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Effect of Alkali and Membrane Area on the Simultaneous Recovery of Nitrogen and Phosphorous from Digestate by Membrane Technology and Chemical Precipitation

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Abstract: Nutrient recovery from the agri-food sector waste is an increasingly recognized option within the framework of the bioeconomy. Membrane technologies and chemical precipitation are among the best valued options for their economic and practical feasibility. In this study, the combination of gas-permeable membrane (GPM) technology for the recovery of nitrogen (N) and the chemical precipitation for phosphorous (P) recovery from anaerobically digested swine manure is evaluated. This work studies the effect of the membrane area and the addition of alkali on N and P recovery efficiencies. Specifically, two different membrane area ratios (180 and 100 g of N per m^2 of membrane) with and without the addition of alkali were studied. High nutrient recovery efficiencies, of 77% for N and 80% for P, were obtained after 10 days of experiment with a ratio of 180 g N per m^2 of GPM and the addition of NaOH (1.5 N), along with the precipitant agent ($MgCl_2$) for P precipitation. Hence, a combined configuration was proposed to perform an effective simultaneous recovery of N and P with the minimum amount of membrane needed in a short time.

Keywords: waste valorization; ammonia; phosphate; gas-permeable membrane; circular economy

1. Introduction

Nutrient recovery and reuse from the main waste streams are at the core of the international sustainability strategies [1]. The objectives are to reduce the dependence on fossil-based fertilizers and the environmental and economic problems derived from waste mismanagement, while also closing the nutrient cycles [2–4]. Livestock waste provides over 70% of the total N and P when used as organic fertilizer (manure) [3]. However, manure must be managed properly to avoid environmental impacts, such as particulate matter formation, acidic rain, and eutrophication, due to emissions into the air, soil, and water bodies of ammonia (NH_3), methane (CH_4), nitrous oxide (N_2O) nitrates, and nitrites (NO_3^- NO_2^-) [4]. The stabilization of manure is also an important factor when using it as an organic fertilizer. The anaerobic digestion (AD) is a well-known process and widely used manure management system, which has proved useful to reduce greenhouse emissions [5]. Manure treatment with the AD process results in biogas (renewable energy) and digestate production, which is a more stable substance than manure, which can be used as organic fertilizer and contains the same amount of original nutrients as the manure, since anaerobic digestion does not remove them [3,6]. Thus, the application of digestate may also cause environmental issues due to nutrient losses when it is not properly managed, such as an excess of N and P in soils and water bodies, resulting in eutrophication, decreased biodiversity, and toxicity [3]. Therefore, it is important to consider the application of innovative treatment technologies for the recovery of nutrients from the digestate. This

would allow the environmental impacts to be minimized and the recovered nutrients to be stored, transported, and applied more easily where needed.

According to Buckwell and Nadeu [3], the average production of digestate in the EU 27 is 56 million tons annually, 80% of which is used for agriculture as organic fertilizer. Therefore, the digestate is a nutrient-rich by-product and is also currently the largest output product obtained from manure treatment. Interest in the application of innovative technologies to reduce the environmental impacts of poor manure management is increasing, alongside economic investments to optimize nutrient recovery.

Among the most known technologies for N recovery from digestate, such as air stripping, ion exchange or chemical precipitation, the novel gas-permeable membrane (GPM) technology has recently been recognized as one of the most effective technologies from an energetic, economic, and environmental perspective [7–9]. On the basis of literature reviews that considered such relevant factors as recovery performance, operating conditions, and energy and chemical demand, the GPM technology stood out due to its high capacity for N recovery, its low energy requirement, and no need of post-treatment. In this sense, it has been reported that the GPM technology presented a recovery efficiency of over 98%, and an energy cost within a range of 0.17 to 1.2 kWh per kg of N recovered and a chemical cost of 1.41$ per kg of N recovered [7–9]. In addition, Beckinghausen [7] compared the operations costs of N recovery (energy and chemicals) using different N recovery technologies, with the potential sales revenue of the obtained product. They found that the GPM technology presented a total benefit of 284.45$ per ton of ammonium salt produced. The GPM technology consists of a hollow tubular microporous hydrophobic gas-permeable membrane submerged in ammonia (NH_3)-rich wastewaters, while an acidic trapping solution is recirculating inside the membrane. The NH_3 passes through the membrane by diffusion and is captured by the acidic trapping solution, which becomes an ammonium salt solution, a valuable bio-based organic fertilizer [10].

