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Research article

A biorefinery approach to recover nutrients, proteins, and methane from raw swine manure

Paula Calvo-de Diego [a], María Cruz García-González [a], Berta Riaño [b], Matias B. Vanotti [c], Mercedes Sánchez-Bascones [a], Beatriz Molinuevo-Salces [a,*]

[a] Department of Agroforestry Sciences, ETSIAA, University of Valladolid, Avenida Madrid 44, 34004, Palencia, Spain
[b] Agricultural Technological Institute of Castilla y León (ITACyL), Ctra. Burgos, Km. 119, Valladolid, 47071, Spain
[c] United States Department of Agriculture, Agricultural Research Service, Coastal Plains Soil, Water and Plant Research Center, 2611 W. Lucas St., Florence, SC, 29501, USA

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ABSTRACT

The livestock industry is expanding rapidly, generating large amounts of manure rich in nutrients and energy. This study develops a novel integrated biorefinery approach that combines multiple technologies to enable the simultaneous recovery of nutrients, proteins and energy from pig manure, maximizing resource valorization and economic returns. The technologies included gas-permeable membrane (GPM) to separate the ammonia, solid-liquid separation to separate organic particles, acid-base solubilization to separate phosphorus and proteins (SPP) from the particles, anaerobic digestion (AD) to produce biogas and combinations thereof. Using the GPM method, nitrogen (N) concentrations were reduced by up to 90 %, with total ammonia nitrogen (TAN) recovery rates ranging from 25 to 27 g N m^{-2} d^{-1}. Solid-liquid separation did not significantly increase pH or N recovery. The SPP method provided a phosphorus extraction efficiency of 114 % and a protein extraction efficiency of 86 % from the solid fraction of pig manure. The methane yield was 1.9 times higher when nitrogen was recovered before AD, while phosphorus and protein removal resulted in methane yields comparable to swine manure (215.5 mL CH_4 g^{-1} VS). A techno-economical study was carried out for the AD treatments proposed in the biorefinery approach. High internal rates of return (IRR) were obtained, 21–37 %, and a return on the investment in 3–5 years was obtained for all the treatments. This integrated strategy demonstrated a comprehensive and economically viable solution for sustainable pig manure management and resource recovery.

1. Introduction

The growth of the livestock industry raises environmental concerns due to the increased production of organic waste. Nutrients like nitrogen (N) and phosphorus (P) in the manure can lead to the eutrophication of waterways if improperly managed. However, these potential pollutants are high-value commodities with various industrial uses. To achieve the goal of a pollution-free environment and renewable "green" energy, it is crucial to seek methods that enable their recovery (Sajjad et al., 2024).

In the case of N, there is much interest in using control technologies to reduce NH_3 emissions through N recovery and subsequent conversion into a fertilizer product. The sale of the fertilizer product would help to partially cover the expenses of its deployment and maintenance (Van der Heyden et al., 2015). Some approaches for N recovery include struvite precipitation, ultrafiltration/ion exchange, ultrafiltration/reverse osmosis, or acid absorption after separation by gas stripping, and gas-permeable membrane (GPM) technology (Perera et al., 2019). In GPM technology (Vanotti and Szogi, 2015), NH_3 gas in the manure passes through the micropores of the membrane, which is hydrophobic. The membranes are immersed in the manure, and NH_3 is extracted before it escapes into the air. On the other side of the membrane, the gas is captured and concentrated by an acidic stripping solution. More specifically, NH_3 reacts with free protons in the acidic solution to form non-volatile NH_4^+, which is then transformed into an advantageous fertilizer, a concentrated non-volatile ammonium salt (Vanotti and Szogi, 2015). Ammonia has been effectively removed from swine manure (SM) using GPM. An important parameter affecting N recovery is the process pH, which determines the equilibrium between ammonium and ammonia gas and the rate of ammonia capture by the membrane

* Corresponding author.
E-mail addresses: paula.calvo.diego@estudiantes.uva.es (P. Calvo-de Diego), mariacruz.garcia.gonzalez@uva.es (M.C. García-González), riairabe@itacyl.es (B. Riaño), matias.vanotti@usda.gov (M.B. Vanotti), mercedes.sanchez@uva.es (M. Sánchez-Bascones), beatriz.molinuevo@uva.es (B. Molinuevo-Salces).

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Nomenclature:

AD	Anaerobic digestion
ATM	Ammonia trapped manure
BMP	Biochemical methane potential
CAPEX	Capital costs
$CVCH_4$	Methane calorific value
DPP	Discounted payback period
EC	Electrical conductivity
e-PTFE	Expanded polytetrafluoroethylene
GPM	Gas-permeable membrane
HRT	Hydraulic residence time
IRR	Internal rates of return
LF-ATM	Liquid Fraction Ammonia Trapped Manure
LF-SM	Liquid fraction of swine manure
M_{feed}	Volume of substrate treated in the biogas plant
N	Nitrogen
NEV	Net present value
OPEX	Operational costs
P	Phosphorus
PA	Parcial alkalinity
$PECH_4$	Potential energy of methane
RPPSM	Removed Phosphorus & Protein Swine Manure
S_o	Substrate
SF-SM	Solid fraction of swine manure
SM	Swine manure
SPP	Separate phosphorus and proteins
T1	Treatment 1
T2	Treatment 2
T3	Treatment 3
T4	Treatment 4
TA	Total Alkalinity
TAN	Total ammonia nitrogen
TKN	Total nitrogen
TP	Total phosphorus
TS	Total solid
VFA	Volatile fatty acids
VS	Volatile solid
X_o	Inoculum
YCH_4	Methane yield
$\eta_{Electric}$	Electric recovery efficiency
η_{heat}	Heat recovery efficiency

(García-González and Vanotti, 2015a). It has also been demonstrated that low-rate aeration is an effective way of increasing the pH in the manure without adding alkali chemicals. In this way, García-González et al. (2015a) studied aerated and non-aerated conditions for pH control in experiments with manure, recovering 99 % and 66 % of NH_3, respectively. In addition, the concentration of total solids in the manure could affect N recovery; these solids can cause fouling by adhering to the membrane surface or entering the pores, resulting in lower capture efficiency and increased energy consumption (Fillingham et al., 2017). However, Daguerre-Martini et al. (2018) reported that the concentration of organic matter had no direct effect on the NH_3 recovery rate. These authors found a higher pH in the liquid fraction (low solid content) than in the raw SM (high solid content), and pH is a parameter that affects the recovery of NH_3.

In the case of P, it is an essential nutrient for plant growth and development in agricultural production. The lack of P in soils can change crop metabolism, physiology and morphology, reducing yield and quality (Liu et al., 2015; Pandey et al., 2015). For this reason, it is interesting to recover P from manure, as phosphate rock is a non-renewable material that provides 80 % of the P used in producing fertilizers (Cordell et al., 2009). There are different methods of P recovery, such as struvite precipitation, electrodialytic processes, or chemical precipitation (Gonzalez-Garcia et al., 2022). A two-step method has been developed to separate P and proteins (SPP method) from biological materials, including animal manures (Vanotti and Szogi, 2018). Proteins are one of the most important N components in animal feed and are abundant in waste. For every 8.7 kg of protein a pig ingests, 5.8 kg is excreted, representing a significant protein loss. Therefore, it is necessary to recover proteins from manure to maximize the use of this resource (García-González et al., 2015a). The SPP method obtained an efficiency of 100 % in recovering proteins and 100 % in recovering P from swine manure (Vanotti and Szogi, 2018). The SPP method is based on the effect of pH on protein and P solubilization. In this manner, in the first step, an acidic solution is used to dissolve the P contained in wet manure solids separated out by a solid-liquid separator, and phosphorus is extracted from the resulting acidic supernatant. Then, in the second step, an alkaline solution is applied to the acidic precipitate that results from the acid extraction. After the alkaline treatment, the protein is extracted from the resulting basic supernatant (Vanotti and Szogi, 2018).

