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TWO-PHASE NUTRIENT RECOVERY FROM LIVESTOCK WASTEWATERS COMBINING NOVEL MEMBRANE TECHNOLOGIES

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ABSTRACT

The application of new technologies in the agro-industrial sector is needed to close the loop of the nutrient cycle in the food chain. The aim of this work is to study the feasibility of the combination of two nutrient recovery technologies. In a first step, the novel gas-permeable membrane technology recovers N from the wastewater as an ammonium sulfate solution (a bio-based fertilizer). Secondly, the electrodialytic process recovers P, as an electrolyte solution, from which P can then be precipitated as struvite (a slow-release fertilizer). The process was tested in two different livestock wastewaters: swine manure (SM) and anaerobically digested SM (digestate). Recovery efficiencies for N were 53% for SM and 92% for digestate; for P the efficiencies were 100% and 74% for SM and digestate, respectively. The results showed a great potential of combining these novel membrane technologies in livestock wastewaters, promoting the sustainability of the sector in the realm of the bioeconomy.

KEYWORDS: nitrogen, phosphorus, nutrient recovery, livestock wastewater, gas-permeable membrane, electrodialytic process.

1. INTRODUCTION

The new guidelines within the framework of the circular economy, such as the European Farm to Fork strategy [1], point out the need to apply measures in the agro-food sector to pursue the optimization of the use of fertilizers, to limit losses and improve its sustainability. Innovative strategies for the recovery and reuse of nutrients, particularly nitrogen (N) and phosphorus (P), are decisive for better management and diversification of supply sources, thus ensuring nutrient security [2]. The livestock waste is considered one of the waste streams from which more nutrients can be recovered. Specifically, manure has been commonly applied as organic fertilizer directly on the fields, but this practice is limited by economic and environmental factors, such as water and soil pollution, as well as climatic impacts. To valorize the manure, it is being encouraged its use as the main substrate for anaerobic digestion (AD) in biogas plants, to produce renewable energy and minimize methane emissions [1]. The use of the resultant effluent, the digestate, as organic fertilizer is considered the best option for its recycling [3, 4]. However, the AD process does not recover the nutrients from the manure, therefore their loss during application can also lead to environmental problems in nutrient saturated zones. In this line, new technologies are emerging to maximize the nutrient recovery and increase the nutrient reuse efficiency.

In the case of N recovery from wastewaters, air stripping, thermal vacuum stripping and gas-permeable membrane (GPM) technology appear to be the most viable alternatives, attending to the ammonia (NH_3) recovery efficiencies, the lower operational costs and the recovery of N in the form of ammonium fertilizers [5]. The GPM technology has been successfully applied to recover N from swine manure and digestate, obtaining efficiencies of up to 99% at laboratory scale [6 - 12]. The GPM technology consists of a hydrophobic gas-permeable membrane submerged in a liquid waste through which a trapping solution (commonly diluted H_2SO_4) is recirculated. By diffusion, the NH_3 passes through the micropores of the

hydrophobic membrane and is captured in the trapping solution to form an ammonium salt, which can be used as a fertilizer.

Phosphorus recovery from wastewater, both municipal and agricultural, is commonly carried out by struvite precipitation [13]. Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a fertilizer with the same agronomic quality as the mineral source fertilizer, which can be obtained from P rich wastewater streams by the precipitation of magnesium, ammonium and phosphate [13]. Struvite precipitation has also been applied to manure [2, 10]. However, the management of the ratio of reagents and the optimization of the alkalinity and pH are important limitations to achieving a high purity product in effluents as heterogeneous as manure [14, 15]. Therefore, the application of new technologies to extract phosphate (P- PO_4^{3-}) ions for further precipitation can optimize the recovery in the form of high-quality by-products.

In this regard, a novel membrane separation technology (the electrodialytic (ED) process, followed by a chemical precipitation) has been proved to be effective for recovering P from different organic wastes, such as the anaerobically digested organic fraction of municipal solid waste [16 - 18] or sewage sludge [19]. Some studies have applied electrodialysis for nutrient recovery using synthetic solutions or highly pre-treated livestock wastewaters as substrate [20 – 22]. Although the principle of ED is similar to electrodialysis, the former is an historic evolution of waste treatment while the latter evolves from water treatment processes. The consequence of this difference is that the electrodialysis setup, in stacks, is not suited for water or wastewater with a high content of solids, because the suspended material blocks the membranes and the fluid circulation channels. So, its application to wastewater is limited to very few situations, where the content of suspended solids is very low. The only reported experiment trying to combine electrodialysis and ED is the work by Jensen et al [23], in which an adapted electrodialysis cell was used to treat a suspension of fly ash. The ED process allows the extraction of P from the waste matrix before the chemical precipitation, thus obtaining a solution with a high P concentration (electrolyte solution), free of other substances (high

purity), that can then be precipitated as struvite. In the ED process, the wastewater is placed in a compartment with where an electric current is applied, so the charged ions in solution migrate towards the electrode of opposite charge. In the case of P, as it is mainly present as negatively charged species, it will migrate towards the electrode with the positive charge (the anode), being thus extracted from the wastewater. The application of the ED process for P recovery, using real livestock wastewaters as substrate, i.e. swine manure and digestate, has not yet been studied.

The combination of different solutions for the simultaneous recovery of nutrients would allow more effective and sustainable nutrient recycling practices to be achieved [24]. However, technologies for the recovery of N and P are usually applied separately and the combination of different processes is rarely considered [15]. The aim of this work was to study the viability and the potential of the combination of the GPM technology with the ED process in a sequential way of two-phase N and P novel recovery processes from two different wastewaters: swine manure (SM) and anaerobically digested swine manure (digestate). The first phase consisted of recovering N from SM and digestate using the GPM technology to obtain an ammonium sulphate solution that can be used as a bio-based fertilizer. The second phase consisted of applying the ED process to recover P from the SM and digestate, where the N had been already removed, to obtain an electrolyte solution rich in P, which can be used in further operations for the synthesis of a second bio-based fertilizer, such as struvite.

