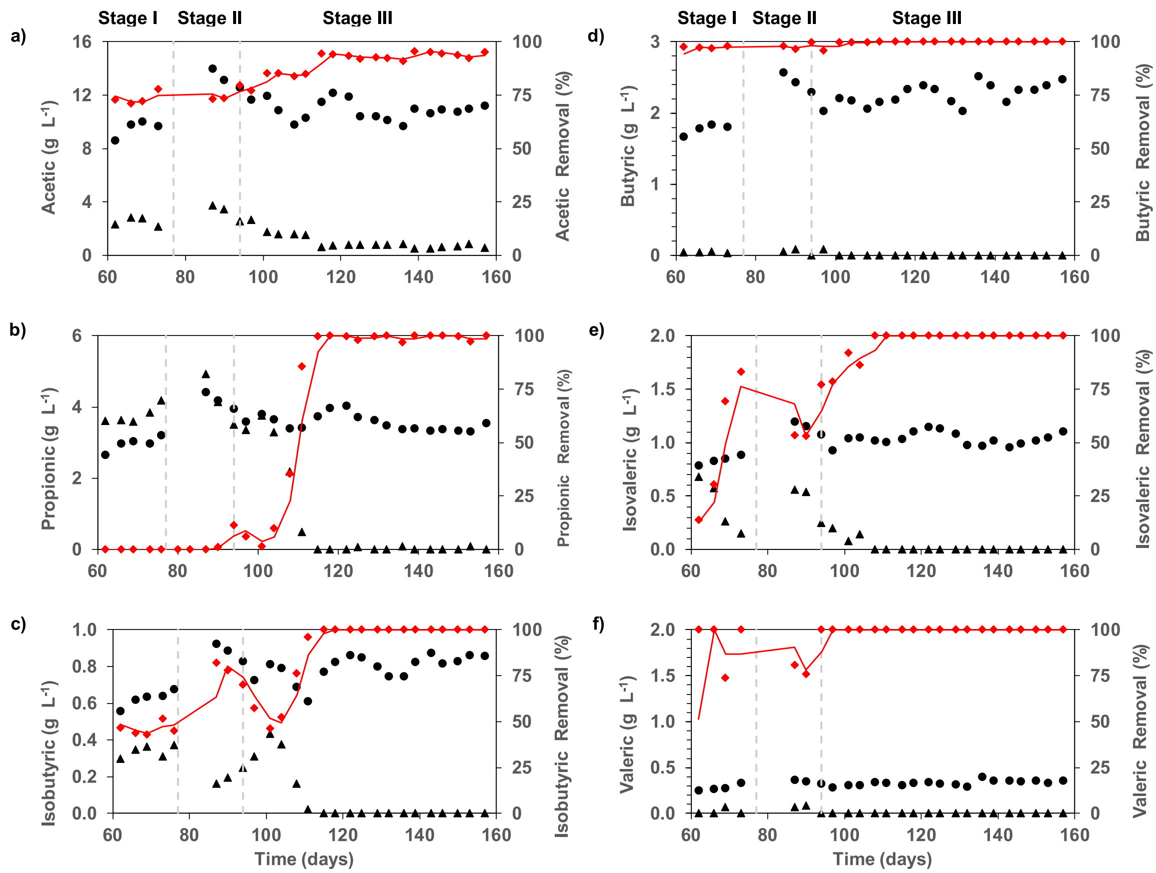


Fig. 6. Time course of the concentrations (a) Acetic, (b) Propionic, (c) Isobutyric, (d) Butyric, (e) Isovaleric and (f) Valeric acids in the feed (●) and effluent (▲), and their corresponding removal efficiency (♦) during the three stages of operation.

concentrations can cause inhibition to the methanogens during swine manure digestion along with a decrease in the buffer capacity and pH of the cultivation broth (Axelsson et al., 2012; Kraemer and Bagley, 2007). (Hansen et al., 1998) concluded that high VFA concentrations caused inhibition of the anaerobic process with a low methane yield of 67 $mLCH_4$ g vS^{-1} during the operation of a CSTR treating swine manure at 25 days HRT. In our particular study, these low VFA concentrations induced by NH_3 extraction further enhanced the anaerobic digestion of swine manure.

4. Conclusions

The anaerobic treatment of piggery wastewater can be enhanced by reducing NH_3 concentrations in the anaerobic broth via membrane assisted NH_3 extraction. Ammonia recovery increases at increasing pH values in the digestate. The concentration of suspended solid in the anaerobic broth did not significantly influence NH_3 extraction under short term operation. NH_3 extraction from the anaerobic digester during continuous pig slurry treatment supported enhancements in COD and vS removal efficiencies of 87 % and 48 %, respectively, and mediated a complete VFA assimilation. In addition, while biogas composition remained constant, the yields of CH_4 increased by 49 %.