The digestate has a higher concentration of ammonium than swine manure [6,11], since organic nitrogen is transformed into ammonium during the AD process. This makes it an interesting candidate as a substrate for applying the GPM technology, which has shown high N recovery efficiencies (over 98% of the N removed from the substrate) in raw and anaerobically digested swine manure [12–14]. An important aspect of the GPM technology is that it can be combined with other nutrient recovery technologies, especially P recovery technologies. In this context, although the combination of nutrient recovery technologies could lead to a greater competitiveness of the systems [15], only a few studies have considered this aspect. Oliveira et al. [16] combined the GPM technology with ion-exchange membranes for the simultaneous recovery of N and P (as total P) from anaerobically digested swine manure, obtaining recovery rates of 19 g N m^{-2} of GPM day^{-1} and 6.3 g P m^{-2} of anion exchange membrane day^{-1}. González-García et al. [17] evaluated the combination of GPM with ion-exchange membranes to recover N and P in a two-step system, obtaining recovery efficiencies of 25.7 g N m^{-2} GPM day^{-1} and 4.4 g P m^{-2} of ion exchange membrane day^{-1} from anaerobically digested swine manure. Vanotti et al. [18] also applied the GPM technology to recover N and P from anaerobically digested swine manure. These authors reported recovery rates of up to 16.7 g N m^{-2} of GPM day^{-1} with a nitrification inhibitor, but without the addition of alkali, and up to 18.1 g N m^{-2} of GPM day^{-1} and 0.5 g precipitated P day^{-1}, with the addition of a nitrification inhibitor and alkali (NaOH). This work showed that, after the N recovery, the resultant substrate presented a high pH, a low concentration of NH_4^+ and a low alkalinity, which are favorable conditions for P precipitation by applying a metal salt [18–20]. In the case of Vanotti et al. [18], they focused on how the application of the GPM technology can influence the type of magnesium phosphate obtained via precipitation. This study considered that premise, of using GPM technology to recover N and chemical precipitation to recover P as magnesium phosphates using $MgCl_2$; however, it also considered other factors affecting nutrient recovery. In particular, the N removal from the digestate and its recovery in the trapping solution creates advantageous conditions for obtaining high

recovery rates of precipitated P as magnesium phosphates [18]. Following this postulation, the aim of the present work was to study the simultaneous recovery of N and P from anaerobically digested swine manure, using the GPM technology for N recovery and the application of a precipitating agent for the recovery of P. To do so, two factors were evaluated: the influence of the membrane area in contact with the digestate for nutrient recovery, and the addition of NaOH as the alkali to act as the pH control agent together with the precipitating agent. The results offer an insight into what could be the best configuration for the combination of these two nutrient recovery techniques.

2. Materials and Methods

2.1. Experimental Set-Up and Operations

Two different sets of experiments were carried out: Set 1 and Set 2 (Table 1).

Table 1. Experimental configurations for N and P recovery.

Experimental Sets		Ratio (g TAN: m^2 of Membrane)	Alkali Addition (NaOH 1.5N)	Nutrient Recovery Configuration Name
Set 1	Experiment 1	180:1	-	N1
				P1
	Experiment 2	180:1	37.5 mL	N2
				P2
Set 2	Experiment 3	100:1	-	N3
				P3
	Experiment 4	100:1	32 mL	N4
				P4

Two plastic vessels' reactors, not hermetically sealed, were used in both sets, with an effective volume of 1.5 L of digestate.