2. MATERIAL AND METHODS

2.1. Swine manure and digestate

The SM was collected from a farm located in Narros de Cuéllar (Segovia, Spain). The manure was a centrate collected after on-farm centrifugation. The digestate was obtained from an

agricultural anaerobic digestion plant. Both wastewaters were collected in plastic containers and stored in the laboratory at 4 ºC until use. The chemical characterization of SM and digestate is shown in Table 1.

2.2. Nitrogen recovery experiment set up

For the N recovery, the experiments were conducted in batch mode. A non-hermetic plastic vessel was used as the container for 700 mL of wastewater, where the GPM was submerged (Fig. 1). The hydrophobic tubular membrane was made of expanded polytetrafluoroethylene (e-PTFE), (Zeus Industrial Products Inc. Orangeburg, SC, USA) with a length of 50 cm and an outer diameter of 5.2 mm. The GPM had a density of 0.95 g cm^{-3}, a wall thickness of 0.64 mm, a porosity lower than 60% and an average pore size length of 12.7 ± 5.9 μm. The ratio of the membrane surface per wastewater volume was 0.004 m^2 L^{-1}. The content of the vessel was continuously agitated using a magnetic stirrer at 250 rpm. Aeration was incorporated using an air pump (Hailea Aco-2201) and a porous stone placed in the bottom of the vessel. This method has been proven to be effective as a substitute of alkali addition to increase pH in order to enhance the N capture by the membrane [8]. The low aeration rate was 0.24 L air L^{-1} min^{-1}. A trapping solution (150 mL H_2SO_4 1N) was continuously recirculated inside the tubular membrane using a peristaltic pump (Pumpdrive 5001, Heidolph, Schwabach, Germany) at a flow rate of 12 L d^{-1}. Daily samples of the trapping solution and the wastewater (5 mL) were taken to monitor pH and total ammonia nitrogen (TAN) content. The amount of TAN in the samples of the acidic solution was taken into account in the mass balance. Initial samples of the wastewater were analyzed to determine the pH, total alkalinity (TA), total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN), total phosphorus (P_t) and soluble phosphorus (P_s). Daily samples were taken to analyse pH and TAN. The experiments were performed at 22ºC and they were conducted in duplicate.

For each batch experiment, the mass of TAN removed was calculated as the difference between the initial and final mass of TAN in the wastewater. The TAN removal and the TAN recovery efficiencies by the GPM system were calculated according to Eq. (1) and Eq. (2), respectively:

$$TAN\ removal\ (\%) = \frac{(Initial\ mass\ of\ TAN - Final\ mass\ of\ TAN)}{(Initial\ mass\ of\ TAN)} * 100 \quad \text{(Eq. 1)}$$

$$TAN\ recovery\ (\%) = \frac{Final\ mass\ of\ TAN\ in\ the\ trapping\ solution}{mass\ of\ TAN\ removed\ from\ the\ wastewater} * 100 \quad \text{(Eq. 2)}$$

The GPM mass transfer coefficient (K_m; m d^{-1}), was calculated as follows [25]:

$$J = K_m\ (C1 - C2) \quad \text{(Eq. 3)}$$

Where J is the TAN mass flux per area (g m^{-2} d^{-1}), and C1 and C2 correspond to the concentrations of free ammonia in the wastewater vessel and in the trapping solution bottle, respectively.

Free ammonia (FA) was calculated using the equation of Hansen et al. (1998), as un-ionized ammonia (Eq. 4):

$$NH_3/tNH_3 = (1 + (10^{-pH}/10^{-(0.09018 + 2729.92/T)}))^{-1} \quad \text{(Eq. 4)}$$

Where, the pH is the pH measured in the wastewaters, NH_3 was the FA content, tNH_3 is the total NH_3 concentration and T was temperature in Kelvin.

The factors that can affect this mass coefficient are related to the flow rate of the trapping solution and the membrane characteristics (e.g. morphology, porosity, pore size or thickness), [25]

2.3. Phosphorus recovery experiment set up

In a second step, the treated effluents from the N recovery process were used for P recovery through the ED process (Fig. 2). These effluents were placed in a cylindrical Plexiglas

laboratory cell, and assembled with 3 compartments. The central compartment (compartment II) contained a specific volume of effluent and was constantly agitated using an overhead stirrer (LBX OS20 series). An initial volume of 230 mL, agitated at 370 rpm, was used for SM. An initial volume of 180 mL, agitated at 460 rpm, was used for the digestate. Compartments I and III contained 500 mL of 0.01M $NaNO_3$ as electrolyte solution to recover anions and cations, respectively. Electrodes were placed in compartments I and III, in the form of a platinum coated titanium bar with a diameter of 3 mm and a length of 5 cm. Each compartment was separated by an ion exchange membrane (IEM). A cation-exchange membrane (CEM; CR67R, SUEZ GE Water & Process Technology) was used between compartments II and III, and an anion-exchange membrane (AEM; AR204R, SUEZ GE Water & Process Technology) between compartments I and II. Each membrane placed in the cell has an effective surface area of 0.005 m^2. This membrane configuration proved to be effective for delaying changes in the pH of the effluent in compartment II, and also allowed P to migrate to the electrolyte solution [27]. The electrolyte solution was recirculated using a peristaltic pump between the compartment and an external reservoir. A power supply (Hewlett Packard E3612A) was used to maintain a constant current of 50 mA. Daily samples of the effluent and electrolyte solution were taken to monitor pH, conductivity and P_t. Both the voltage and the electric current were also monitored daily. At the end of the ED experiments, the volume of electrolytes and effluent were registered and ion exchange membranes and electrodes were immersed in 1M and 5M HNO_3, respectively, during 48 h to release any P attached to them.