CRediT authorship contribution statement

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

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.

Acknowledgements

This work was supported by the Regional Government of Castilla y León and the European FEDER Program (VA088G19, CL-EI-2021-07, UIC 315 and UIC 082) and the Spanish Ministry of Science and Innovation (PID2019-109403RB-C21/AEI/10.13039/501100011033). Fanny Rivera thanks University of Valladolid for her PhD Contract. The technical assistance of Enrique Marcos, Araceli Crespo and Beatriz Muñoz is also gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2022.127829.

References

Andriani, D., Wresta, A., Atmaja, T.D., Saepudin, A., 2014. A review on optimization production and upgrading biogas through CO 2 removal using various techniques. Appl. Biochem. Biotechnol. 172, 1909–1928. https://doi.org/10.1007/s12010-013-0652-x.

Angelidaki, I., Ahring, B.K., 1994. Anaerobic thermophilic digestion of manure at different ammonia loads: Effect of temperature. Water Res. 28, 727–731. https://doi.org/10.1016/0043-1354(94)90153-8.

APHA, 2005. Standard Methods for the Examination of Water, 21st ed. American Public Health Association, Washington D.C.

Axelsson, L., Franzén, M., Ostwald, M., Berndes, G., Lakshmi, G., Ravindranath, N.H., 2012. Perspective: Jatropha cultivation in southern India: Assessing farmers' experiences. Biofuels Bioprod. Biorefining 6, 246–256. https://doi.org/10.1002/bbb.

Brennan, B., Briciu-Burghina, C., Hickey, S., Abadie, T., al Ma Awali, S.M., Delaure, Y., Durkan, J., Holland, L., Quilty, B., Tajparast, M., Pulit, C., Fitzsimons, L., Nolan, K., Regan, F., Lawler, J., 2020. Pilot scale study: First demonstration of hydrophobic membranes for the removal of ammonia molecules from rendering condensate wastewater. Int. J. Mol. Sci. 21 (11), 3914.

Chang, I.-S., Le Clech, P., Jefferson, B., Judd, S., 2002. Membrane fouling in membrane bioreactors for wastewater treatment. J. Environ. Eng. 128, 1018–1029. https://doi.org/10.1061/(asce)0733-9372(2002)128:11(1018).

Chen, Y., Cheng, J.J., Creamer, K.S., 2008. Inhibition of anaerobic digestion process: a review. Bioresour. Technol. 99, 4044–4064. https://doi.org/10.1016/j.biortech.2007.01.057.

Darestani, M., Haigh, V., Couperthwaite, S.J., Millar, G.J., Nghiem, L.D., 2017. Hollow fibre membrane contactors for ammonia recovery: Current status and future developments. J. Environ. Chem. Eng. 5, 1349–1359. https://doi.org/10.1016/j.jece.2017.02.016.

Değermenci, N., Ata, O.N., Yildiz, E., 2012. Ammonia removal by air stripping in a semi-batch jet loop reactor. J. Ind. Eng. Chem. 18, 399–404. https://doi.org/10.1016/j.jiec.2011.11.098.

Dube, P.J., Vanotti, M.B., Szogi, A.A., García-González, M.C., 2016. Enhancing recovery of ammonia from swine manure anaerobic digester effluent using gas-permeable membrane technology. Waste Manag. 49, 372–377. https://doi.org/10.1016/j.wasman.2015.12.011.

European Parliament and Council, 2016. DIRECTIVE (EU) 2016/2284 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending Directive 2003/35/EC and repealing Directive 2001/81/EC. Off. J. Eur. Union L 344, 1–31.

Eykens, L., De Sitter, K., Dotremont, C., Pinoy, L., Van der Bruggen, B., 2016. Characterization and performance evaluation of commercially available hydrophobic membranes for direct contact membrane distillation. Desalination 392, 63–73. https://doi.org/10.1016/j.desal.2016.04.006.

Gao, S., Zhao, M., Chen, Y., Yu, M., Ruan, W., 2015. Tolerance response to in situ ammonia stress in a pilot-scale anaerobic digestion reactor for alleviating ammonia inhibition. Bioresour. Technol. 198, 372–379. https://doi.org/10.1016/j.biortech.2015.09.044.

García, D., de Godos, I., Domínguez, C., Turiel, S., Bolado, S., Muñoz, R., 2019. A systematic comparison of the potential of microalgae-bacteria and purple phototrophic bacteria consortia for the treatment of piggery wastewater. Bioresour. Technol. 276, 18–27. https://doi.org/10.1016/j.biortech.2018.12.095.

Garcia-González, M.C., Vanotti, M.B., 2015. Recovery of ammonia from swine manure using gas-permeable membranes: Effect of waste strength and pH. Waste Manag. 38, 455–461. https://doi.org/10.1016/j.wasman.2015.01.021.

