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Improved anaerobic digestion of swine manure by simultaneous ammonia recovery using gas-permeable membranes

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ABSTRACT

In feedstocks containing high ammonia (NH_3) concentration, removal of the NH_3 during the anaerobic digestion (AD) process can improve AD process performance. In the present study, the effect of NH_3 removal using gas-permeable membrane (GPM) technology on AD process performance and biogas production was investigated using swine manure feedstock. Batch and semi-continuous AD experiments were carried out under mesophilic conditions. In the reactor with NH_3 recovery, total ammonia nitrogen (TAN) concentration was reduced 28% in batch experiments and 23% on average in the semicontinuous experiment compared with the reactor without NH_3 recovery. Free ammonia (FA) concentrations were also decreased by 23% and 4% on average in batch and semicontinuous experiments, respectively. These reductions in TAN and FA by GPM system positively impacted both the quality and quantity of the biogas produced by AD of swine manure. Specifically, the specific methane yield increased 9% in the batch experiment and 17% on average in the semicontinuous experiment. Furthermore, higher percentages of methane in biogas were obtained during AD retrofitted with GPM system, 24% increase in the batch experiment and 11% on average in the semicontinuous experiment (range 8.3-13.6%). Simultaneously, a uniform TAN recovery rate of 6.7 g N TAN per m^2 of membrane and per day was obtained for the 205 days of semicontinuous operation; ammonia nitrogen was recovered in the form of ammonium sulphate solution. Therefore, the AD-GPM configuration produces beneficial results on biogas quantity and quality while recovering ammonia nitrogen in form of ammonium sulphate.

1. Introduction

The amount of entire manure production in the EU27 is about 1.4 billion tonnes (AMEC, 2014). Anaerobic digestion (AD) is a powerful strategy to minimize the negative environmental impacts of manure management (Hijazi et al., 2020). AD has been largely studied and it is widely applied for manure treatment in Europe. The major benefit of AD is the production of renewable energy in the form of methane whilst reducing greenhouse gas emissions from manure management (Grando et al., 2017). However, AD treatment does not reduce total N concentration in the manure and, therefore, it does not solve the problem of excesive N in the surplus areas of the EU and similar regions of intensive animal production around the world. Another problem with AD of manure is the inhibition of methanogens by high ammonia (NH_3) concentration in these residues that severely reduces the production of biogas (Angelidaki and Ahring, 1993). It is suggested that the methanogens inhibition is due to free ammonia (FA) that can freely permeate microbial cellular membrane (Chen et al., 2008). Different approaches have been used to decrease NH_3 inhibition of AD due to high ammonia nitrogen concentration: 1. through the adaptation of AD microorganisms, 2. the co-digestion with carbon-rich wastes, 3. the dilution of the reactor content, and 4. the reduction and recovery of total ammonia nitrogen (TAN) concentration from the raw material prior or during the AD process (Lauterbock et al., 2012). Methods that reduce TAN concentration from AD by recovering it are desirable for economic and environmental reasons (Darestani et al., 2017; Romero et al., 2016). Such approach could not only improve the AD process due to removal of one of the main inhibitors, but also transform waste in valuable by-products allowing a circular flow of the N cycle (Robles et al., 2020; Toopa et al., 2017).

Different methodologies have been recently developed to recover TAN in the AD process. Serna-Maza et al. (2015) reported side-stream stripping during AD of domestic food waste using a

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Table 1
Chemical characteristics of the swine manure used in the batch AD experiment and in the semi-continuous AD experiment. Standard deviation is shown in parenthesis.

		Batch experiment	Semi-continuous experiment			
Parameter	Units	-	Period I	Period IIa	Period IIb	Period III
pH	-	8.0 (0.0)	6.9 (0.4)	6.7 (0.2)	7.7 (0.3)	7.1 (0.5)
Alkalinity	mg $CaCO_3$ L^{-1}	n.d.	8914 (776)	8412 (332)	12119 (2620)	10779 (2377)
SCOD	g L^{-1}	3.7 (0.1)	19.8 (3.6)	8.8 (2.8)	9.7 (1.1)	10.6 (2.8)
TVFA	g L^{-1}	n.d.	13.8 (0.4)	5.6 (0.2)	1.7 (1.1)	1.6 (2.5)
Ratio TVFA/SCOD		n.d.	0.70	0.64	0.18	0.15
TS	g L^{-1}	60.8 (1.4)	88.5 (17.4)	81.5 (4.3)	87.0 (13.3)	80.9 (8.7)
VS	g L^{-1}	46.7 (1.9)	73.2 (15.1)	68.3 (6.1)	65.6 (6.2)	56.1 (7.9)
TKN	mg N L^{-1}	2134 (1)	3623 (438)	1679 (531)	3043 (421)	2562 (567)
TAN	mg N L^{-1}	1165 (7)	1982 (141)	802 (111)	2078 (312)	1730 (413)