The recovery of P_t from the corresponding effluent was calculated as follows in Eq (5):

$$Pt\ recovery\ (\%) = \frac{Final\ mass\ of\ Pt\ in\ the\ anolyte\ solution}{Initial\ mass\ of\ Pt\ in\ the\ effluent} \quad *100 \qquad \text{(Eq. 5)}$$

2.4. Analytical methods

TS, VS, TAN and TKN determinations were performed according to the APHA methodology [28]. TS content was determined by drying the sample to a constant weight at 103–105 ºC. The TS residue was ignited at 550 ºC 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. TA was calculated by measuring the amount of 0.1 N-H_2SO_4 needed to get the pH of the sample of 4.5, expressed as mg $CaCO_3$ L^{-1}. The chemical determination of P_t and P_s was made according to the vanadomolybdophosphoric acid colorimetric method, at a wavelength of 470 nm (spectrophotometer T80+ SW, PG instruments), after the pretreatment of the samples according to the Danish Committee [29]. A HANNA (Combo) probe was used to monitor pH and conductivity.

3. RESULTS

3.1. Nutrient recovery from swine manure

3.1.1. Nitrogen recovery from swine manure

In the first set of experiments, nutrient recovery from SM was tested. In this phase, the TAN concentration in the SM decreased from an initial concentration of 3900 mg N L^{-1} to 1550 ± 102 mg N L^{-1} (Fig. 3a). The initial volume of SM was 700 mL, as mentioned in section 2.2, but it decreased to a final value of 528 ± 0.1 mL due to water evaporation. The mass of TAN removed was 1912 mg N and the TAN removal efficiency was for 70%. The TAN concentration in the trapping solution achieved a value of 7024 ± 92 mg N L^{-1} on day 13 (Fig. 3a). During the experiment, the volume of the trapping solution decreased from an initial value of 150 mL to a final value of 120 mL due to water evaporation. The total mass of TAN recovered in the trapping solution was 1004 mg N (i.e., 843 mg of N in the acidic solution and 161 of sampling), therefore the TAN removal rates accounted for 147.1 mg N d^{-1}. This

recovered N accounted for 53% of the mass of TAN removed during the experiment. The loss of TAN by the system due to volatilization was 47%.

It was calculated the mass transfer coefficient (K_m) using Eq. 3, resulting in a value of 2.69 x 10^{-4} m s^{-1}.

3.1.2. Phosphorus recovery from swine manure

The initial concentration of P_t in the SM was 1000 ± 135 mg L^{-1} and it decreased to a final value of 70 ± 2 mg L^{-1} (Fig. 3b). The initial pH value was 7.6 and the final value was 5.2. In this experiment, the voltage increased systematically after day 2, reaching the maximum allowed by the equipment around day 4, after which the experiment was halted because it was no longer possible to maintain the current at the reference value (50 mA). At this point, the electrical conductivity of SM was low (0.14 mS cm^{-1}), indicating that there were no more ions available for electromigration. No P_t was detected in the cathode compartment (compartment III) and the P_t mostly moved across the anion-exchange membrane into the anode compartment (compartment I), meaning that P_t is mainly present as a negatively charged compound. Initially, there were 230 ± 31 mg of P_t in the SM, and that amount decreased to 10 ± 0.25 mg at the end of the experiment. The final mass of P_t in the anolyte solution was 251 ± 2 mg, and the mass balance at the end of the experiment calculated in the anolyte was of 105%. Therefore, all the P_t present in the SM migrated through the membrane to the anolyte solution, and the recovery efficiency was 100%.

3.2. Nutrient recovery from digestate

3.2.1. Nitrogen recovery from digestate

In the second set of experiments, nutrient recovery from digestate was tested. The initial TAN concentration in digestate was 3319 ± 48 mg N L^{-1} and it decreased to a value of 214 ± 1 mg N L^{-1} on day 8 (Fig. 4a). The initial volume of digestate was 700 mL, but it decreased to a

final value of 543 ± 0.1 mL due to water evaporation. Taking this into account, the TAN removed was 2197 mg N, which means a removal efficiency of 95%. The TAN concentration in the trapping solution achieved a value of 9383 ± 435 mg N L^{-1}. There was no water evaporation in the acidic bottle in this case. The amount of TAN recovered was 2028 mg N (i.e., 1667 mg N content in the acidic solution and 361 mg N contained in the 5 mL samples taken each day), which shows a TAN recovery rate of 275.9 mg N d^{-1} in the digestate. A TAN recovery efficiency of 92% was achieved. The loss of TAN by the system due to volatilization was 1% in this case.

In this case, the mass transfer coefficient (K_m) presented a value of 2.16 x 10^{-3} m s^{-1}.

3.2.2. Phosphorus recovery from digestate

The P recovery in digestate was performed for 7 days. The initial concentration of P_t in the digestate was 1323 ± 208 mg L^{-1} and it decreased to a concentration of 50 ± 13 mg L^{-1} on day 7 (Fig. 4b). The pH values at the beginning and end of the experiment were 8.7 and 6.4, respectively.

The mass of P_t in digestate was 238 ± 37 mg at the beginning of the experiment, decreasing to 11 ± 3 mg at the end. The mass of P_t in the anolyte solution at the end of the experiment was 177 ± 3 mg, so a recovery efficiency of 74% was achieved.

4. DISCUSSION

4.1. Performance of the two-phase nutrient recovery technology

For the N recovery experiments, the TAN recovery rates, expressed in terms of mass of TAN recovered per membrane area and day, were 8.0 g N m^{-2} d^{-1} for the SM and 25.7 g N m^{-2} d^{-1} for the digestate. This value for the SM is similar to that found by García-González et al. [8],

who reported a TAN recovery rate of 9.5 g N m^{-2} d^{-1} when applying the GPM technology for N recovery from raw SM in batch mode.

For the digestate, the obtained TAN recovery rate is in the range of 22.7-30.7 g N m^{-2} d^{-1} found by Dube et al. [30], when they used GPM technology to recover N from anaerobically digested swine manure in batch mode.

The pH is the most determinant factor for N recovery using GPM technology [5, 8]. The pH values for each experiment of N recovery can be seen in Figure 5. The average pH values in the first 8 days of experiment are 8.4 ± 1.5 for SM and 8.4 ± 0.2, therefore a similar N recovery would be expected. The low N recovery in the swine manure compared with the digestate could be explained due to a deficient agitation. A constant stirring of the feed has been reported as important factor for the membrane to capture the available ammonia [31]. Therefore, a higher concentration of ammonia available in the SM, but without being able to be captured by the membranes could explain the differences between the two recovery rates. To minimize the losses of N in form of NH_3 in the N recovery phase of the experiment with digestate, different measures were taken. These measures were: the use of a new cover for the plastic vessel, (not hermetic but capable of reducing the air outlet to a minimum), and a monitoring for constant and uniform agitation. The pH monitorization showed that these measures were enough to prevent high volatilization during the N recovery.