González-García, I., Riaño, B., Molinuevo-Salces, B., Vanotti, M.B., García-González, M. C., 2021. Improved anaerobic digestion of swine manure by simultaneous ammonia recovery using gas-permeable membranes. Water Res. 190, 116789.

Guldhe A., et al., 2017. Phytoremediation Potential of Bioenergy Plants. Springer, Singapore. 10.1007/978-981-10-3084-0_2.

Guo, J., Lee, J.-G., Tan, T., Yeo, J., Wong, P.W., Ghaffour, N., An, A.K., 2019. Enhanced ammonia recovery from wastewater by Nafion membrane with highly porous honeycomb nanostructure and its mechanism in membrane distillation. J. Membr. Sci. 590, 117265.

Hansen, K.H., Angelidaki, I., Ahring, B.K., 1998. Anaerobic digestion of swine manure: inhibition by ammonia. Water Res. 32, 5–12. https://doi.org/10.1016/S0043-1354(97)00201-7.

Hansen, K.H., Angelidaki, I., Ahring, B.K., 1999. Improving thermophilic anaerobic digestion of swine manure. Water Res. 33, 1805–1810. https://doi.org/10.1016/S0043-1354(98)00410-2.

Hasanoğlu, A., Romero, J., Pérez, B., Plaza, A., 2010. Ammonia removal from wastewater streams through membrane contactors: Experimental and theoretical analysis of operation parameters and configuration. Chem. Eng. J. 160, 530–537. https://doi.org/10.1016/j.cej.2010.03.064.

Hejnfelt, A., Angelidaki, I., 2009. Anaerobic digestion of slaughterhouse by-products. Biomass and Bioenergy 33, 1046–1054. https://doi.org/10.1016/j.biombioe.2009.03.004.

Hendriksen, H.V., Ahring, B.K., 1991. Effects of ammonia on growth and morphology of thermophilic hydrogen-oxidizing methanogenic bacteria. FEMS Microbiol. Lett. 85, 241–246. https://doi.org/10.1111/j.1574-6968.1991.tb04730.x.

Jiang, A., Zhang, T., Zhao, Q.B., Li, X., Chen, S., Frear, C.S., 2014. Evaluation of an integrated ammonia stripping, recovery, and biogas scrubbing system for use with anaerobically digested dairy manure. Biosyst. Eng. 119, 117–126. https://doi.org/10.1016/j.biosystemseng.2013.10.008.

Jonsson, O., Erik, P., Jan, K., Rolf, E., Hakan, S., Staffan, I., 1997. Sustainable gas enters the european gas distribution. Water.

Kang, J.N., Wei, Y.M., Liu, L.C., Han, R., Yu, B.Y., Wang, J.W., 2020. Energy systems for climate change mitigation: a systematic review. Appl. Energy 263, 114602. https://doi.org/10.1016/j.apenergy.2020.114602.

Kraemer, J.T., Bagley, D.M., 2007. Improving the yield from fermentative hydrogen production. Biotechnol. Lett. 29, 685–695. https://doi.org/10.1007/s10529-006-9299-9.

Kunatsa, T., Xia, X., 2022. A review on anaerobic digestion with focus on the role of biomass co-digestion, modelling and optimisation on biogas production and enhancement. Bioresour. Technol. 344, 126311.

Licon Bernal, E.E., Maya, C., Valderrama, C., Cortina, J.L., 2016. Valorization of ammonia concentrates from treated urban wastewater using liquid-liquid membrane contactors. Chem. Eng. J. 302, 641–649. https://doi.org/10.1016/j.cej.2016.05.094.

López, J.C., Arnáiz, E., Merchán, L., Lebrero, R., Muñoz, R., 2018. Biogas-based polyhydroxyalkanoates production by Methylocystis hirsuta: a step further in anaerobic digestion biorefineries. Chem. Eng. J. 333, 529–536. https://doi.org/10.1016/j.cej.2017.09.185.

Mahmud, H., Kumar, A., Narbaitz, R.M., Matsuura, T., 2000. A study of mass transfer in the membrane air-stripping process using microporous polypropylene hollow fibers. J. Memb. Sci. 179, 29–41. https://doi.org/10.1016/S0376-7388(00)00381-1.

McCarty, P.L., 1964. Anaerobic Waste Treatment Fundamentals. Public. Work. 95, 91–94.

Molinuevo-Salces, B., Riaño, B., Vanotti, M.B., García-González, M.C., 2018. Gas-permeable membrane technology coupled with anaerobic digestion for swine manure treatment. Front. Sustain. Food Syst. 2, 1–12. https://doi.org/10.3389/fsufs.2018.00025.