n.d.: not determined

stripping extraction column that treated the content of the reactor and the biogas. The recovery of ammonium with phosphate species from aqueous residues using struvite ($MgNH_4PO_4 \bullet 6H_2O$) precipitation has been also researched (Uludag-Demirer et al., 2005). However, in livestock wastewater less than 15% of the N contained in the influent could potentially be recovered through struvite because of the very high N to P ratio in these effluents (Vanotti et al., 2017). Gas permeable membrane (GPM) separation has been successfully applied for N recovery from manure before AD and after AD from anaerobically digested effluents (García González et al., 2015a; García González et al., 2015b; Molinuevo-Salces et al., 2018; Riaño et al., 2019; Vanotti and Szogi, 2010; Vanotti and Szogi, 2015). In this vein, Munasinghe-Arachchige and Nirmalakhandan (2020) used a multicriterion analysis to rank five N-recovery technologies (ammonia stripping, ultrafiltration and ion exchange, struvite precipitation, ultrafiltration and reverse osmosis, and GPM separation) considering 10 performance criteria giving priority to energy and economic aspects. Results of this analysis indicated the GPM technology as the preferred option for N recovery from waste streams followed by struvite precipitation. Similarly, Beckinghausen et al. (2020) indicated GPM technology had lower energy requirements per kg of N recovered (0.22 to 1.2 kWh kgN^{-1}) compared to typical ammonia stripping/acid absorption (23.6 to 49.6 kWh kgN^{-1}). In the GPM process, gaseous NH_3 in manure passes through a hydrophobic gas-permeable membrane and is concentrated in an acidic solution circulating on the other side of the membrane. The availability of NH_3 in the waste, where NH_3 and $NH_4{}^+$ are in equilibrium, determines the efficiency of this technology. Main factors affecting the process are the pH, temperature and TAN concentration in the livestock waste (Riaño et al., 2019).

Few studies have investigated the use of GPM systems inside AD reactors to eliminate ammonia inhibition and improve biogas production. Shi et al. (2019) studied the combination of AD with GPM technology using food wastes. They found that a reduction of 57% free ammonia (FA) concentration inside the AD reactor due to N capture by GPM favoured methanogens abundance and increased biogas production by 58%. Lauterböck et al. (2012) also studied the combination of AD with GPM separation using slaughterhouse waste. It led to a reduction of 70% FA concentration in the mixed liquor and a higher biogas yield, averaging 57% increase compared with a control AD reactor without N recovery.

The present study also investigated the combination of AD with GPM technology and its effectiveness to relieve ammonia inhibition and improve AD process performance and biogas production, but it differs from previous studies in the substrate used: swine manure; this is another high-ammonia, strategically important waste requiring solutions. The AD-GPM experiments with swine manure were conducted using batch and semi-continuous operation.

2. Materials and methods

2.1. Origin of manure and inoculum

Swine manure (SM) was collected from a finishing farm located in Salamanca (Spain). The collected manure was put in plastic containers, transported the same day to ITACyL laboratory in Valladolid (Spain), and stored in the laboratory at 4 °C for further use. Table 1 shows the chemical characteristics of the SM used; it contained high concentrations of total Kjeldahl nitrogen (TKN) (1679 to 3623 mg N L^{-1} mg L^{-1}), TAN (802 to 2078 mg N L^{-1}) and alkalinity (8412 to 12119 mg $CaCO_3$ L^{-1}). Alkalinity is important to sustain N removal by gas-permeable membrane process because the N uptake by the GPM acidifies the manure (Daguerre-Martini et al., 2018). The inoculum used was obtained from an anaerobic digester of the municipal wastewater treatment plant in Valladolid (Spain). The inoculum had a concentration of 16.3 g VS (volatile solids) L^{-1}.

2.2. Experimental set-up

Two laboratory-scale, stirred-tank AD reactors (working volume of 2000 mL) were first operated in batch mode (10 days), and then in semicontinuous mode (205 days) (Fig. 1). Reactor R1 was the reference reactor (control treatment) that provided AD treatment to swine manure without NH_3 recovery. Reactor R2 was the membrane reactor (NH_3 removal and recovery treatment) that provided AD of swine manure coupled with GPM recovery of the NH_3. Two ports placed on the top of each reactor were used one for influent feeding and effluent withdrawing, and the other one for biogas collecting. The biogas production was measured daily by displacement of water. The temperature of both reactors was kept constant (38 °C) using a water jacket connected to a temperature-controlled water bath. The methane volumes were converted to standard temperature and pressure (STD, 0°C and 1 atm).

The GPM module retrofitted to the AD (membrane reactor) consisted of: 1. a tubular gas-permeable membrane submerged in the anaerobic reactor liquid; 2. a peristaltic pump, and 3. a stripping acidic solution reservoir/N concentration tank. The tubular gas-permeable membrane was made of e-PTFE material (hydrophobic) with a length of 53 cm, an outer diameter of 5.2 mm and a wall thickness of 0.56 mm. The e-PTFE membrane density was 0.95 g cm^{-3}, and the ratio of membrane area exposed to the anaerobic reactor liquid per reactor volume was 0.004 m^2 L^{-1}. The peristaltic pump (Pumpdrive 5001, Heidolph, Schwabach, Germany) continuously recirculated, in a closed-loop, an acidic solution between the inside of the membrane and the N concentration tank (Fig. 1). The acidic solution flow rate was 12 L d^{-1}. The N concentration tank consisted of a 570 mL glass vessel hermetically sealed containing an acidic solution (150 mL of 0.5 mol L^{-1} H_2SO_4). It was replaced with bigger vessels during the experiments to accommo-