In the case of the P recovery, the rates in terms of mass of P_t per area of membrane and day were 12.5 g P_t m^{-2} d^{-1} for the SM and 4.4 g P_t m^{-2} d^{-1} for the digestate. This difference could be attributed to the different chemical forms of P in both wastewaters. Specifically, the SM initially presented 34% more of P_s than the digestate (Table 1), which made the extraction of the P easier for the SM during the process. P recovery from the digestate could be improved by lowering the pH in the last few days of the experiment to solubilize the P molecules [16]. The high recovery efficiencies obtained of P in the SM and digestate in 4 and 7 days

respectively, is in line with previous studies [19, 32] and suggest the great potential that the ED process has for P recovery from livestock wastewater.

Regarding the by-products obtained, the liquid ammonium solution obtained with the application of the GPM technology presented a final N concentration 1.8 times higher than SM and 2.8 times higher than digestate. The electrolyte solution obtained from the ED process achieved Pt concentrations 1.6 times higher than the SM and 1.2 times higher than the digestate. In addition to being more concentrated in N and P than the initial wastewaters, the solutions contain only the target nutrients, in soluble form and with low level of impurities, therefore are ready to be transformed into fertilizers. Hence, by combining the proposed technologies, it was possible to recover two main macronutrients in two separate fractions that can be used independently or together, providing versatility to different applications. Obtaining these solutions separately can help in the planning of a more efficient use of nutrient sources for fertilization applications, avoiding the excess of nutrients and their losses in the environment, therefore avoiding the related environmental problems.

This study has suggested the possibility of interesting advantages of the combination of the GPM and ED processes compared to the application of the single ED process. The application of GPM technology in the first step removed of NH_4^+ from solution, reducing the number of soluble ions present. Because of this, the second step is improved, being faster and more energy efficient since less energy is wasted in the transport of ions other than PO_4^{3-}, [27]. In addition, if NH_4^+ is not removed, changes in pH taking place in the second step might lead to the unwanted precipitation of magnesium ammonium phosphate, which would reduce the recovery rates of P. The conditions used in the work thus favor the subsequent extraction of P_t using the ED process, both in time as well as in efficiency. This represents a significant improvement from an economic and energy point of view, since the membrane will be less

time in contact with the wastewater, minimizing the fouling risk and, at the same time, greatly reducing the amount of energy used in the ED process. This work being just a proof of concept, further research is needed in this line to explore this advantage and to improve nutrient recovery efficiency.

4.2. Comparison with other technologies

In this section, the performance of the GPM technology and the ED process are compared with other N and P recovery technologies. As the GPM and the ED are physic-chemical technologies, for questions of consistency, only physic-chemical technologies were considered, thus excluding biological treatments. Tables 2 and 3 present a summary of the N and P recovery technologies, respectively. For the comparison of the operational cost (energy and chemicals), the calculations took the economic studies conducted on the corresponding sources as the basis.

Regarding the N recovery, air stripping, ion exchange and adsorption and struvite precipitation are the most known technologies for N recovery from livestock wastewaters (Table 2). In the case of air stripping, this technique can present high operational costs due to the high requirements of chemicals and energy, as well as the high pH values, gas pressurization and temperature needed in the process [31, 33]. Liao et al. [34] reported a removal efficiency of 90% at a constant temperature of 22ºC and a pH of 11.2 with constant aeration (Table 2). However, to increase the pH of the manure to near 12, large amounts of lime (2 g L^{-1} manure) were needed, which may increase the costs, with the added risk of calcium carbonate formation. On larger scales (pilot plants), these operational costs, especially the energy costs, can increase significantly [35]. In the case of the ion exchange/adsorption technology, despite the high recovery rates, the manure may need to be pre-treated [36], while the addition of

chemicals is needed (zeolites), in contrast to the GPM technology. There is also a risk of interference from different ions (K^+) and the suspended solids present in livestock wastewaters, which could affect the recovery efficiencies, as reported by Milan et al. [37]. In the case of struvite precipitation, the removal rates are lower compared to the other technologies (Table 2), though it is more commonly used for P recovery than for N recovery [36]. The addition of chemicals (Mg_2^+, PO_4^{3-} and alkalis) for pH adjustment would increase the operational costs, since their amount is highly dependent on the type of wastewater and the molar ratio of the reagents [5]. In comparison with the mentioned technologies, the GPM technology presents high recovery rates with low operational costs (Table 2). It requires low energy [5] and the use of alkalis for pH increment can be substituted by aeration [9, 11, 12, 307, 8, 23]. In addition, there is no need for a pre-treatment of the wastewaters [8]. It can be integrated with anaerobic digestion to enhance the biogas production, while recovering N in the process [33, 34]. For this study, based on the studies of Riaño et al. [12] and Molinuevo et al. [38], and considering the TAN initial concentration ant the recovery results obtained for each wastewater, the costs would be of 3.07 € per kg of N for SM and 3.85 € per kg of N for digestate (Table 2). The major disadvantage of the GPM technology is related to the total capital investment and the cost of the membranes. In any case, Beckinghausen et al. [40] evaluated the different N recovery techniques from wastewaters, determining that the GPM technology has the higher total benefit (284 $ per tonne of ammonium sulfate produced). Additionally, Munasinghe-Arachchige and Nirmalakhandant, [31] estimated the profit for N recovery of the GPM technology compared to air stripping, ion exchange and struvite precipitation, with the result that the GPM technology presented the highest profit. The growing interest in wastewater treatment and nutrient recovery and reuse, the it is expected that investments for larger scale installations would also grow.