Once the above treatments are applied (i.e. N recovery by GPM technology from the liquid fraction followed by P and protein recovery by the SPP method from the solid fraction), a substantial amount of organic matter remains in the manure. One of the possible valorization treatments for this resulting organic biomass is anaerobic digestion (AD). AD is a biological treatment that processes biomass and produces biogas that can be used as a biofuel. This treatment contributes to reducing greenhouse gases and odor and producing renewable energy (Molinuevo-Salces et al., 2020b). Some biomass characteristics can affect the AD process; therefore, biochemical methane potential (BMP) tests are carried out to evaluate the methane potential of different biomasses (Cárdenas-Cleves et al., 2018). Previous studies have investigated AD performance coupled to GPM membranes. According to González-García (2021), AD systems retrofitted with GPM demonstrated increased methane content in biogas, with a 24 % improvement observed in batch experiments and an average increase of 11 % (from 8.3 % to 13.6 %) in semicontinuous experiments. These findings suggest that integrating multiple nutrient recovery technologies can significantly enhance the efficiency of the AD process.

A biorefinery constitutes a processing facility that amalgamates diverse biomass conversion technologies to convert renewable biological resources-such as crops, agricultural residues, and organic waste-into a wide array of valuable products, encompassing fuels, chemicals, materials, and energy (Thongchul et al., 2022). In the last years, different studies have been conducted to develop biorefinery systems to valorize organic by-products. For example, Gallipoli et al. (2024) investigated anaerobic digestion followed by thermally enhanced solid–liquid separation for food waste treatment and Aguiar et al. (2020) developed a biorefinery process for corn obtaining phosphorus and protein.

This research aims to investigate a new biorefinery approach that recovers ammonia, phosphorus, and proteins and produces methane from raw SM. First, the use of GPM technology for nitrogen recovery in the form of ammonium salt was studied. Second, protein and phosphorus recovery using the SPP method was evaluated. Finally, the resulting by-products' biochemical methane production (BMP) was studied.

2. Material and methods

2.1. Origin of substrates and inoculum

Raw SM was collected from a fattening pig farm located in Segovia province, Spain. It was stored in plastic bottles, transported to the laboratory, and refrigerated at 4 °C until use. Solid-liquid separation was carried out on the SM to obtain a liquid fraction (LF-SM) and a solid fraction (SF-SM). The solid-liquid separation was done in two steps: a filtration step with a 0.250 mm mesh light sieve and a centrifugation step at 10,000 rpm for 10 min and at 10 °C. Table 1 shows the chemical composition of SM, LF-SM, and SF-SM.

Anaerobic sludge, collected from the municipal wastewater treatment plant of Valladolid (Spain), was used as inoculum for the BMP experiments. It was stored in plastic bottles, transported to the laboratory, and refrigerated at 4 °C until use. The inoculum had a total solid (TS) and a volatile solid (VS) concentration of 2.37 ± 0.16 and 1.48 ± 0.13 %, respectively.

2.2. Experimental design

Four treatments (T1 to T4) with increased complexity were evaluated, as shown in Fig. 1. In treatments T1 and T2, no solid-liquid separation was carried out, whereas in treatments T3 and T4, a solid-liquid separation step was performed up-front, creating a separated liquid stream (Liquid Fraction Swine Manure, LF-SM) and a separated solids stream (Solid Fraction Swine Manure, SF-SM).

In T1, raw SM was directly subjected to anaerobic digestion (AD), and only a biogas product was obtained. In T2, raw SM was subjected to ammonia recovery using GPM technology, and the resulting manure effluent with low ammonia (called Ammonia Trapped Manure (ATM)) was subsequently treated by AD. The treatment produced an ammonia salt concentrate and biogas. In T3, the separated liquid fraction LF-SM rich in soluble ammonia was subjected to ammonia recovery using GPM technology. The resulting effluent with low ammonia (called Liquid Fraction Ammonia Trapped Manure, LF-ATM) was mixed with the previously separated SF-SM rich in volatile solids (VS) and treated by AD. In T4, the LF-SM was subjected to ammonia recovery using GPM technology as in T3. In addition, the SF-SM was subjected to phosphorus and protein extraction using the SPP method, leaving a by-product with low phosphorus and proteins called Removed Phosphorus & Protein Swine Manure (RPPSM). The resulting by-products from the liquid and solid streams (LF-ATM and RPPSM) were combined, and the mixture was treated by AD to produce biogas.

Table 1
Chemical composition of SM, LF-SM and SF-SM. The standard deviation of duplicate analyses is shown in parentheses. N.d. stands for not determined.

	SM	LF-SM	SF-SM
pH	7.82	8.15	9.27
TS (%)	4.47 (0.09)	1.72 (0.06)	10.92 (0.24)
VS (%)	3.26 (0.06)	0.97 (0.04)	9.16 (0.16)
TP (mg L^{-1})	453.25 (34.70)	82.09 (1.83)	1736.24 (153.31)
TAN (mg N L^{-1})	4568 (0.08)	4766 (82.73)	3893 (67.58)
Parcial Alkalinity (mg $CaCO_3$ L^{-1})	6118	6665	n.d.
Total Alkalinity (mg $CaCO_3$ L^{-1})	14820	14470	n.d.
EC (mS cm^{-1})	28.7	32.3	n.d.

The chemical abbreviations are SM: swine manure, LF-SM: liquid fraction of swine manure and SF-SM: solid fraction of swine manure, TS: total solids, VS: volatile solids, TP: total phosphorus, TAN: total ammonia nitrogen, EC: electrical conductivity.

2.3. Ammonia recovery using the GPM method

The ammonia recovery using GPM technology was carried out in duplicate reactors. The experimental setup (Fig. 2) consisted of: 1) a 1 L flask with an effective volume of 0.7 L of SM (T2) or LF-SM (T3 and T4), depending on the treatment that was being carried out, 2) a 0.5 L flask containing 0.2 L of 1N-H_2SO_4, 3) magnetic stirrer to ensure homogenization of SM or LF-SM, 4) an aquarium air pump (Marina 60, model 1110, China) with continuous air flow connected to porous stones, 5) an airflow meter (Aalborg, Orangeburg, NY, USA) to control the airflow rate from the pump, 6) a tubular hydrophobic and microporous gas-permeable membrane (GPM) that was submerged in the manure liquid, and 7) a peristaltic pump (Heidolph, Peristaltic Pump, Hei-FLOW Value 01 EU, Germany) to circulate the acidic solution through the tubular membrane continuously.