The same precipitating agent was added to both sets of experiments: $MgCl_2$ (as $MgCl_2 \cdot 6H_2O$, Panreac). To calculate the necessary amount of $MgCl_2$, the initial concentration of the total P in the digestate (0.473 g P L^{-1}) was considered in order to obtain a molar ratio of Mg:P of 1.2:1. As a result, 0.551 g of $MgCl_2 \cdot 6H_2O$ was added at the beginning of the experiments. Therefore, the P precipitated at the same time as the N recovery was carried out by the GPM technology.

In Set 1, the nutrient recovery efficiency, with a membrane ratio of 180 g total ammonia nitrogen (TAN) per m^2 of membrane, both without the addition of alkali (Exp. 1) and with the addition of alkali (NaOH 1.5N) at the beginning of the experiment (Exp. 2), was studied.

In Set 2, the nutrient recovery efficiency with a membrane ratio of 100 g of TAN per m^2 of membrane, both without the addition of alkali (Exp. 3) and with the addition of alkali at the beginning of the experiment (Exp. 4), was evaluated (Table 1). The 180 g TAN:m^2 membrane ratio was selected based on the previous work of Vanotti et al. [18] as reference. The 100 g TAN:m^2 membrane ratio was selected as a new configuration, with a higher membrane area, in order to study the effect of this factor on the N capture. The optimal pH value considered for the N recovery was 9.2 [18]. To reach this pH value, 37.5 mL of NaOH 1.5 N were added to the digestate in Exp. 2 and 31.0 mL of NaOH 1.5 N in Exp. 4.

2.2. Origin of the Digestate

The digestate was obtained from a biogas plant located in Juzbado (Salamanca, Spain). This biogas plant was designed to treat mainly raw livestock waste from nearby farms, as well as agricultural waste from the area, such as cereal dust, harvest remains, etc. These residues are transported to the plant, stored, and then enclosed in an airtight concrete

tank—or digester—which, in the absence of oxygen and through a process of anaerobic digestion, transforms these wastes into biogas and digestate. The plant works in the mesophilic range (35 °C) and with an average hydraulic retention time of 75 ± 5 days, producing approximately 6000 m^3 of digestate per year [14]. The digestate from the plant was collected and stored in a plastic container in the ITACyL laboratory at 4 °C for later use. The chemical characterization of the digestate is presented in Table 2.

2.3. Nutrient Recovery Process

The recovery process of N and P occurred simultaneously inside the reactors that contained the digestate. The chemical reagents were added at the beginning of the experiment, for P precipitation and pH control (when applicable). Each nutrient recovery process is described in detail in the following sections.

2.3.1. Nitrogen Recovery Process

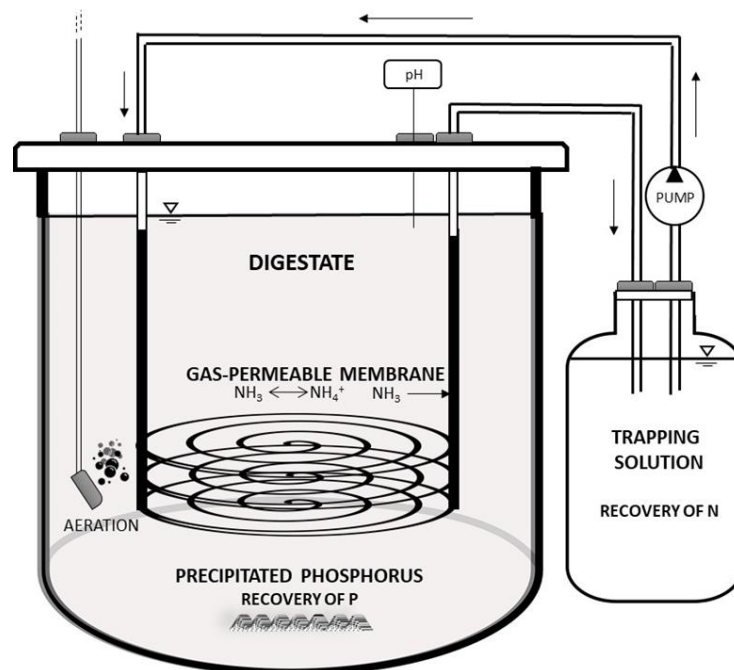The GPM was completely submerged in the digestate (Figure 1).