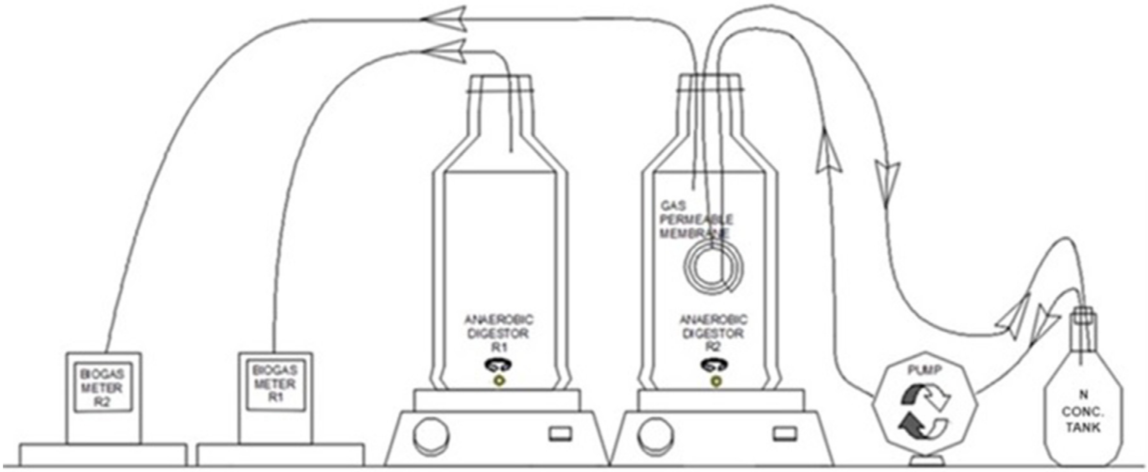

Fig. 1. Schematic showing the experimental set-up: R1 is the reference AD reactor (control). R2 is the membrane AD reactor (AD coupled with GPM module for ammonia recovery).

date the increase of the volume of the acidic solution with time as a consequence of the occurrence of osmotic distillation, as previously reported by Riaño et al. (2019). The pH of the acidic solution was monitored daily and whenever the pH reached 2, concentrated H_2SO_4 (96–98%, Panreac) was added into the N concentration tank to an endpoint of $pH < 2$. The pH 2 was selected as the upper set point based on Vanotti and Szogi (2015) that indicated that NH_3 recovery in closed-loop GPM system is optimized when the pH of the stripping tank solution is kept below 2.

2.3. Batch experiment

An AD batch experiment was carried out for 10 days. Both AD reactors (membrane and reference) were fed using the same 1:1 substrate (So) to inoculum (Xo) ratio (expressed as g VS: g VS). The 1:1 So/Xo ratio was recommended by Molinuevo-Salces et al. (2018) to study the effect of ammonia recovery on anaerobic digestion under stable operation. In order to achieve this ratio in anaerobic reactors, and due to the different VS concentrations of inoculum and swine manure (Table 1), the volume of inoculum and substrate (swine manure) added in each reactor were 1 L and 0.35 L, respectively. The amounts of VS added from inoculum and swine manure were thus identical (16.3 g VS). The addition of water was required to get a final volume of 2 L, achieving the desired So:Xo ratio. The reactors were continuously agitated using magnetic stirrers, and the mixing speed was kept between 500 and 700 rpm. The volume of biogas produced was daily monitored and biogas composition was weekly analysed. The specific methane yield was calculated as N mL CH_4 produced per g VS added in the substrate. Initial and final samples of the content of the reactors were taken for TAN determination. Acidic solution samples of 3 mL were daily collected from the N concentration tank and analysed for pH and TAN determinations. In the batch experiment, pH of the stripping solution did not reach 2, and addition of concentrated H_2SO_4 was not needed.

2.4. Semi-continuous experiment

The semi-continuous experiment was carried out for 205 days. Both reactors were initially filled with 2 L of inoculum. After that, manure was added to the reactors once per day, every weekday, using manual feeding. Both reactors were fed with the same mixed manure substrate and amount. The reactors were continuously agitated with magnetic stirrers in the first stage of the experiment, at a mixing speed between 500 and 700 rpm, and thereafter they were daily agitated using manual stirring due to the high content of fibers and solids in the manure. Prior to each feeding event, a volume equal to the feeding volume was removed to maintain a constant reactor volume. The volume of the membrane reactor was daily checked and any water loss due to osmotic distillation was replenished.

Three different periods (I to III) were established for the AD semi-continuous experiment based on the organic loading rate (OLR) and the hydraulic retention time (HRT). The same conditions were applied to both reactors. During period I (0-62 days) the reactors were operated with HRT = 20 days, OLR = 3.7 ± 0.8 g VS L^{-1} d^{-1}, and feeding rate = 100 mL d^{-1}. During period II (63-128 d) the HRT was decreased to 15 days and OLR increased to 4.3 - 4.6 g VS L^{-1} d^{-1}, with a feeding rate of 133 mL d^{-1}. The composition of manure varied greatly among the two different batches received during period II, as a result of swine manure production (Table 1). For this reason, period II was separated in the data analysis into period IIa (with a high ratio total volatile acids (TVFA)/soluble chemichal demand (SCOD)) of 0.64, and low ammonia content) and period IIb (with a low ratio TVFA/SCOD ratio of 0.18, and high ammonia content) (Table 1). The OLR was similar: 4.6 ± 0.4 and 4.3 ± 0.4 g VS $L^{-1}d^{-1}$ for periods IIa and IIb, respectively. During period III (129-205 d) HRT was increased back to 20 days with OLR = 2.8 ± 0.4 g VS L^{-1} d^{-1}, with a feeding rate of 100 mL d^{-1}.

The volume of biogas produced was daily measured and the biogas composition was weekly measured. Influent and effluent samples were taken twice a week and analysed for total alkalinity (TA), partial alkalinity (PA), total solids (TS), VS, TVFA, SCOD, TAN, and TKN. Within each period, data collected after one HRT were used for average calculations of AD process parameters. Acidic solution samples of 3 mL were daily collected from the N concentration tank to monitor pH and TAN. To maintain the pH under 2, concentrated H_2SO_4 was added in the acidic solution whenever it was needed. A total volume of 102 mL of acid was used (10 mL in period I, 12 mL in period IIa, 20 mL in period IIb and 60 mL in period III). The volume of the acidic solution was also daily measured in order to calculate the mass of TAN recovered by the GPM system in the membrane reactor.