The GPM was made of expanded polytetrafluoroethylene (e-PTFE) (Zeus Industrial Products Inc., Orangeburg, SC, USA) with an outside diameter of 5.2 mm, a wall thickness of 0.64 mm, a polymer density of 0.95 g cm^{-3}, an average pore size of 2.5 µm and a bubble point of 207 kPa. The membrane had a length of 0.56 m. The membrane's surface area was 0.0091 m^2, the length-to-effective volume ratio was 0.8 m L^{-1}, and the area-to-manure volume ratio was 0.013 m^2 L^{-1}, as described by Molinuevo-Salces et al. (2018). The membrane was immersed in SM or LF-SM. An airflow rate of 0.24 $L_{air}L_{manure}^{-1}min^{-1}$ was used to increase the pH of the manure (Vanotti and Szogi, 2015; Garcia-González and Vanotti, 2015). The SM or LF-SM was continuously stirred using magnetic stirrers throughout the experiment. However, due to the high TS content of SM (Table 1), it wasn't always possible to achieve good homogenization. The GMP experiments had a duration of 9 days. The temperature in the SM and LF-SM varied between 24.5 and 29.1 °C and 20.0–26.1 °C, respectively. The acidic solution (i.e. 1N-H_2SO_4) was continuously recirculated through the membrane at a flow rate of 6.25 L d^{-1}. To ensure the N recovery in the acidic solution, the pH of the acidic solution was kept below 2 by adding H_2SO_4 (98 %) (Lahav et al., 2008; Rothrock et al., 2010).

The resulting effluent (called Ammonia Trapped Manure (ATM)) was stored at 4 °C. Samples of 9 mL of SM or LF-SM were taken daily to measure the temperature, conductivity, total ammonia nitrogen (TAN), and pH. In addition, total alkalinity (TA) was measured twice during the experiment, once at the beginning and once at the end. The concentrations of TS, and VS were measured at the beginning and end of the experiment. Each day, 5 mL of sample was taken from the acidic solution to measure the temperature, the TAN content, and the pH. The amount of water captured by the membrane by osmotic distillation was measured every day by weighing the flask containing the acidic solution before sampling (Riaño et al., 2019).

2.4. Protein and phosphorus recovery using the SPP method

The method developed by Vanotti and Szogi (2018) for recovering proteins and phosphorus from biological materials was used. A diagram with the different steps of this methodology used in T4 is presented in Fig. 3. First, 2907 g of raw SM were centrifuged for 30 min at 20 °C to separate the manure into two fractions: a liquid fraction rich in soluble ammonia (LF-SM) (2250 g), which was used for ammonia recovery and a solid fraction (SF-SM) (656.9 g), rich in proteins and phosphorus, that was used for the SPP extraction. The phosphorus and protein extraction procedure is carried out in 2 steps (Vanotti and Szogi, 2018): an acidic extraction with sulfuric acid (H_2SO_4) 0.25M and an alkaline extraction with sodium hydroxide (NaOH) 0.4M. The extractions were replicated 4 times using a quantity of 2.4 g dry basis of SF-SM for each replicate. 20 mL of diluted H_2SO_4 was added and stirred for 30 min to solubilize the phosphorus and precipitate the proteins. The samples were then centrifuged for 30 min at 20 °C to separate into two fractions: a liquid fraction called acid extract with a pH of 0.95(0.03), which was stored, and an acid solid fraction. The acid solid was rinsed with 20 mL of

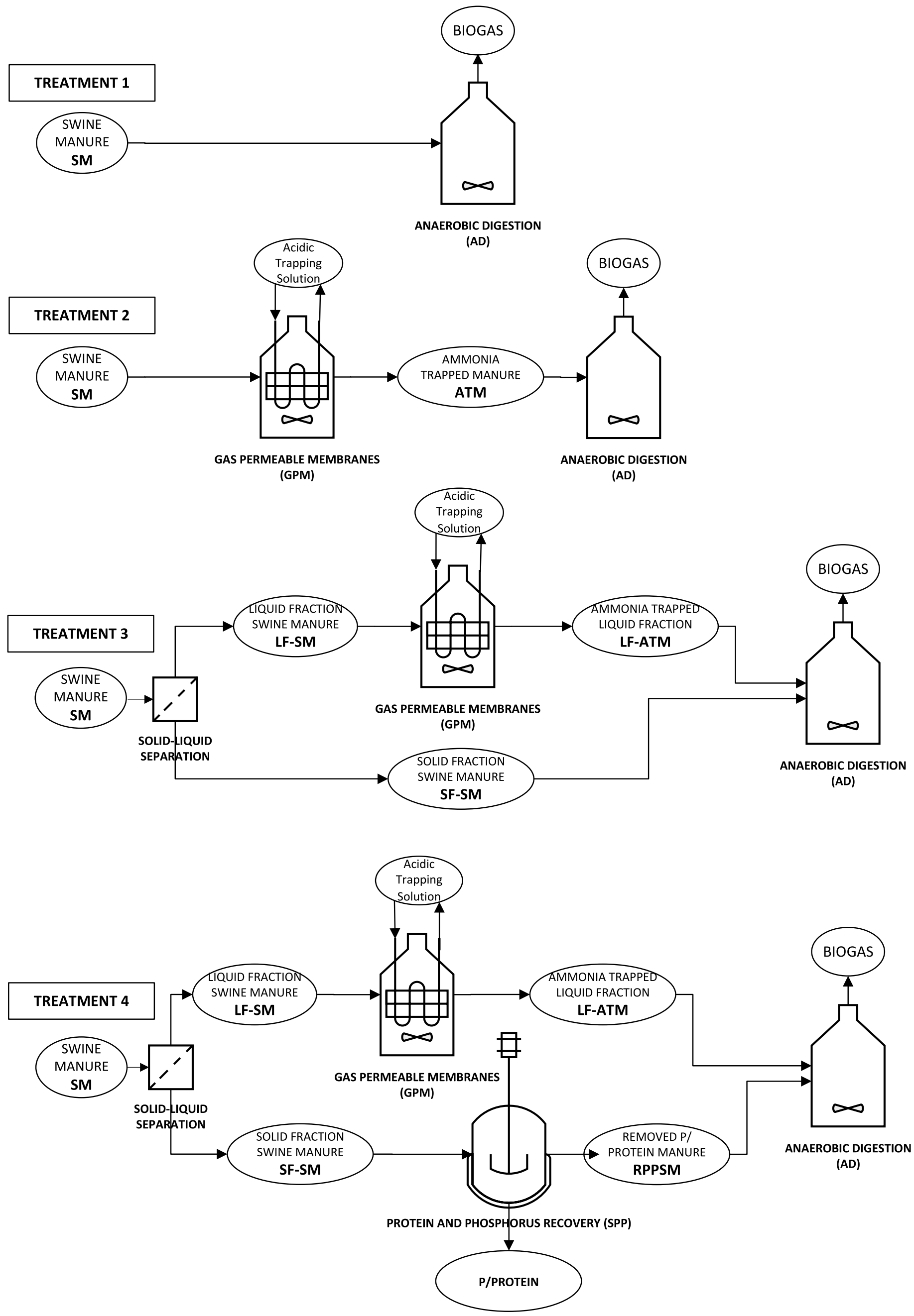

Fig. 1. Diagram of the four treatments evaluated (T1-T4).

distilled water and vortexed for 1 min. Then, the sample was centrifuged for 30 min at 20 °C to separate into two fractions: a liquid called rinsed acid extract with a pH of 1.44(0.06),which was stored and a rinsed acid solid (Fig. 3).