For P recovery, such technologies as struvite precipitation and ion exchange and adsorption have been successfully proven (Table 3). In the case of struvite precipitation, the economic balance strongly depends on the type of wastewater and its P concentration, the molar ratios of the chemicals used for precipitation, and the use or not of alkali for precipitation [41]. While the recovery rates on a laboratory scale can be very high, the efficiency of the technology applied on a pilot scale varied (Table 3). For example, Dewaele [42] reported a recovery efficiency of 100% and the securing of struvite with a higher commercialization purity. However, Saerens et al. [43] obtained lower recovery rates (up to 15%) and the recovered struvite with enough quality for P reuse was only 5% (Table 3). With very different results on P recovery rates, the use of chemicals and the operating conditions of each work will be determinant for the economic feasibility of this technology. In the case of adsorption and ion exchange, these technologies present high P recovery efficiencies and a high quality of P, and they do not need chemicals to be added for pH adjustment [14]. Bottini and Rizzo [44] reported an operational cost of 8.3 € per kg of P recovered, only considering the chemical costs (Table 3). For the treatment of effluent from a wastewater treatment plant (WWTP) using ion exchange technology at a pilot plant, Liberti et al. [45] reported a P removal of 60%, using a combination with struvite at pilot plant scale (REM NUT technology) with an operational cost of 366,900 € per year for the recovery of approximately 285 tonnes of struvite; while the high costs of resins and other chemicals were highlighted. In addition, they have the limitation of reaching the saturation of the adsorbent medium and the selectivity is limited, [14].

For the ED process, an important part of the process cost depends on the current density applied, since it directly affects the energy costs [46]. Zhang et al. [47] reported a consumption of 1 kWh electricity to extract 60 g of phosphate. The cost of chemicals in that case would account for 21 € per kg of struvite obtained being reported [27]. This process presents the lowest operational costs of the reviewed options (Table 2), and for P recovery can be

completed with the precipitation of struvite, in such a way that a precipitate of great purity is obtained [17]. In this study, based on the study of Zhang et al. [47] and considering the initial P_t concentration and the recovery results obtained for each wastewater, the costs would be of 3.3 € per kg of P for SM and 4.2 € per kg of P for digestate.

In view of the results, the costs of the recovered nutrients need to decrease to approach the prices of mineral fertilizers (0.76 € per kg for monoammonium phosphate and 0.42 € per kg for urea ammonium phosphate [48]). The operational costs and the investment for the novel nutrient recovery technologies are still high, since these technologies are in the early stages of application. Nevertheless, the nutrient recovery technologies provide a source of renewable fertilizers, diminishing the dependence on external mineral sources, which can improve national and global food security, while also contributing to closing the loops in the biological cycles [49]. It also worth mentioning that, in the agriculture and wastewaters sector, the production of competitive bio-based fertilizers presents important economic barriers that need to be addressed, as the chemical fertilizer price does not consider many externalities, while these are indeed considered for recovered by-product pricing [24]. Therefore, the by-products have to compete with cheap fertilizers, where the costs and environmental impacts of production are not taken into account [24].

5. CONCLUSIONS

The results showed a great potential for this two-phase membrane technology configuration. The GPM technology applied in the first step achieved TAN recovery rates of 8.0 g N m^{-2} d^{-1} for the SM, and 25.7 g N m^{-2} d^{-1} for the digestate, which correspond to recovery efficiencies of 53% and 94% for SM and digestate, respectively. The ED process, applied in a second step, achieved rates of 12.5 g P_t m^{-2} d^{-1} for the SM and 4.4 g P m^{-2} d^{-1} for the digestate, which implies a P recovery of 100% and 74% for SM and digestate, respectively, in a short period

of time. The processes also delivered two different valuable bio-based marketable fertilizers: ammonium sulfate solution and P rich solution. Therefore, the combination of the GPM and ED technologies can be considered a compelling methodology for a more effective and sustainable nutrient management.

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Conflict of Interest Statement:

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Tables

Table 1. Chemical characterization of swine manure (SM) and digestate used in the present study. Data are means of two replicates, standard deviation is shown in brackets.

	SM	Digestate
pH	7.58 (0.04)	8.19 (0.02)
Conductivity (mS cm^{-1})	30	28
Ca+	1617 (76)	5119 (309)
K+	4294 (942)	5926 (804)
Mg+	960 (21)	1626 (23)
TA (mg $CaCO_3$ L^{-1})	20035	22014
TKN (mg N L^{-1})	5842 (117)	4721 (43)
TAN (mg N L^{-1})	3900 (301)	3319 (48)
TS (g L^{-1})	56.5 (5.3)	87.6 (3.5)
VS (g L^{-1})	42.5 (4.3)	55.6 (7.9)
Pt (mg L^{-1})	1000 (135)	1323 (208)
Ps (mg L^{-1})	170.5 (8.2)	126.6 (1.5)

Table 2. Comparison of the GPM technology with other technologies for N recovery.

Technology	Type of wastewater	Scale	TAN concentration (mg N L^{-1})	N removal (%)	N recovery (%)	Operational costs (€ per kg of N recovered)	Source
Air stripping	Swine manure	Lab.	2192	90	91	1.8 [a]	Liao et al. [34]
	Anaerobically digested swine manure	Pilot-plant	2500	50	100	33.3 [b]	Baldi et al. [35]
Ion exchange and adsorption (zeolites)	Anaerobically digested swine manure	Lab.	600	91	100	8.8 [a]	Milan et al. [37]
	Digestate of sludge (WWTP*)	Pilot plant	1500	94	100	5.5 [a]	Lubensky and Ellersdorfer [50]
Struvite precipitation	Swine manure	Lab.	2110	80	100	6.6 [a]	Romero-Güiza et al. [4]
	Swine manure	Pilot plant	2010	75	100	7.5 [b]	Astals et al. [51]
GPM technology	Swine manure	Pilot-plant	2774	90	62	3.1 [b]	Molinuevo- Salces et al. [52]
	Anaerobically digested swine manure	Pilot-plant	2980	57	58	3.9[b]	Riaño et al., 2021 [12]
	Swine manure	Lab.	3900	70	53	6.2	This study
	Anaerobically digested swine manure	Lab.	3319	93	94	3.5	This study

[a]Calculations based on of Zarebska et al. (2015)
[b]Calculations based on the economic study of the source
*Wastewater treatment plant

Table 3. Comparison of the ED process with other technologies for P recovery.