2.5. Analytical methods and statistical analysis

Analyses of SCOD, TS, VS, TAN, TKN and TVFA, were performed in duplicate in accordance with APHA (2005). For the analysis of SCOD a closed reflux colorimetric method was used. TS content was determined by drying the sample to a constant weight at 103–105 °C. The TS residue was ignited at 550 °C to constant weight and the weight lost on ignition was the VS content. TAN was measured according to the distillation and titration method. TKN was measured according to the Kjeldahl digestion, distillation, and titration method. Both TAN and TKN concentrations are expressed in N units.

The volatile fatty acids concentrations (acetate, propionate, butyrate, iso-butyrate, valerate, iso-valerate, and caproate), were determined using a gas chromatograph (Agilent 7890A, USA) equipped with a Teknokroma TRB-FFAP column of 30 m length and 0.25 mm i.d. followed by a flame ionization detector (FID). The carrier gas was helium (1 mL min^{-1}). The temperature of the detector and the injector was 280°C. The temperature of the oven was set at 100°C for 4 min, then increased to 155°C for 2 min and thereafter increased to 210°C. TVFA were calculated as the sum of those acids concentration after applying the COD conversion factor.

To measure total and partial alkalinity (TA, PA), a pH meter Crison Basic 20 (Crison Instruments S.A., Barcelona, Spain) was used. TA and PA were obtained by measuring the amount of 0.5 mol L^{-1} H_2SO_4 needed to bring the sample to a pH of 4.3 and 5.75, respectively, and expressed as mg $CaCO_3$ L^{-1}. Intermediate alkalinity (IA) was calculated by subtracting PA from TA. The optimal IA/PA ratio would be of 0.3 (Ripley et al., 1986).

Biogas composition was analysed using a gas chromatograph (Agilent 7890A, USA) with a thermal conductivity detector, provided by a HP-Plot column (30 m 0.53 mm 40 μm) followed by a HP-Molesieve column (30 m 0.53 mm 50 μm). The carrier gas was helium (7 mL min^{-1}). The injection port temperature was set at 250°C and the detector temperature was 200°C. The temperature of the oven was set at 40°C for 4 min and thereafter increased to 115°C.

Free ammonia (FA) was calculated as un-ionized ammonia, using the equation of Hansen et al. (1998) (Eq. (1)):

$$NH_3/tNH_3 = \left(1 + \left(10^{-pH}/10^{-(0.09018+2729.92/T)}\right)\right)^{-1} \quad (1)$$

where NH_3 was the FA content, tNH_3 is the total NH_3 concentration, T was the manure reactor temperature (in Kelvin), and pH was measured in the effluent.

Resistances against NH_3 gas diffusion by the membrane (structure and pores), is defined by the K_m value (Samani-Majd and Mukhtar, 2013). The mass transfer coefficient (K_m; m d^{-1}) was calculated using Eq. (2) (Samani-Majd and Mukhtar, 2013).

$$J = K_m(C1 - C2) \quad (2)$$

where J is the mass flux per area (g m^{-2} d^{-1}), and C1 and C2 are the FA concentrations in the membrane reactor and in the N concentration tank, respectively. C2 was assumed to be zero for calculations, since pH of the acidic solution was maintained below 2 during the whole experiment and, consequently, FA concentration was zero.

Results obtained were analysed using one-way analysis of variance (ANOVA) with significance at $p < 0.05$.

3. Results and discussion

3.1. Batch AD experiment

At the beginning of the AD experiment, TAN concentration in both reactors was 1166 mg N L^{-1}. By coupling a GPM system to the anaerobic reactor, TAN was consistently removed from the membrane reactor and recovered as $(NH_4)_2SO_4$ in the acidic solution, up to 548 mg N at day 10 (Fig. 2). The slope present in Fig. 2 leads to a rate of TAN captured of 50.2 mg N per day. In terms of membrane area, the TAN recovery rate obtained was 5.8 g N m^{-2} d^{-1}. TAN concentration in the acidic solution increased to 1227 mg L^{-1} at day10. After 10 days, the membrane reactor had a lower concentration of TAN compared with the reference (749 ± 16 mg N L^{-1} vs. 1033 ± 27 mg N L^{-1}), which implied a reduction of 28%. Similarly, a reduction of FA concentration of 23% was evidenced in the membrane reactor when comparing with the reference reactor (121 mg L^{-1} vs. 157 mg L^{-1}). The pH in the membrane reactor after 10 days was 8.05.

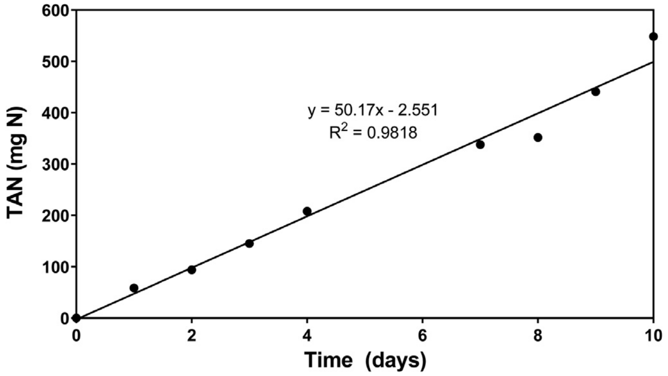

Fig. 2. Mass of TAN captured by GPM module during the batch AD experiment.