After the acidic treatment, the resulting rinsed acid solid was mixed with 20 mL of NaOH 0.4M and homogenized with a magnetic stirrer and a disperser (Hielscher Ultrasonics (Teltow, Germany) probe-type ultrasonicator model UIP1000hdT (1000 W, 20 kHz)) for 20 and 10 min, respectively, where proteins were solubilized and recovered. The homogenate was then centrifuged 30 min at 20 °C to separate into two fractions: a liquid fraction called alkali extract with a pH of 12.77(0.09) and a solid fraction, called alkali solid. The alkali solid was rinsed, adding 20 mL of distilled water, and vortexed for 1 min. Then, the samples were centrifuged for 30 min at 20 °C to separate into two fractions: a liquid called rinsed alkali extract with a pH of 10.66(1.82), which was stored, and a rinsed alkali solid. The resulting solid by-product was named Recovered Phosphorus Protein Swine Manure (RPPSM) corresponding with rinsed alkali solid in Fig. 3 and it was stored at 4 °C for further use. The (RPPSM) was used for AD in the T4.

After the procedure, the acid extracts, rinsed acid extracts, alkali extracts, and rinsed alkaline extracts were placed in plastic bottles and cooled to 4 °C until chemical analysis. Total phosphorus (TP) and protein contents were measured in all the fractions.

2.5. *Anaerobic digestion tests using biomethane potential (BMP)*

BMP tests were carried out in triplicate, using 0.57 L bottles. The BMP was carried out as the final process of the 4 treatments studied (T1 to T4, Fig. 1). The four AD substrates used were: 1) SM in T1, 2) ATM in T2, 3) LF-ATM + SF-SM in T3, and 4) LF-ATM + RPPSM in T4. To obtain

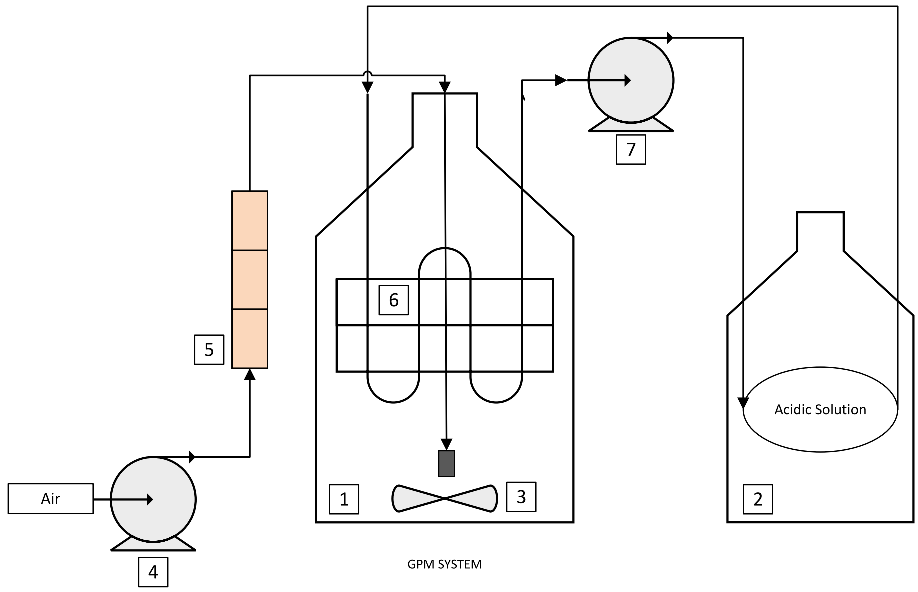

Fig. 2. Process diagram of GPM system. 1) 1 L flask with SM or LF-SM, 2) 0.5 L flask containing 0.2 L of H_2SO_4, 3) magnetic stirring, 4) aquarium pump connected to porous stones, 5) air flow meter, 6) e-PTFE membrane and 7) peristaltic pump.

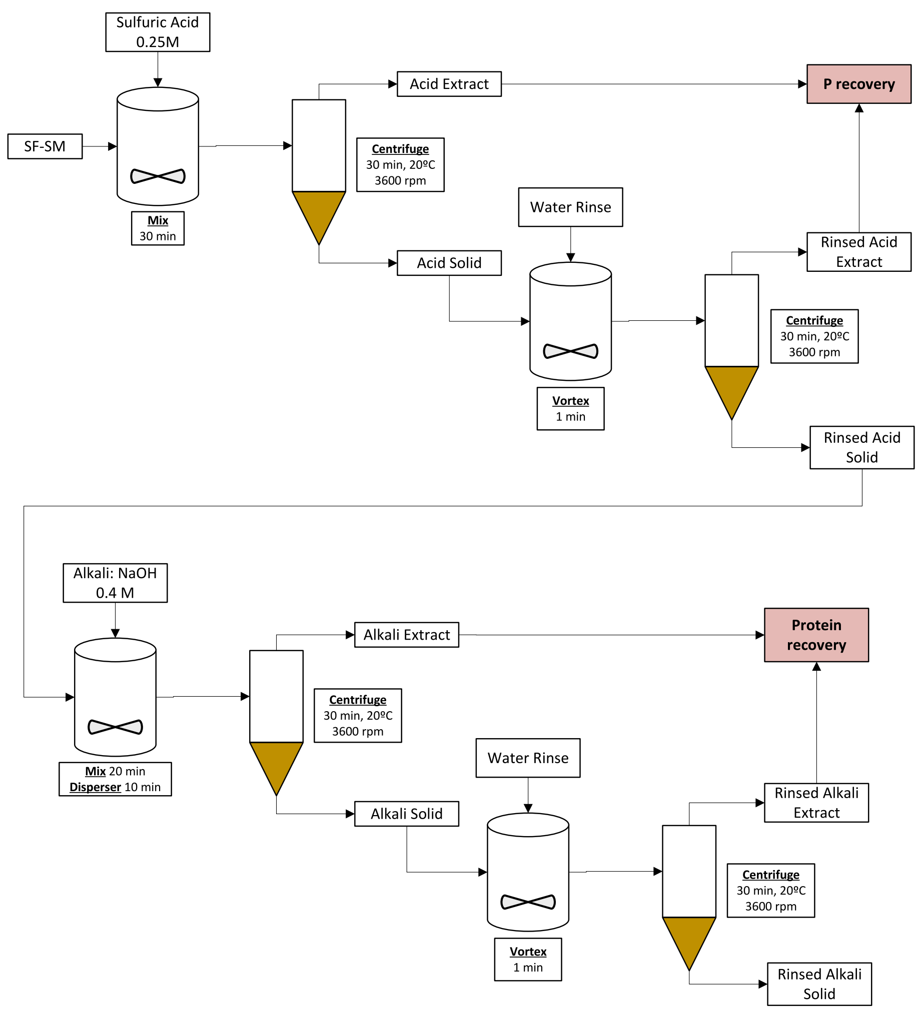

Fig. 3. Steps used to recover phosphorus and proteins from manure following the SPP method.

a substrate/inoculum (So/Xo) ratio of 1, expressed in g VS g VS^{-1}, each substrate was combined with an inoculum. Due to the different amounts of biomass obtained in the treatments, tests were carried out with different amounts of inoculum and substrate. For the biomass of T1 and T3, 100 g of inoculum was used; for the biomass of T2 and T4, 25 g of inoculum was used. The substrate/inoculum ratio was used to calculate the amount of substrate. Additionally, blanks containing only the inoculum were used to verify the endogenous methane production. The appropriate mixtures were put into bottles, which were then sealed with an aluminium top and a rubber septum. Nitrogen was evacuated for 5 min to maintain anaerobic conditions. The bottles were incubated at 37.1 ± 1.3 °C for 46 days. The amount of biogas produced by the substrates was calculated by monitoring the overpressure in the bottle's headspace. The composition of the biogas was measured once a week. The concentrations of TS, and VS, TAN, total nitrogen (TKN), pH and conductivity were measured at the beginning and end of the experiment.