Technology	Type of waste water	Scale	Pt concentration (mg P L^{-1})	Pt removal (%)	Pt recovery (%)	Operational costs (€ kg of P recovered[1])	Source
Struvite precipitation	Digestate + centrate of WWTP	Pilot plant	1200	83	100	5.3 [b]	Dewaele [42]
	Digested sludge	Pilot plant	250	70	15	15.9 [b]	Saerens et al. [43]
Ion exchange	Sludge from WWTP	Lab.	472	95	100	8.3 [b] (only chemical costs)	Bottini and Rizzo [44]
	Sludge from WWTP (	Pilot plant	n.f.	60	100	9.4 [b]	Liberti et al. (45)
ED process	Digestate sludge	Lab.	2030	95	93	3.6 [b]	Zhang et al. [47]
	Swine manure	Lab.	1000	100	100	3.3	This study
	Anaerobically digested swine manure	Lab.	1323	74	100	4.5	This study

[b]Calculations based on the economic study of the source
*Waste water treatment plant
n. f. = not found

Figures

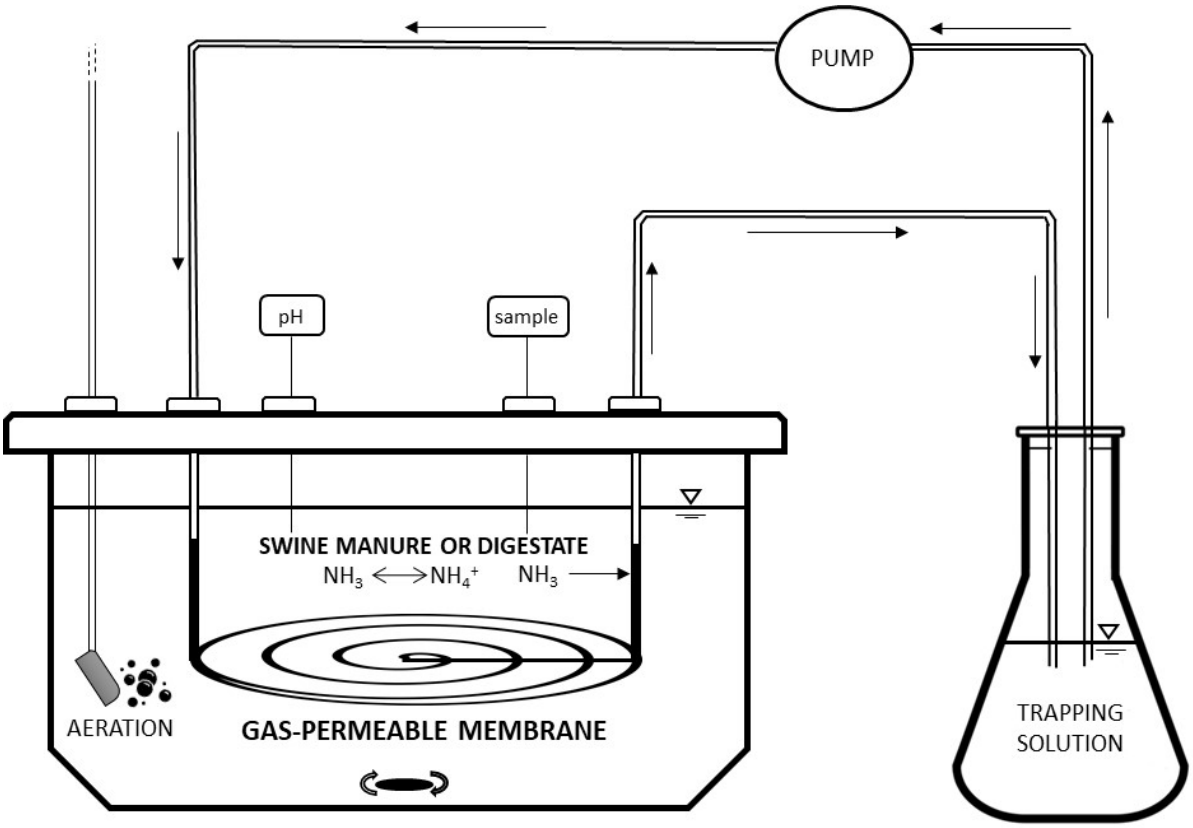

Figure 1. Experimental set up for N recovery.