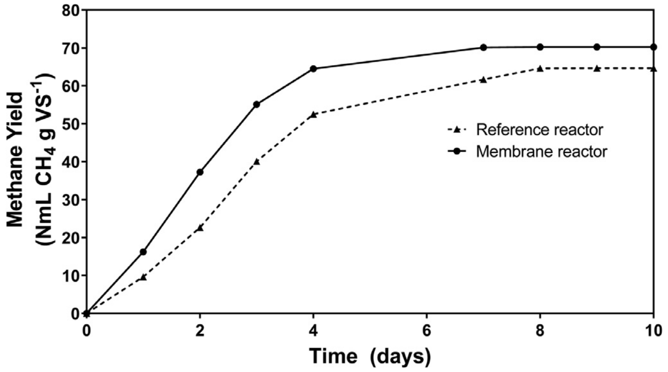

Fig. 3. Accumulated specific methane yields for the membrane reactor and the reference reactor obtained in the batch AD experiment.

The reductions in TAN and FA by GPM impacted the biogas quantity and quality. The accumulated specific methane yields, expressed as NmL CH_4 produced per gram of VS added in the substrate, are presented in Fig. 3. Specific methane yield for the membrane reactor with NH_3 recovery was 9% higher compared to the reference reactor without NH_3 recovery. More specifically, the membrane reactor presented a methane yield of 70 NmL CH_4 g VS^{-1} compared with a yield of 64 NmL CH_4 g VS^{-1} by the reference reactor. Furthermore, the biogas obtained in the membrane reactor had a higher percentage of CH_4 (78%) compared to the reference reactor (63%).

The results of this batch experiment confirmed that the AD-GPM combination can produce beneficial results on both the biogas quantity and quality using swine manure feedstocks.

3.2. Semi-continuous AD experiment

3.2.1. Ammonia concentration in the reactors

Semi-continuous reactors (membrane and reference reactors) were operated for 205 days through three periods. The continuous ammonia capture by the gas-permeable system in the membrane reactor worked well and throughout the experiment. Thus, TAN in the membrane reactor was lower than in the reference reactor during the whole experimental period (Fig. 4). Maximum TAN concentration in the reference reactor was 2040 mg N L^{-1} whereas in the membrane reactor was 1666 mg N L^{-1}. TAN concentration in

Table 2
Average TAN and FA concentration in the reference and the membrane reactors during the semi-continuous AD experiment. Standard deviations are shown in parenthesis.

Period	TAN concentration (mg N L^{-1})			FA concentration (mg NH_3 L^{-1})		
	Reference reactor	**Membrane reactor**	**% Decrease by GPM**[1]	**Reference reactor**	**Membrane reactor**	**% Decrease by GPM**[1]
Period I (0-62 d)	1846 (165)	1488 (100)	19.4	68.0 (25.2)	63.1 (20.3)	7.2
Period IIa (63-83 d)	1234 (103)	827 (61)	33.0	38.4 (18.0)	17.7 (2.7)	53.9
Period IIb (84-128 d)	1806 (204)	1404 (118)	22.3	53.2 (20.5)	60.8 (16.8)	-
Period III (129-205 d)	1524 (212)	1125 (148)	26.2	32.3 (21.3)	29.3 (19.8)	9.3
All (0-205 d)	1677 (260)	1289 (228)	23.1	49.0 (26.3)	47.2 (25.2)	3.7

[1] % Decrease by GPM = [1 - (membrane reactor/reference reactor)] * 100

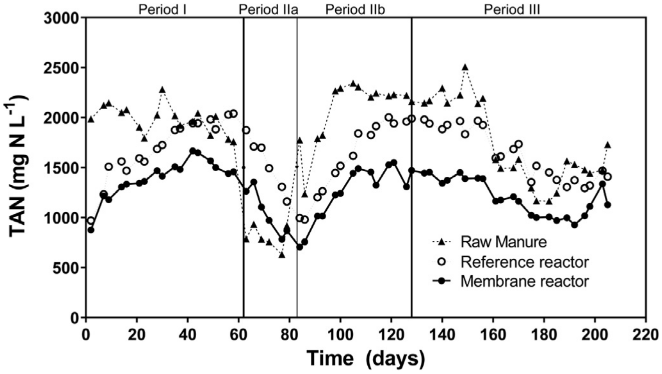

Fig. 4. Evolution of TAN concentration during the semi-continuous experiment for the raw manure, and the two AD reactors: the reference reactor and the membrane reactor. Treatment comparisons are provided in Table 2.

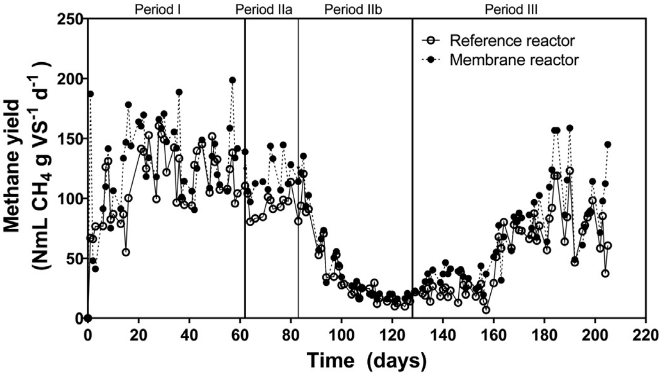

Fig. 5. Specific methane yields in the semi-continuous experiment for the reference reactor and the membrane reactor. Treatment comparisons are provided in Table 3.

the membrane reactor with an active ammonia capture system was reduced by 23% (range 19-33%) compared to the reference reactor without TAN recovery (Table 2). Free ammonia concentrations in the membrane reactor were also lower than those obtained in the reference reactor (Table 2). A reduction of FA concentration up to 54% was detected in the membrane reactor compared with the reference reactor. Inhibitory concentrations for methanogenic microorganisms range between 1500 and 7000 mg L^{-1} for TAN and between 53 and 1450 mg L^{-1} for FA (Shi et al., 2019; Yenigün and Demirel, 2013). In the present study, the recovery of NH_3 in the membrane reactor allowed mantaining TAN and FA concentrations below these reported inhibition levels for most of the experimental time.