Figure 1. Experimental set up for simultaneous recovery of N and P. Design based on Vanotti and Szogi [10].

The experimental design was intended for optimal membrane performance. The membrane used was *Aeos™ ePTFE porous tubing*. This tubular membrane was made of expanded polytetrafluoroethylene (e-PTFE), (Zeus Industrial Products Inc., Orangeburg, SC, USA), with a diameter of 5.2 mm, a wall thickness of 0.56 mm and a density of 0.95 g cm^{-3}. In the first set of experiments (Set 1), the length of the membrane was 1.6 m and the membrane surface area to the volume of the digestate was 0.0175 m^2 L^{-1}. In the second set of experiments (Set 2), the length of the membrane was 3 m and the membrane surface area to the volume of the digestate was 0.0314 m^2 L^{-1}. A peristaltic pump (Pumpdrive 5001, Heidolph, Schwabach, Germany) was used to continuously recirculate the trapping solution through the membrane at a flow rate of 12 L d^{-1}. A magnetic stirrer was placed at the bottom of the vessel to ensure the homogenization of the digestate. The N recovery tank consisted of a glass bottle containing 250 mL of trapping solution (H$_2$SO$_4$ 1 N). The pH of the trapping solution was monitored on a daily basis and, whenever the pH reached 2, concentrated H$_2$SO$_4$ (96–98%, Panreac) was added to an endpoint of pH < 2 to ensure an efficient N capture. As pH is the determining factor for free ammonia (FA) availability,

it is therefore crucial for the N recovery. To ensure FA availability in the digestate, a low aeration was applied to maintain high pH values [13]. Aeration was applied in both sets of experiments using an air pump with a porous stone placed in the bottom of the reactor (Hailea Aco-2201), and an aeration rate of 0.36 L air L^{-1} min^{-1} controlled with a rotameter (Aalborg, Orangeburg, NY, USA). To ensure the previously mentioned optimal pH value (9.2), the alkali was added at the beginning of the experiments. All the experiments were carried out at room temperature (20 °C). Daily samples of the digestate and the trapping solution were taken to monitor pH and TAN content. Furthermore, samples were taken at the beginning and end of the experiments to analyze the content of P, TA, TS, VS, TKN, Mg, Ca, and K.

In each set of experiments, the TAN removal, the TAN recovery efficiency, and the average TAN recovery rate by the GPM system in the digestate were calculated according to Equations (1)–(3) as follows:

$$\text{TAN removal (\%)} = \frac{(\text{Initial mass of TAN} - \text{Final mass of TAN})}{(\text{Initial mass of TAN})} \times 100 \tag{1}$$

$$\text{TAN recovery efficiency (\%)} = \frac{\text{Final mass of TAN in the trapping solution}}{\text{mass of TAN removed from the digestate}} \times 100 \tag{2}$$

$$\text{Average TAN recovery} \left(\text{g N m}^{-2}\ \text{day}^{-1}\right) = \frac{\begin{array}{c}\text{mass of TAN recovered}\\ \text{in the trapping solution}\end{array}}{\begin{array}{c}\text{m}^2\ \text{of membrane and}\\ \text{days of experiment}\end{array}} \times 100 \tag{3}$$

Free ammonia (FA) was calculated using the equation of Hansen et al. [21], as un-ionized ammonia Equation (4):

$$\frac{\text{NH}_3}{\text{tNH}_3} = \left(1 + \left(10^{-\text{pH}}/10^{-(0.09018+2729.92/\text{T})}\right)\right)^{-1} \tag{4}$$

where, NH_3 was the FA content, tNH_3 is the total considered NH_3 concentration, and both pH and T (in Kelvin) of the digestate were measured daily. The N recovery experiments were stopped once a minimum TAN removal of 90% was reached.