2.6. Chemical analyses

The concentrations of TS, VS, TP and TKN were measured according to standard methods (APHA, 2005). TS was determined after drying for 24 h at 105 °C and VS was determined after ignition for 4 h at 550 °C. TAN was analyzed by steam distillation followed by collection of the distillates in borate buffer and titration with 0.1M HCl. A Kjeltec 8100 apparatus (Foss Iberia S.A., Barcelona, Spain) was used for distillation. pH, Electrical Conductivity and total alkalinity were monitored using a GLP22 electrode (Crison Instruments S.A., Barcelona, Spain). Total alkalinity (TA) was determined by measuring the amount of standard sulfuric acid needed to bring the sample to pH of 4.5. Parcial alkalinity (PA) was determined by measuring the amount of standard sulfuric acid needed to bring the sample to pH of 5.75. Proteins were determined by multiplication with TKN and a conversion factor of 6.25 (Pervaiz and Sain, 2011).

The composition of biogas was determined 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 used 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. Methane values were expressed at normal conditions (i.e. 0 °C and 1 atm).

2.7. Statistical analyses

An analysis of variance (ANOVA) was used to determine the statistical analysis of the experimental data (TAN initial, TAN remained, TAN removed, TAN volatilized, TAN recovered in the acidic solution, TAN removal efficiency, TAN recovery over removed and TAN Recovery Rate) for SM and LF-SM before and after GPM technology. To determine statistical significance, the 95 % confidence interval of differences ($p < 0.05$) was chosen.

2.8. Techno-economic study

A techno-economic study of the four treatments proposed in this study was carried out. For this purpose, the calculations were made for a farm with 2800 swine, which generates an amount of 6.12 m^3 of SM per animal per year, resulting in an annual amount of SM to be treated of 17,136 m^3 (Riaño et al., 2023).

All the proposed treatments contain anaerobic digestion (AD) as a part of their process, but the volume of materials to be treated by AD varied according to the treatments applied in each case. In this way, for T1 all the SM produced in the farm was subjected to AD. After liquid-solid separation, the LF-SM was 77.4 % of mass SM and the SF-SM was the 22.6 %. For T2, 80.7 % of the SM volume was considered for AD, since some material loss was observed during the GPM treatment. For T3, 88.9 % of the LF-SM volume and 100 % of the SF-SM was considered for AD, since some material loss was observed during the previous treatments. For T4, 88.9 % of the LF-SM volume and 90 % the SF-SM (10 % of volume loss during P and protein extraction was estimated) were considered for AD. The AD would be performed according to the results obtained in the BMP tests in this study, at 38 °C with an HRT of 15 days (Section 3.3). Due to maintenance shutdowns, the biogas plant would operate 85 % of the year (310 days). To calculate the volume of the reactor, a security factor of 1.4 was applied. Therefore, AD reactors of 1161, 937, 1062 and 1035 m^3, would be needed for T1, T2, T3 and T4, respectively.

The methane production (m^3 d^{-1}) and the potential energy for each treatment were calculated using Eq. (1) and Eq. (2), respectively:

$$\textit{Methane production}\left(m^3 d^{-1}\right) = \frac{M_{feed} * Y_{CH_4}}{\textit{Working days per year}} \tag{1}$$

where $M_{feed}\left(m^3 year^{-1}\right)$ is the annual volume of substrate treated in the biogas plant; Y_{CH_4}(m^3 CH_4 t^{-1} VS d^{-1}) is the methane yield; Working days per year are 310 days.

$$PE_{CH_4}\left(kWh\ m^{-3}\right) = \textit{Methane production} * CV_{CH_4} \tag{2}$$

where $CV_{CH_4}\left(kWh\ m^{-3}\right)$ is methane calorific value (i.e. 9.96kWh m^{-3}) (Riaño et al., 2023).

A combined heat and power system of 100 kW was chosen for the simultaneous production of electricity and heat. Net electricity production and net heat production were determined with Eqs. (3) and (4):

$$\textit{Net electricity production}\left(kWh\ d^{-1}\right) = PE_{CH_4} * \eta_{Electric} \Big/ 100 \tag{3}$$

$$\textit{Net heat production}\left(kWh\ d^{-1}\right) = PE_{CH_4} * \eta_{heat}\ / 100 \tag{4}$$

where $\eta_{electric}$ is the electric recovery efficiency being 30 % and η_{heat} is the heat recovery efficiency being 50 % according with a combined power and heat system was used for electricity and heat production simultaneously (Riaño et al., 2023).

The revenues were calculated considering the electricity production and the sales of the solid fraction of the digestate. The average selling price of electricity in Spain in 2024 was 0.1833 € kWh^{-1} and the price of the solid fraction of the digestate was 5 € t^{-1} of solids. (Riaño et al., 2023). It was assumed that the solid fraction obtained after a solid-liquid separation of the digestate was 25 % of the total volume.

The capital costs (CAPEX) were calculated considering the digestor and the equipment required in the biogas plant such as plumbing equipment, electrical equipment and installation, engineering works and the purchase of a solid-liquid separator.

The digestor price was estimated according to Imeni et al. (2019) with Eq. (5):

$$\textit{Digestor Price}\ (€) = 329.05 * \textit{Digestor size} + 181,815 \tag{5}$$

The estimation of the costs of plumbing equipment, electrical equipment and installation, engineering works, civil works and the solid-liquid separator was performed according to Riaño et al. (2023).

The operational costs (OPEX) were calculated considering the electricity consumption and maintenance costs. The estimation of the plant's internal electricity consumption was calculated by multiplying its daily usage, which was calculated to be 5 % of the electricity produced. (Riaño et al., 2023).

To estimate the net revenues of the AD process, the net present value (NPV), the internal rate of return (IRR) and the discounted payback period (DPP) were calculated. A discount rate of 7 % and a project life of 25 years were chosen to calculate those values (Imeni et al., 2019).

Besides the revenues obtained in the AD systems, the incomes that could be obtained from applying the GPM method to recover the ammonia and the SPP method to recover phosphorus and proteins were calculated. Regarding the GPM system used in treatments T2, T3, and

T4, a cost of 2.07 € per N kg recovered (Molinuevo-Salces et al., 2020a) and a sale price for the obtained ammonium sulfate of 2.66 € kg^{-1} of N (Dube et al., 2016) were considered. To estimate the revenues of the SPP method of phosphorus and protein extraction in T4, the cost of the necessary chemicals and the price of sale of the resulting products were estimated for the SF-SM needed to be treated. The price of the chemicals was estimated to be 0.29 € kg^{-1} of H_2SO_4 (98 %) and 0.19 € kg^{-1} of NaOH (100 %) (Dube et al., 2016). The equipment to perform SPP process would comprise different tanks, pipes and tubes, an industrial disperser and a centrifugation device. An initial investment of 25,000 € has been estimated for the whole SPP process. In the case of the products, a price of 2.81 € kg^{-1} of P was considered, according to González-García et al. (2023). The price of protein depends on its origin and consumption, so it was assumed that the protein would be used for fish consumption (aquaculture). In this way, a protein similar to the protein from soybean meal, which is the No. 1 protein source used in aquaculture worldwide, was considered. The price of soybean meal at 47 % protein is 472 € t^{-1}, which is equivalent to 1004 € t^{-1} (1 €/kg) of protein at 100 % protein. (MAPA, 2024).