Molinuevo-Salces, B., Riaño, B., Vanotti, M.B., Hernández-González, D., García-González, M.C., 2020. Pilot-scale demonstration of membrane-based nitrogen recovery from swine manure. Membranes (Basel). 10, 1–13. https://doi.org/10.3390/membranes10100270.

Montalvillo, M., Silva, V., Palacio, L., Calvo, J.I., Carmona, F.J., Hernández, A., Prádanos, P., 2014. Charge and dielectric characterization of nanofiltration membranes by impedance spectroscopy. J. Memb. Sci. 454, 163–173. https://doi.org/10.1016/j.memsci.2013.12.017.

Panichnumsin, P., Nopharatana, A., Ahring, B., Chaiprasert, P., 2010. Production of methane by co-digestion of cassava pulp with various concentrations of pig manure. Biomass and Bioenergy 34, 1117–1124. https://doi.org/10.1016/j.biombioe.2010.02.018.

Procházka, J., Dolejš, P., MácA, J., Dohányos, M., 2012. Stability and inhibition of anaerobic processes caused by insufficiency or excess of ammonia nitrogen. Appl. Microbiol. Biotechnol. 93, 439–447. https://doi.org/10.1007/s00253-011-3625-4.

Resch, C., Wörl, A., Waltenberger, R., Braun, R., Kirchmayr, R., 2011. Enhancement options for the utilisation of nitrogen rich animal by-products in anaerobic digestion. Bioresour. Technol. 102, 2503–2510. https://doi.org/10.1016/j.biortech.2010.11.044.

Reyes, I.P., Díaz, J.P., Horváth, I.S., 2015. Anaerobic Biodegradation of Solid Substrates from Agroindustrial Activities — Slaughterhouse Wastes and Agrowastes. Biodegrad. Bioremediation Polluted Syst. - New Adv. Technol. 10.5772/60907.

Rivera, F., Pr, P., Hern, A., Palacio, L., 2022. A Systematic Study of Ammonia Recovery from Anaerobic Digestate Using Membrane-Based Separation.

Siles, J.A., Brekelmans, J., Martín, M.A., Chica, A.F., Martín, A., 2010. Impact of ammonia and sulphate concentration on thermophilic anaerobic digestion. Bioresour. Technol. 101, 9040–9048. https://doi.org/10.1016/j.biortech.2010.06.163.

Silva, V., Martín, Á., Martínez, F., Malfeito, J., Prádanos, P., Palacio, L., Hernández, A., 2011. Electrical characterization of NF membranes. A modified model with charge variation along the pores. Chem. Eng. Sci. 66, 2898–2911. https://doi.org/10.1016/j.ces.2011.03.025.

Sung, S., Liu, T., 2003. Ammonia inhibition on thermophilic anaerobic digestion. Chemosphere 53, 43–52. https://doi.org/10.1016/S0045-6535(03)00434-X.

Temkin, A., Evans, S., Manidis, T., Campbell, C., Naidenko, O.V., 2019. Exposure-based assessment and economic valuation of adverse birth outcomes and cancer risk due to nitrate in United States drinking water. Environ. Res. 176, 108442 https://doi.org/10.1016/j.envres.2019.04.009.

Wang, Y., Zhang, Y., Wang, J., Meng, L., 2009. Effects of volatile fatty acid concentrations on methane yield and methanogenic bacteria. Biomass Bioenergy 33, 848–853. https://doi.org/10.1016/j.biombioe.2009.01.007.

Xu, P., Bellona, C., Drewes, J.E., 2010. Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation: Membrane autopsy results from pilot-scale investigations. J. Memb. Sci. 353, 111–121. https://doi.org/10.1016/j.memsci.2010.02.037.

Ye, W., Lu, J., Ye, J., Zhou, Y., 2021. The effects and mechanisms of zero-valent iron on anaerobic digestion of solid waste: a mini-review. J. Clean. Prod. 278, 123567 https://doi.org/10.1016/j.jclepro.2020.123567.

Yenigün, O., Demirel, B., 2013. Ammonia inhibition in anaerobic digestion: a review. Process Biochem. 48, 901–911. https://doi.org/10.1016/j.procbio.2013.04.012.

Yeon, S.H., Sea, B., Park, Y.I., Lee, K.H., 2003. Determination of mass transfer rates in PVDF and PTFE hollow fiber membranes for Co2 absorption. Sep. Sci. Technol. 38, 271–293. https://doi.org/10.1081/SS-120016575.

Zarebska, A., Nieto, D.R., Christensen, K.V., Norddahl, B., 2014. Ammonia recovery from agricultural wastes by membrane distillation: Fouling characterization and mechanism. Water Res. 56, 1–10. https://doi.org/10.1016/j.watres.2014.02.037.