3.2.2. Influence of NH_3 recovery on methane yield and biogas composition

The reactors were semi-continuously operated for 205 days through three periods under different OLR and HRT. Fig. 5 shows the daily methane yields for both reactors during the whole study. The average methane produced, average specific methane yield and average methane content for each reactor in each experimental period are listed in Table 3.

Both the daily methane produced and the specific methane yield obtained were higher in the membrane reactor compared with that obtained in the reference reactor in all the studied conditions (Fig. 5; Table 3). The specific methane yield is one of the most relevant process performance parameters in AD, due to its direct relation with the economic efficiency of the process.

Regarding period I, average specific methane yield for the membrane reactor with NH_3 recovery was significantly higher ($p < 0.05$) than for the reference reactor, accounting for 138 ± 27 NmL CH_4 g VS^{-1} d^{-1} and 126 ± 21 NmL CH_4 g VS^{-1} d^{-1}, respectively. A decrease in the HRT from 20 to 15 days in period IIa resulted in a reduction in methane yield to values of 125 ± 15 and 98 ± 13 NmL CH_4 g VS^{-1} d^{-1} for the membrane reactor and the reference reactor, respectively (Fig. 5; Table 3). Significant differences ($p = 0.03$) were found between reactors, where the membrane reactor presented a higher methane production than the reference reactor. Although a drastic drop in methane production occurred in period IIb, with an average methane of 24 ±10 NmL CH_4 g VS^{-1} d^{-1} for membrane reactor and 22 ±11 NmL CH_4 g VS^{-1} d^{-1} for reference reactor, the reduction in methane production was no related with the performance of the GPM system because the reduction affected both membrane and reference reactors. This reduction was due to a new batch of SM influent with a different composition than in period IIa (Table 1). In period IIa manure presented a TVFA/SCOD ratio of 0.64, and it decreased to 0.18 in period IIb, leading to a reduction in biodegradability. Period IIa showed a considerable higher methane production and stable operation than period IIb, working at the same HRT (15 days) and OLR (4.4-4.5 g VS L^{-1} d^{-1}). Thus, in this study, the reduction in methane yield from period IIa to period IIb was not due to the low HRT and subsequent low SRT inside the reactor. This result was in agreement with that obtained by Bayrakdar et al. (2018), who also experienced sudden and unexpected changes in methane production during AD of chicken manure when the manure batch was changed. From day 129, in the period III, the HRT was increased again to the previous value in period I of 20 days, to try to recover the anaerobic process. From this point, methane production gradually increased in both reactors (Fig. 5), achieving an average methane yield of 81± 37 NmL CH_4 g VS^{-1} d^{-1} for membrane reactor and 66 ± 28 NmL CH_4 g VS^{-1} d^{-1} for reference reactor. Thus, methane yield was 1.2-fold higher in the membrane reactor than in the reference reactor, with a similar behaviour than that obtained in period I and period IIa. As an overall, the methane produced and the specific methane yield increased 17% higher (range 10-28%) on average in the membrane reactor than in the reference reactor. These results are in accordance with those found in literature who indicated that the combination of AD with GPM could increase methane yield by 13-129% depending on operational conditions and digested feedstocks (Lauterböck et al., 2012; Shi et al., 2019).

Table 3
Methane production, specific methane yields and methane content in the biogas in the reference and the membrane reactor during semi-continuous AD experiment. Standard deviations are shown in parenthesis.

	Methane produced (NmL CH_4 d^{-1})		Specific methane yield (NmL CH_4 g^{-1} $VS^{-1}d^{-1}$)			Methane percentage in the biogas (%)		
Period	Reference reactor	Membrane reactor	Reference reactor	Membrane reactor	% Increase by GPM[1]	Reference reactor	Membrane reactor	% Increase by GPM[1]
Period I (0-62 d)	924 (154)	1012 (196)	126.2 (21.0)	138.2 (26.8)	9.5	51.8 (3.7)	56.1 (2.3)	8.3
Period IIa (63-83 d)	888 (122)	1132 (137)	97.7 (13.4)	124.7 (15.0)	27.6	45.9 (-)	52.1 (-)	13.5
Period IIb (84-128 d)	189 (92)	207 (90)	21.7 (10.6)	23.7 (10.3)	9.2	39.7 (4.8)	44.8 (4.8)	12.8
Period III (129-205 d)	372 (158)	455 (206)	66.3 (28.1)	81.1 (36.7)	22.2	46.3 (3.2)	52.6 (4.6)	13.6
All (0-205 d)	519 (330)	608 (379)	75.3 (44.6)	88.3 (51.2)	17.3	45.9 (4.9)	51.4 (4.8)	11.4

[1] % Increase by GPM = [(membrane reactor-reference reactor)/reference reactor)] * 100