3. Results and discussion

3.1. Nitrogen recovery by GPM technology: effect of TS content on ammonia recovery

Fig. 4 presents the removal of TAN in SM (T2) (Fig. 4A) and in LF-SM (T3 and T4) (Fig. 4B) and the recovery by the GPM technology as ammonium salt. It can be observed that, for both substrates (SM and LF-SM), as the TAN content in the manure decreased, the concentration of TAN in the acidic trapping solution increased (Fig. 4). More specifically, for SM, the concentration of TAN in SM decreased from 4567.5 ± 0 to 667 ± 300 mg N L^{-1}, while the concentration of TAN in the acidic trapping solution increased from 0 to 10,466 ± 126 mg N L^{-1}. In the case of LF-SM, the concentration of NH_4^+-N decreased from 4765.5 ± 0 to 583 ± 113.1 mg N L^{-1}, while at the same time, the concentration of TAN in the acidic trapping solution increased from 0 to 10,872 ± 0 mg N L^{-1} during the 9 days of the experiment. From these results it can be seen that the trend, both in removal and in the recovery of N, was similar for both substrates, SM and LF-SM. These results are in line with those obtained by García-González et al. (2015a), working with swine manure, where the ammonium concentration decreased from 2270 ± 0 to 20 ± 30 mg N L^{-1} in 18 days.

The removal efficiencies of TAN were 89.4 % and 90.2 %, for SM and LF-SM, respectively (Table 2). Percentages of 71.4 and 73.2 % of the removed N were recovered as ammonium salt, for SM and LF-SM, respectively (Table 2). TAN recovery rates were 24.9 and 26.9 g m^{-2} d^{-1} in SM and LF-SM, respectively. Moreover, the results obtained here are like those reported in Riaño et al. (2019), who observed a TAN recovery rate of 27.1 g m^{-2} d^{-1} under similar operational conditions.

A two-factor analysis of variance (ANOVA) was carried out to determine if there were significant differences between the results obtained for SM and LF-SM. For a 95 % confidence interval there were no significant differences between both substrates in TAN removal, TAN recovery in the acidic solution and TAN Recovery Rate. These results indicate that the solid-liquid separation and resulting lower concentration of total solids in the manure had no effect on GPM performance. The results obtained in this study are consistent with those of Daguerre-Martini et al. (2018), who showed that similar ammonia recovery rates can be achieved over a range of total solid concentrations. In their study, they observed consistent ammonia recovery efficiencies of over 90 % for digestates with total solid contents ranging from 0.8 to 23.3 g L^{-1}. In our study, similar results were found for raw swine manure.

3.2. Recovery of protein and phosphorus by the SPP method

With initial concentrations of phosphorus (1736 mg L^{-1}) and protein (20,735 mg L^{-1}) in SF-SM, an amount of 2.4 g dry basis of SF-SM was taken for each of the 4 replicates. The initial amounts of phosphorus and protein in SF-SM were 38.07 ± 0.07 and 454.67 ± 0.87 mg, respectively (Tables 3 and 4). In the first step of the SPP method (i.e. acidic extraction), 29.41 ± 2.77 and 62.93 ± 0.83 mg of phosphorus and protein, respectively, were recovered, corresponding to 77.2 % and 13.8 % recovery, respectively. The pH values were 0.95 ± 0.03 and 1.43 ± 0.06 for acidic extract and rinsed acidic extract, respectively. In the second step of the SPP method (i.e. alkaline extraction), 14.15 ± 0.86 mg of phosphorus and 327.55 ± 50.02 mg of protein were extracted, giving a recovery of 37.1 % and 72.0 % recovery, respectively. The pH values were 12.77 ± 0.09 and 11.93 ± 1.27 in the alkali extract and rinsed alkali extract, respectively. The SPP method resulted in a phosphorus recovery efficiency of 114 % and a protein recovery efficiency of 86 %.

As mentioned above, different technologies have been investigated to recover P from livestock wastewater. Struvite precipitation resulted in P recoveries of up to 90 % from anaerobic digestate and swine manure (Gonzalez-Garcia et al., 2022) while the electrodialysis process achieved up to 93 % P recovery (Zhang et al., 2013). Furthermore, the combination of technologies has led to high P recoveries. For example, a study carried out by Chen et al. (2023) used an electrochemical method combined with a vivianite method using a sacrificial iron anode to recover P from pig manure, achieving up to 90 % recovery at pH of 5. Zhang et al. (2013) reported a P recovery of 90.4 % at pH 3 from anaerobic sludge by using electrodialysis. When comparing the results obtained with the SPP method in this study with those of other phosphorus recovery technologies, the SPP method resulted in higher recovery efficiencies. Also, the SPP method allows for high protein recovery in addition to P recovery.

Protein recoveries of up to 86 % were obtained with the SPP method. Callejo-López et al. (2020), who used a two-step method with an alkaline reaction and enzymatic treatment, achieved 81 % protein recovery

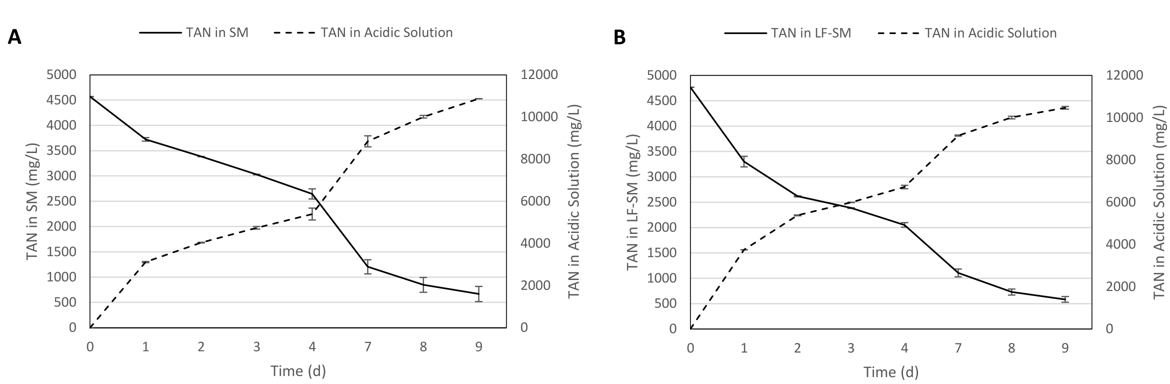

Fig. 4. Removal of TAN and recovery as ammonium salt in A) SM and B) LF-SM.

Table 2
Nitrogen mass balance using the GPM system for SM and LF-SM.

	TAN Initial	TAN remained	TAN removed	TAN volatilized	TAN recovered in the acidic solution	TAN removal efficiency	TAN recovery over Removed	TAN Recovery Rate
	mg N					%		$g\ m^{-2}\ d^{-1}$
SM	3197.3	337.9(78.1)	2859.4(156.1)	817.6	2041.8(175.6)	89.4	71.4	24.9
LF-SM	3335.9	327.7(61.6)	3008.1(0.0)	804.8	2203.3(27.5)	90.2	73.2	26.9

Table 3
Mass balance of phosphorus from SF-SM using SPP method.