2.3.2. Phosphorus Recovery Process

The recovery of P (as total phosphorus) through precipitation was studied for each set of experiments, under the different favorable conditions created by the N recovery treatment.

Initial and final samples of the digestate were taken to determine the total P recovered. The concentration of the Mg^+, Ca^+ and K^+ ions was also analyzed at the end of the experiments, to verify whether there was any interference in the formation of the magnesium phosphates. In addition, the P recovery efficiency was also calculated, as follows Equation (5):

$$\text{P recovery efficicency (\%)} = \frac{\text{mass of P recovered in the solid fraction}}{\text{initial mass of P in the digestate}} \times 100 \tag{5}$$

Table 2. Chemical characterization of the digestate at the beginning and end of the experiments. Standard deviations are shown in brackets.

Experiments		Parameters											
		pH	TA (mg CaCO$_3$ L^{-1})	TAN (mg N L^{-1})	TKN (mg N L^{-1})	TCOD (mg O$_2$ L^{-1})	SCOD (mg O$_2$ L^{-1})	TS (g L^{-1})	VS (g L^{-1})	Mg$^+$ (mg L^{-1})	Ca$^+$ (g L^{-1})	K$^+$ (g L^{-1})	P (mg P L^{-r1})
Exp. 1	Initial	8.25 (-)	27,439 (-)	3318 (29)	5271 (7)	74,537 (681)	30,889 (1467)	82.1 (2.3)	45.3 (1.3)	932.8 (15)	8.1 (0.4)	3.1 (0.2)	473 (2)
	Final	8.53 (0.04)	25,585 (513)	243 (16)	2489 (167)	73,493 (248)	16,857 (891)	65.2 (17.1)	44.2 (4.9)	-	-		266 (5)
Exp. 2	Initial	8.21 (-)	40,664 (-)	3419 (9)	5553 (55)	77,857 (240)	35,894 (469)	88.9 (1.2)	51.9 (3.2)	940.2 (4.6)	8.5 (0.1)	2.9 (0.1)	426 (2)
	Final	9.16 (0.08)	22,138 (8844)	270 (129)	2419 (139)	55,495 (3568)	19,423 (1674)	74.2 (0.5)	19.7 (7.9)	-	-	-	139 (8)
Exp. 3	Initial	8.31 (-)	49,796 (-)	3365 (25)	5446 (121)	69,376 (3694)	32,394 (1358)	80.0 (6.5)	40.1 (5.5)	992.9 (1.1)	10.9 (1.1)	3.7 (0.6)	467 (1)
	Final	8.47 (0.06)	45,560 (197)	227 (5)	2489 (197)	70,600 (1766)	17,037 (1146)	79.6 (0.7)	24.5 (4.8)	-	-	-	243 (4)
Exp. 4	Initial	8.85 (-)	41,683 (-)	3511 (20)	5784 (10)	70,395 (449)	32,564 (228)	84.1 (0.8)	47.7 (0.3)	979.1 (9.9)	9.2 (0.2)	2.2 (0.1)	410 (33)
	Final	9.35 (0.01)	22,857 (8591)	291 (1)	2577 (163)	68,989 (66)	15,572 (777)	78.1 (0.7)	21.8 (3.2)	-	-	-	13 (16)

Considering TA as total alkality; TKN as total Kjeldahl nitrogen; TCOD as total chemical oxygen demand; SCOD as soluble chemical oxygen demand; TS as total solids; VS as volatile solids; Mg as Magnesium; Ca as calcium; K as potassium; and P as total phosphorus.