Table 4
Average pH, IA/PA ratio and TVFA concentration in the membrane and reference reactors during the semi-continuous AD experiment. Standard deviations are shown in parenthesis.

	pH		IA/PA ratio		TVFA (mg L^{-1})	
Period	Reference reactor	Membrane reactor	Reference reactor	Membrane reactor	Reference reactor	Membrane reactor
Period I (0-62 d)	7.4 (0.2)	7.4 (0.2)	0.42 (0.10)	0.43 (0.09)	453 (382)	1341 (667)
Period IIa (63-83 d)	7.4 (0.2)	7.2 (0.1)	0.17 (0.10)	0.27 (0.01)	255 (-)	70 (-)
Period IIb (84-128 d)	7.2 (0.2)	7.4 (0.1)	0.48 (0.22)	0.39 (0.10)	87 (33)	69 (12)
Period III (129-205 d)	7.1 (0.3)	7.1 (0.3)	0.67 (0.30)	0.63 (0.26)	62 (36)	44 (33)

Table 5
Average SCOD and VS removals in reference and membrane reactor during semi-continuous experiment. Standard deviations are shown in parenthesis.

	SCOD removal (%)		VS removal (%)	
	Reference reactor	Membrane reactor	Reference reactor	Membrane reactor
Period I	60.9 (6.3)	58.4 (6.0)	50.8 (6.8)	50.3 (6.9)
Period IIa	50.8 (3.4)	52.9 (0.2)	60.1 (13.6)	63.7 (5.7)
Period IIb	21.6 (6.1)	14.5 (9.9)	27.2 (16.1)	43.1 (14.7)
Period III	31.2 (10.8)	33.9 (9.3)	24.4 (8.8)	22.4 (8.1)

An evaluation of the AD with and without N recovery on the basis of energy was carried out to assess if the improvements reported here in terms of methane volume and methane composition are justified in relation to the extra energy expended in acid recirculation in the GPM process. The calculations are based on a biogas plant for a medium-size pig farm with 2800 sows and an annual manure production of 17136 m^3 (6.12 m^3 of manure per saw per year) and the following conditions:

- A methane yield of 75.3 NmL g VS^{-1} for the system without N recovery and 88.3 NmL g VS^{-1} for the system with N recovery (this study, Table 3).
- The AD is carried out at 38°C, with an HRT of 20 days and wet conditions (6.5%).
- The biogas plant works 7500 hours per year (i.e. 313 days).
- A methane calorific value of 10 kWh Nm^{-3} was chosen. The power recovery system was estimated to have an efficiency of 30% for electricity.
- The system with N recovery requires extra energy for the recirculation of the acidic solution with an electrical consumption of 13.2 kWh per day (Molinuevo-Salces et al., 2020).

The daily methane production obtained after treating on-farm the produced swine manure is 266 Nm^3 CH_4 per day for the AD reactor without N recovery and 278 Nm^3 CH_4 per day for the AD reactor with N recovery. These would represent a net electricity production of 795 and 832 kWh day^{-1} for the AD reactors without and with N recovery, respectively. Thus, the difference in the net electricity production between both systems would be 37 kWh per day higher in the AD system with N recovery. The system with N recovery would need extra energy (13.2 kWh per day) for the recirculation of the acidic solution. Therefore, a positive energy balance (23.8 kWh per day) was obtained from AD coupled with N recovery using GPM technology.

The performance of anaerobic process was also evaluated in terms of pH, ratio IA/PA and TVFA concentration (Table 4). No significant differences were found between membrane and reference reactors in these parameters. Average pH values in both reactors remained in the range of 7.1-7.4 (Table 4). No significant differences were found between membrane and reference reactors in IA/PA ratios for any experimental period, and the value of this parameter presented a high variability during each experimental period; for these reasons, the effect of this parameter on ammonia removal could not be clearly discussed. TVFA concentrations were very variable, with no significant differences between reactors, although lower concentrations of TVFA were detected in membrane reactor (exception made for the period I).

The removal efficiencies of SCOD and VS were similar in both reactors, with no significant differences except for period IIb, when the membrane reactor had a VS removal of 43.1% in contrast with the reference reactor, with a VS removal of 27.2%, which implies a better removal efficiency (58%) for the membrane reactor (Table 5).

The biogas quality (methane percentage) was also monitored and the results are shown in Table 3. Results showed a higher methane content in the membrane reactor with NH_3 recovery system than in the reference reactor in all experimental periods. More specifically, methane content was up to 14% higher in the membrane reactor than in the reference reactor. This result obtained with manure agreed with those reported by Shi et al. (2019) who observed higher methane content in a reactor that combined AD with GPM technology using food wastes compared with a reference reactor without NH_3 recovery. The highest methane content in biogas was obtained during period I in both reactors (52% for the reference reactor and 56% for the membrane reactor).

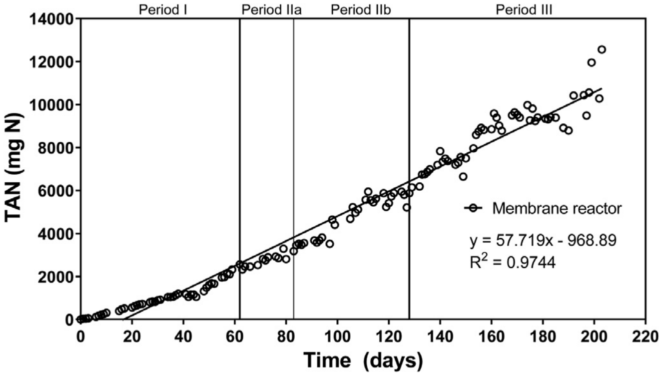

Fig. 6. Mass of TAN recovered from digestate during semi-continuous operation of the membrane reactor that used AD with GPM.