		Phosphorus		Total P Recovery
		mg	%	%
	SF-SM (Initial)	38.07 (0.07)	100	
Acidic Extraction	**Acid Extract**	29.41 (2.77)	77.24 (7.22)	114.4 (9.43)
	Rinsed Acid Extract	14.15 (0.86)	37.16 (2.23)	
Alkali Extraction	**Alkali Extract**	0	0	0
	Rinsed Alkali Extract	0	0	

Table 4
Mass balance of protein from SF-SM using SPP method.

		Protein		Total Protein Recovery
		mg	%	%
	SF-SM (Initial)	454.67 (0.87)	100	
Acidic Extraction	**Acid Extract**	62.93 (0.83)	13.84	13.84(7.58)
	Rinsed Acid Extract	0.0	0.0	
Alkali Extraction	**Alkali Extract**	292.85 (44.85)	64.41 (9.87)	72.04(11.14)
	Rinsed Alkali Extract	34.70 (13.01)	7.63 (2.86)	
Extraction Total Recovery		391.40	85.88	85.88(38.52)

from microalgae biomass. The pH of the media reported in that study was 13.4 and 12.8 for alkaline and enzymatic, respectively. In the present work, a higher recovery was achieved without reaching such a high pH in the treatments. On the other hand, Hernández et al. (2018) achieved 54.5 % protein recovery from slurry-fed microalgae using ultrasound and an alkaline treatment at pH 12, and Lorenzo-Hernando et al. (2019) achieved protein recovery from 53.5 % to 77.9 % from slurry-fed microalgae using alkaline hydrolysis at pH 12 and acid precipitation. Using the SPP method, Vanotti and Szogi (2018) obtained 87 % P recovery and 103 % protein recovery from spirulina algae with an acid step (citric acid) at pH 3.1 and a second alkaline extraction at pH 12.8. So, the SPP method is a very effective method for the recovery of protein from manure slurry solids and algae, and it also achieves good recovery of P, thus contributing to a high recovery of both compounds.

3.3. Biogas production

Four experiments were carried out in triplicate corresponding to the raw materials of the four treatments (T1, T2, T3 and T4). The four substrates were: 1) SM from T1, 2) ATM from T2, 3) LF-ATM + SF-SM from T3 and 4) LF-ATM + RPPSM from T4 (Fig. 1) with a substrate/inoculum (So/Xo) ratio of 1, expressed in g VS g VS^{-1}. The initial and final chemical characterization of the four mixtures inoculum-substrate is shown in Table 5.

Regarding the initial pH, T1 exhibited a higher pH compared to T2 and T4. This difference can be attributed to the processing methods applied: In T2, the entire volume of SM was treated with GPM to recover N. In T4, the LF-SM was treated with GPM for N recovery, while the SF-SM underwent solid-phase (P) extraction (SPP) to extract P and proteins. These treatments resulted in lower initial pH values for T2 and T4. A similar outcome would be expected for T3, however, it displayed a pH comparable to T1. This can be explained by the fact that while the LF-SM in T3 was treated with GPM for N recovery, the SF-SM did not undergo any pretreatment, thus retaining its N content. Consequently, T2 and T4 exhibited the lowest TAN concentrations among the treatments. As expected, the pH increased during anaerobic digestion. The first generation of volatile fatty acids (VFAs) during the breakdown of organic matter can cause a slight decrease in pH. However, as the process of digestion continues, these VFAs are consumed by methanogenic bacteria, leading to an increase in pH (Esposito et al., 2012). The final pH achieved in the BMP trials was between 7.8 and 8.2.

Fig. 5 shows the evolution of the specific methane yield over the digestion time. Specific methane yields of 219 ± 11, 407 ± 46, 316 ± 66 and 216 ± 28 NmL CH_4 g^{-1} VS added were obtained for T1, T2, T3 and T4, respectively. Methane yields in terms of volume of methane per volume of effluent were calculated, obtaining values of 7.21, 13.21, 9.09 and 10.79 L CH_4 per liter of treated effluent for T1, T2, T3 and T4, respectively. An analysis of variance (ANOVA) was carried out to determine if there were significant differences between the four treatments. For a 95 % confidence interval there were significant differences between them. Different studies have reported specific methane yields for swine manure ranging from 130 to 360 mL CH_4 g^{-1} VS (Hamilton, 2012; Santos et al., 2022). These methane yields are influenced by several factors, including the chemical composition of the substrate, the

Table 5
Initial and final chemical characterization of the four mixtures inoculum-substrate.

		pH	EC	TAN	TKN	TS	VS
		–	$mS\ cm^{-1}$	$g\ L^{-1}$	$g\ L^{-1}$	%	%
T1	**Initial**	7.81	11.52	1.67 (0.00)	3.18(0.19)	1.54 (0.37)	1.22 (0.06)
	Final	8.04	13.37	1.96 (0.03)	3.36(0.10)	1.36 (0.00)	0.82 (0.00)
T2	**Initial**	7.55	7.81	0.87 (0.00)	1.98(0.02)	1.96 (0.03)	1.41 (0.08)
	Final	8.2	10.42	1.17 (0.02)	2.13(0.04)	1.41 (0.01)	0.81 (0.00)
T3	**Initial**	7.82	7.72	1.02 (0.12)	2.22(0.21)	1.93 (0.11)	1.41 (0.08)
	Final	7.8	10.32	1.22 (0.02)	2.05(0.19)	1.48(0.09)	0.89(0.16)
T4	**Initial**	7.45	6.28	0.73 (0.02)	1.98(0.06)	1.94(0.22)	1.49(0.14)
	Final	7.97	8.11	0.95 (0.01)	2.03(0.26)	1.22(0.10)	0.48(0.36)

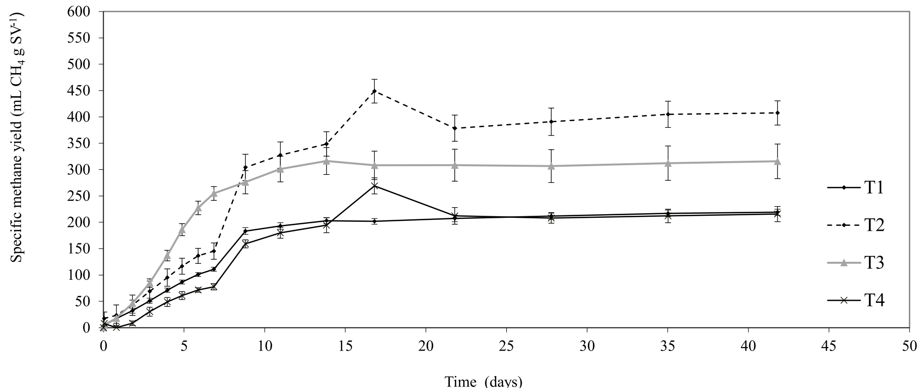

Fig. 5. Specific methane yield for T1, T2, T3 and T4. Data is means of triplicated experiments.