2.4. Analytical and Statistical Methods

Analyses of the TAN, TS, VS, TCOD, SCOD, TKN, and P were performed in duplicate, in accordance with APHA Standard Methods [22]. For the TS content, a sample was dried to a constant weight at 105 °C. The TS residue was ignited at 550 °C to a constant weight, and therefore the weight lost on ignition was the VS content. The TAN was measured according to the distillation and titration method. The TKN was measured according to the Kjeldahl digestion, distillation, and titration method. The TA was calculated by measuring the amount of 0.1 N H_2SO_4 needed to get the pH of a sample of digestate to 4.5, expressed as mg $CaCO_3$ L^{-1}. The chemical determination of the P concentration was carried out according to the vanadate-molybdate acid colorimetric method, at a wavelength of 470 nm (spectrophotometer Thermo Scientific, model Helλos γ), after the pre-digestion of the samples according to the Method 4500 PC [22]. The concentration of Ca^+, Mg^+ and K^+ in the digestate was determined using microwave acid digestion (model CEM MARSX), with HNO_3 at 65%, followed by the inductively coupled plasma (ICP) analysis (Method 3125, [22]).

The results obtained for TAN recovery and for P recovery were analyzed using one-way analysis of variance (ANOVA), with significance at $p < 0.05$, to determine the significant differences in the experimental configurations.

3. Results

3.1. Nitrogen Recovery and Phosphorus Precipitation in Experiments 1 and 2 (Set 1)

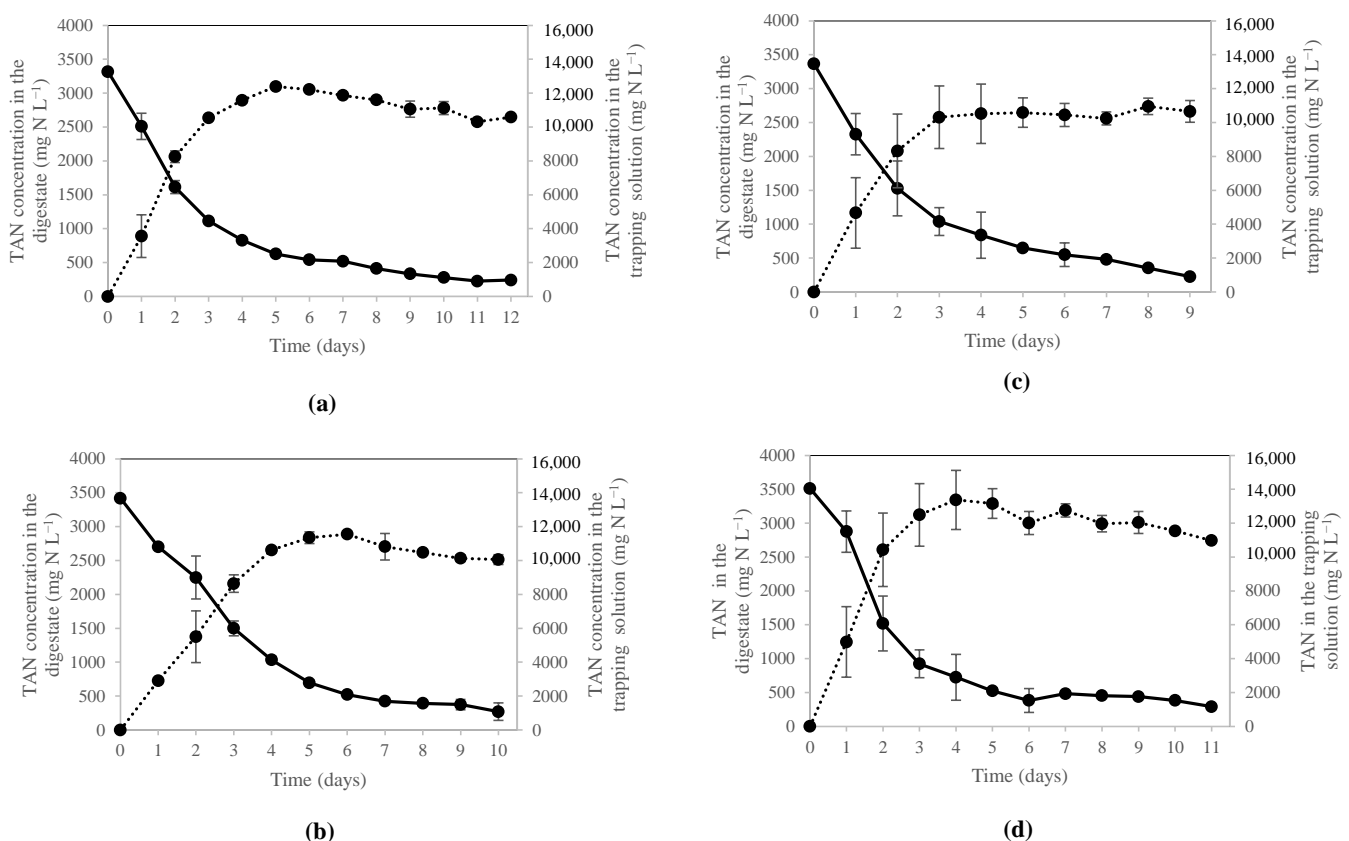The performance of the experiments can be seen in Figure 2.