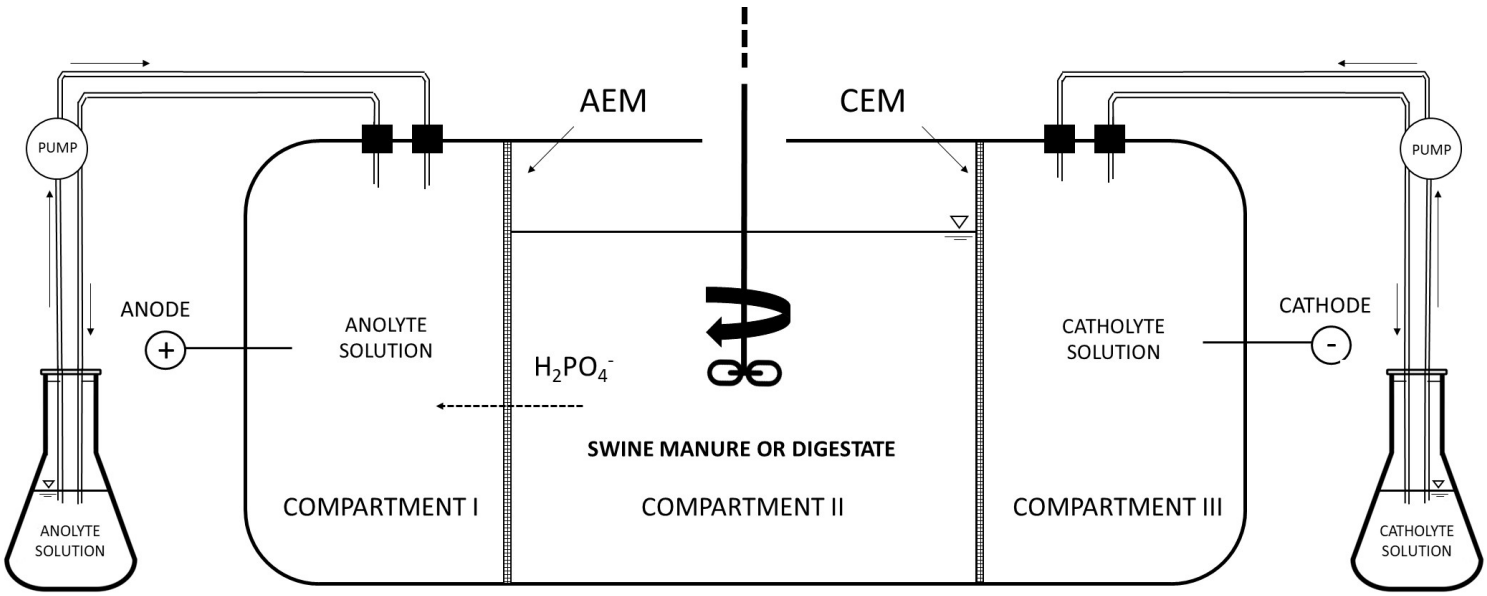

Figure 2. Experimental set up for P extraction (AEM – anion exchange membrane; CEM – cation exchange membrane).

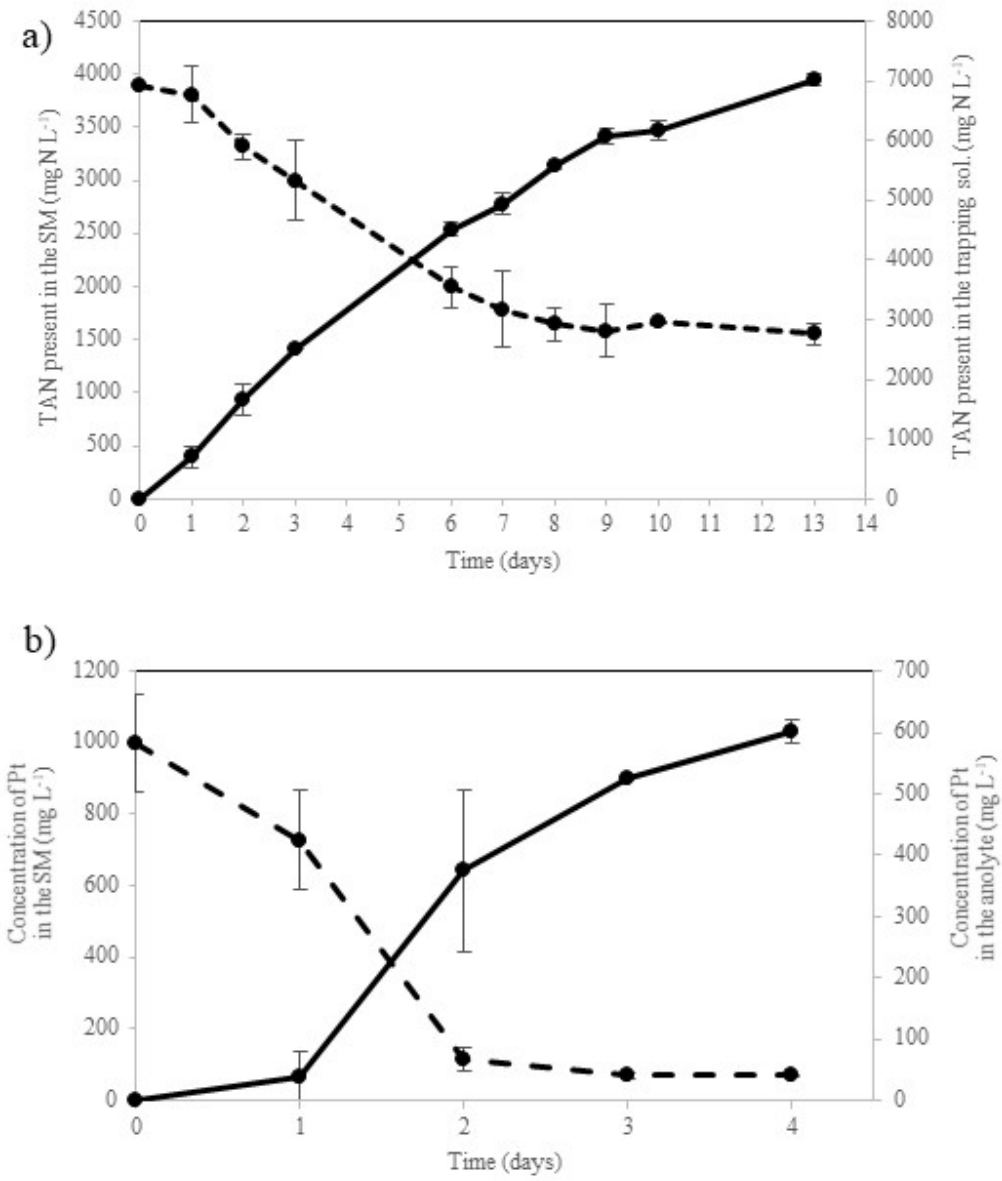

Figure 3. a) Concentration of TAN in the SM (discontinuous line) and in the trapping solution (continuous line) during the experiment for N recovery.

b) Concentration of P_t in the SM (discontinuous line) and in the anolyte (continuous line) during the experiment for P recovery.