ratio substrate to inoculum, pH, temperature or the presence of inhibitors. Higher TS and VS concentrations generally lead to higher methane yields. The substrate to inoculum ratio (So/Xo) also plays a crucial role, with optimal ratios typically falling between 0.5 and 1.0 (Santos et al., 2022). In this case, the So/Xo was 1. pH plays a crucial role, with optimal values for methane production between 7.0 and 7.8. The presence of inhibitors, particularly ammonia, can have a significant effect on methane production. High concentrations of TAN above 200 mg L^{-1} can inhibit methanogenesis, so that reducing methane yields (Mutegoa et al., 2020). This inhibitory effect of ammonia can be seen by comparing the specific methane yields obtained in T1 (219 NmL CH_4 g^{-1} VS) with those obtained in T2 (407 NmL CH_4 g^{-1} VS) and T3 (316 NmL CH_4 g^{-1} VS). Thus, in T2, the recovery of N from the manure using GPM membranes resulted in an increase in the methane potential of the resulting manure (i.e. ATM) if compared to the raw SM (T1). However, the addition of the solid fraction to the anaerobic digestion in T3 reduced the specific methane yield, probably due to the recalcitrant nature of the organic matter in this solid fraction of the manure. In the case of T4, the specific methane production was 216 NmL CH_4 g^{-1} VS, probably due to the removal of proteins during the SPP treatment, which resulted in a reduction in methane production.

3.4. Techno-economic study

The experimental results obtained in the BMP experiments (Section 3.3) were used for the estimations of a techno-economic study. Table 6 presents the results obtained in the techno-economic study of the AD process for treatments T1, T2, T3 and T4. Specific methane yields of 219 ± 11, 407 ± 46, 316 ± 66 and 216 ± 28 NmL CH_4 g^{-1} VS were used for T1, T2, T3 and T4, respectively.

Net present values (NPV), calculated with a discount rate of 7 %, of 1,030,673 €, 1,841,715 €, 1,549,331 € and 883,673 €, were obtained for T1, T2, T3 and T4, respectively. All the obtained values were positive values, indicating that the money return is higher than the initial inversion (CAPEX), being T2 the treatment that obtained the best results. If these results are compared to those obtained by Riaño et al. (2023), who carried out a techno-economic study for the manure of the same number of animals in co-digestion with pepper waste obtaining a NPV of 569,359 €, our results are up to three times higher (T2). It can therefore be seen that the previous use of gas permeable membrane technology improves the AD process, as can also be seen when comparing T1 and T2. The internal rate of return (IRR) explained that the discount rate would turn NPV to zero, the values of IRR obtained

Table 6
Techno-economic study of AD processes for treatments T1, T2, T3 and T4.

		Treatment 1	Treatment 2	Treatment 3	Treatment 4
Biogas and energy production					
Raw materials	m^3/year	17,136	13,831	15,673	15,284
Methane production	m^3/day	794	1212	1064	708
Potential energy (PE)	kWh/d	7910	12,072	10,598	7055
Net electricity production	kWh/d	2373	3622	3179	2116
Net heat production	kWh/d	3955	6036	5299	3527
Revenues					
Electricity production	€/year	134,824	205,777	180,652	120,254
Sales of solid fraction of digetate	€/year	21,420	17,289	19,592	19,105
Total	€/year	156,244	223,066	200,243	139,359
Capital Costs (CAPEX)					
Digestor price	€	563,785	490,119	531,179	522,507
Plumbing equipment	€	15,000	15,000	15,000	15,000
Electrical equipment and installation	€	20,000	20,000	20,000	20,000
Engineering works	€	15,000	15,000	15,000	15,000
Civil works	€	7000	7000	7000	7000
Solid liquid separator	€	15,000	15,000	15,000	15,000
Total	€	620,785	547,119	588,179	579,507
Operation costs (OPEX)					
AD electricity consumption	€/year	6741	10,289	9033	6013
Solid-liquid separator electricity consumption	€/year	590	590	590	590
Maintenance cost	€/year	7200	7200	7200	7200
Total	€/year	14,531	18,079	16,823	13,803
Economic Idexes					
NPV	€	1,030,673	1,841,715	1,549,331	883,673
IRR	%	23	37	31	21
DPP	year	4	3	4	5

were 23 %, 37 %, 31 % and 21 % for T1, T2, T3 and T4, respectively. The discounted payback period (DPP) indicates the number of years after which the cumulative discounted cash inflows cover the initial investment. DPP values of 4, 3, 4 and 5 years were obtained for T1, T2, T3 and T4, respectively. Those can be considered as short periods, considering that the calculations have been performed for 25 years of project life.

The income that could be obtained from the application of the GPM system and the SPP method was calculated. For the GPM treatment, the potential net income obtained from the sale of recovered N, considering that 39,119 kg N/year, 32,325 kg N/year and 32,325 kg N/year were extracted for T2, T3 and T4, were 23,080, 19,072 and 19,072 €/year, respectively. The best net revenue potential was obtained for T2. In the case of the SPP method at T4, the potential income obtained from extracted P, taking into account that 6784 kg of P/year would be extracted, would be −7335 €/year and the potential income obtained from protein, taking into account that 81,031 kg of protein/year would be extracted, would be 69,966 €/year. Therefore, the potential net income from the SPP method would be 59,138 euros/year. For the first year of operation, the estimated initial investment of 25,000 € should be considered. This initial investment includes different tanks, pipes and tubes, an industrial disperser and a centrifugation device needed for the first year and the energy costs involved in the SPP process. The potential net income from P extraction gave negative results, which means that only the P extraction part has costs, but this is compensated by the potential net income from protein extraction, which gives a positive potential net income in the SPP method. Even so, T2 still gives better potential net revenues considering all treatments. The use of chemicals in the SPP method could be optimized to reduce the use of sulfuric acid in this method, or direct protein extraction could be carried out. On the other hand, the SPP method could be included in the T2 process after AD to extract P and protein from the solid fraction of the digestate in order to obtain higher potential net revenues in this treatment.

4. Conclusions

This study presents the results of a biorefinery approach for the valorization of raw pig manure, combining different technologies for the recovery of nutrients, protein and methane. Ammonium was removed from the manure using gas-permeable membrane technology, with recovery rates in the range of 25–27 g N m^{-2} d^{-1}. The combination of P and protein extraction using the SPP method achieved recovery efficiencies of 114 % and 86 % for P and protein respectively. The recovery of nitrogen before AD resulted in a 1.9-fold increase in methane yield when compared to the methane yield of raw pig manure (215.5 mL CH_4 g^{-1} VS). Furthermore, recovering phosphorus and proteins resulted in a methane yield like that of raw pig manure. A techno-economical study was carried out for the AD treatment proposed in the biorefinery approach, a return of the investment in 3–5 years was obtained in all cases. In conclusion, this biorefinery concept is highlighted as a potential valorization approach for pig manure, resulting in the recovery of nutrients, protein and energy in the form of methane.

CRediT authorship contribution statement

Paula Calvo-de Diego: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **María Cruz García-González:** Writing – review & editing, Validation, Resources, Project administration, Funding acquisition. **Berta Riaño:** Writing – review & editing, Validation, Resources, Data curation. **Matias B. Vanotti:** Writing – review & editing, Visualization, Conceptualization. **Mercedes Sánchez-Bascones:** Writing – review & editing, Funding acquisition. **Beatriz Molinuevo-Salces:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Beatriz Molinuevo Salces reports financial support was provided by Spanish Scientific Research Council. Beatriz Molinuevo Salces reports financial support was provided by European Union. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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