3.2.3. Performance of the N recovery system

By coupling a gas-permeable membrane system in the membrane reactor, ammonia was consistently removed from the reactor and recovered as ammonium sulphate in the acidic solution. TAN concentration in the acidic solution increased slowly from the start to a value of 2008 mg N L^{-1} on day 24, and it continued increasing to reach a final value of TAN captured of 3525 mg N L^{-1} on day 205 of the experiment (data not shown). During the experiment, the volume of the acidic solution increased from an initial value of 150 mL to a final value of 3000 mL due to the diffusion of water vapor through the membrane (i.e. osmotic distillation) that occurs as a consequence of the differences in vapor pressure between both sides of the membrane. The water capture rate was 1.7 L of water per day and per m^2 of membrane surface and it led to a continuous dilution of the acidic solution and, consequently, to a decrease in its TAN concentration. The difference of temperature between the liquids (acidic solution and digestate) in both sides of the membranes highly influences on osmotic distillation. Water capture by the membrane could highly influence on the economy of the process. The resultant acidic solution could not present a nitrogen concentration as high as expected, being required a further process to concentrate ammonium sulphate and to reduce transportation cost of this fertilizer. In addition, the design of the N concentration tank that must foresee increasing volume of the acidic solution. Heating the acidic solution has been proposed as an effective strategy to counteract osmotic distillation, allowing the obtention of a higher TAN concentration in the acidic solution for its use as fertilizer (Riaño et al., 2019). The ammonium sulphate can be used as fertilizer in its liquid form, for fertigation, not being necessary to precipitate it for application and thus avoiding the use of extra energy, and only being necessary a system of storage and transport for its further use.

There are two main considerations with regards to the performance of the membrane: one is the long-term functionality, and the other is the specific N removal rate per membrane area. Regarding the functionality over time, a uniform linear (R^2=0.9744) TAN recovery rate by the gas-permeable membrane that led to an average mass recovery rate of 6.7 g N m^{-2} d^{-1} during the whole experimentation time of 205 days was evidenced regardless of the ammonium loading rate and TAN content in membrane reactor experienced during this long run (Fig. 6). This result agreed with those reported by Riaño et al. (2019) who also obtained a uniform TAN recovery rate when treating swine manure using a gas-permeable membrane technology in a semi-continuous mode for 50 days. In contrast, Shi et al. (2019) detected membrane fouling and hydrophobicity loss during AD combined with GPM technology using food waste feedstocks for 146 days. It should be highlighted that no cleaning measures were applied on the membrane in the present study. Regarding the TAN recovery rate per membrane area, the values obtained in this study (4.8 to 6.6 g N m^{-2} d^{-1}) were lower than obtained in other studies; for instance, García-González et al. (2015) obtained an average TAN recovery rate of 9.5 g m^{-2} d^{-1} when treating raw swine manure with GPM at batch fed mode. Riaño et al (2019) reported a TAN recovery rate of 27.1 g N m^{-2} d^{-1} from swine manure using GPM technology at semi-continuous fed mode. The low TAN recovery rate in the present study could be explained by the low pH values in the membrane reactor during the semi-continuous experiment. The pH is the most critical variable influencing the amount of free NH_3 available to pass through the gas permeable membrane, therefore it is crucial for TAN recovery. García-González and Vanotti (2015) adjusted the pH of the manure to 8.5-9.0 whenever the pH of the manure decreased below 7.7 using sodium hydroxide. Riaño et al. (2019) were able to obtain a pH of 8.5 during their experiment, using aeration as method to increase the pH in the reactor. In the present study, the values of pH in the membrane reactor were under 8 during the whole experimental period (Table 4); however, it was preferable not to use aeration or alkali addition methods to increase the pH in this study, due to the AD operation conditions.

The mass transfer coefficient (K_m; m s^{-1}) has been calculated using Eq. (2), resulting in values of 1.1 × 10^{-6}, 3.9 × 10^{-6}, 1.5 × 10^{-6} and 3.1 × 10^{-6} for period I, IIa, IIb and III, respectively. An average value of 2.2 × 10^{-6} m s^{-1} was obtained. These values are comparable to other K_m values in the range of 1.0-9.2 × 10^{-6} m s^{-1} calculated in other studies using e-PTFE membranes for ammonia recovery from livestock manure (Riaño et al., 2019; Samani- Majd and Mukhtar, 2013). The K_m coefficient is dependent on membrane morphology, including thickness, porosity and pore size, as well as the flow rate of the acidic solution and it is indepent on the TAN concentration in the wastewater (Samani-Majd and Mukhtar, 2013). The results of the present study indicated that GPM technology can successfully perform inside AD reactors with a comparable mass transfer coefficient than that obtained in other GPM reactor configurations.

4. Conclusions

Results showed a great potential of gas-permeable membrane technology to improve AD of swine manure while recovering ammonia from the digestate in the form of an ammonium salt under different operational conditions. By coupling GPM system in the AD digester working under semi-continuous operation, an increase in the methane yield up to 27.6% (on average 16.7%) was detected compared to a control treatment. In addition, higher percentages of methane in biogas (up to 14%) were found during AD with NH_3 recovery. TAN was recovered and transformed in an ammonun sulphate solution at a uniform rate of 6.7 g N m^{-2} d^{-1}. Therefore, the AD-GPM configuration produces beneficial results on both biogas quantity and quality while also recovering ammonia nitrogen in marketable ammonium sulphate.

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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