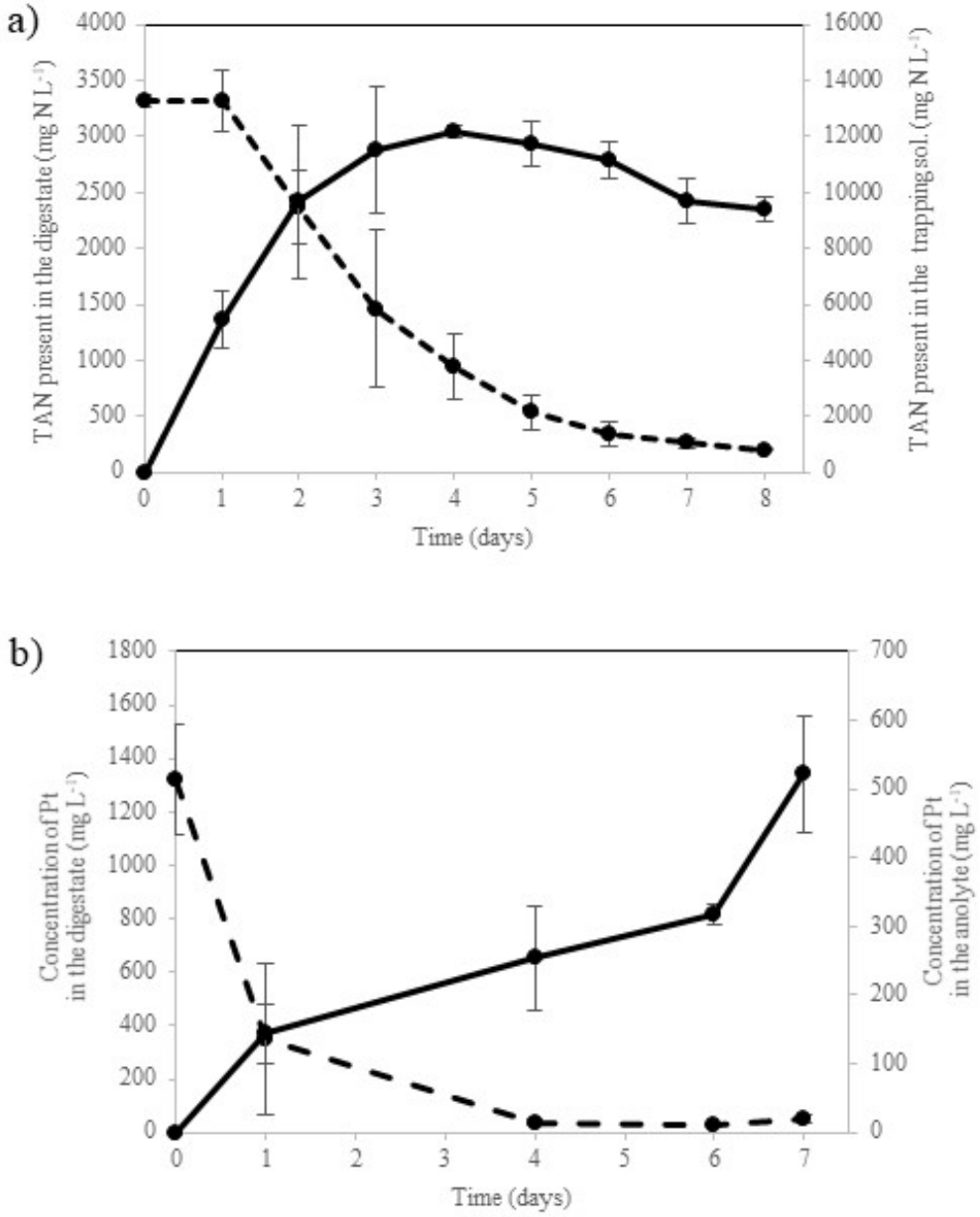

Figure 4. a) Concentration of TAN in digestate (discontinuous line) and in the trapping solution (continuous line) during the experiment for N recovery. b) Concentration of P_t in the digestate (discontinuous line) and in the anolyte (continuous line), during the experiment for P recovery.

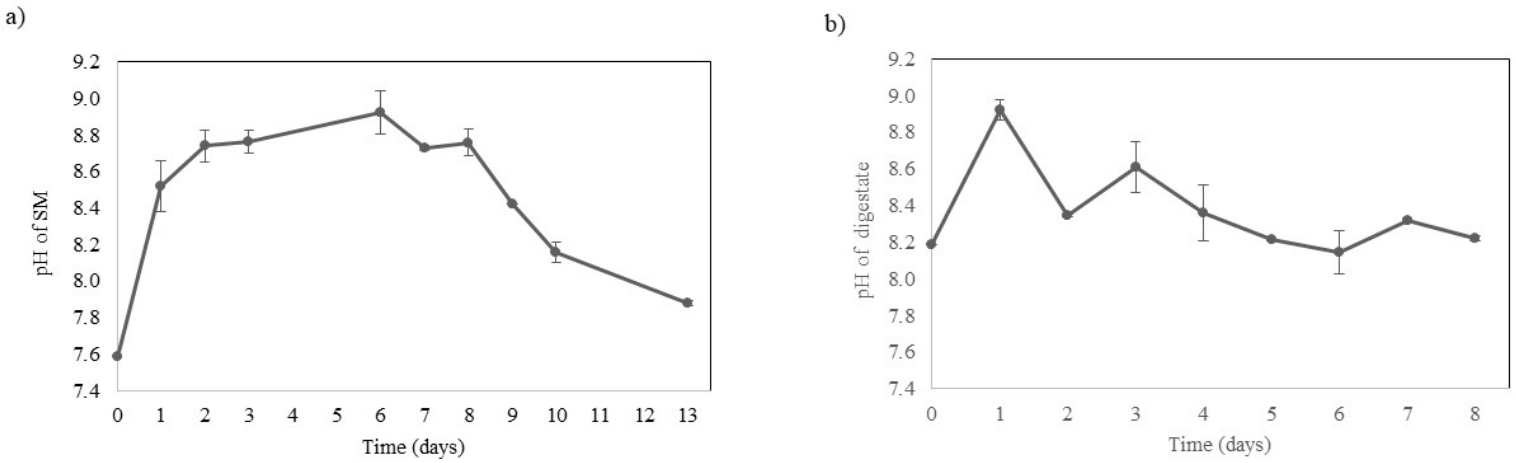

Figure 5. Evolution of the pH of the SM (a) and the digestate (b) during the N recovery experiments