Figure 2. TAN removal in the digestate (continuous line, primary axis) and recovery in the trapping solution (discontinuous line, secondary axis) for the four different configurations, where (**a**,**b**) correspond to a ratio 180 g TAN:1 m² of membrane, and (**c**,**d**) correspond to a ratio 100 g TAN:1 m² of membrane. Also, (**b**,**d**) correspond to the configurations with the addition of alkali.

The N recovery (N1) efficiency of the 180 g TAN:m^2 membrane ratio, without the addition of alkali, was assessed in Exp. 1. The results show that the initial TAN concentration in the digestate of 3318 $\pm$ 29 mg N L^{-1} decreased to 243 $\pm$ 16 mg N L^{-1} in 12 days. This means a removal of 3075 $\pm$ 13 mg N L^{-1}. The mass of TAN removed was 4611 $\pm$ 22 mg N and the TAN removal accounted for 93%. The TAN concentration in the trapping solution achieved a value of 10,581 $\pm$ 0 mg N L^{-1} on day 12 (Figure 2a).

During Exp. 1, the volume of the trapping solution increased from an initial value of 250 mL to a final value of 354.8 $\pm$ 0.6 mL due to the diffusion of water vapor through the membrane (i.e., osmotic distillation). The total mass of TAN recovered in the trapping solution was 3636 $\pm$ 32 mg N, which implied a TAN recovery efficiency of 79% (Table 3). The TAN recovery rate was 11.5 g N m^{-2} d^{-1}.

Table 3. Changes in chemical characteristics of the digestate during the different experiments. Standard deviations are shown in brackets.

Experiments	Parameters							
	Initial TAN in the Digestate (mg N)	Removed TAN from the Digestate (mg N)	Recovered TAN in the Trapping Solution (mg N)	TAN Recovery Efficency (%)	Initial P in the Digestate (mg P)	Recovered P in the Solid Precipitate (mg P)	Recovered P in the Solid Precipitate per Day (mg P day^{-1})	P recovered in the Solid Precipitate (%)
Exp. 1	4976 (44)	4611 (22)	3636 (32)	79 (1)	709 (3)	451 (30)	37.5 (2.4)	64 (5)
Exp. 2	5127 (14)	4734 (198)	3652 (60)	77 (2)	639 (3)	512 (3)	51.2 (0.3)	80 (1)
Exp. 3	5049 (38)	4711 (37)	3986 (213)	85 (4)	700 (1)	523 (77)	58.2 (8.5)	75 (11)
Exp. 4	5268 (30)	4848 (66)	4376 (52)	90 (1)	614 (33)	537 (4)	48.7 (0.4)	88 (5)

The N recovery with a 180 g TAN:m^2 membrane and the addition of 37.5 mL of NaOH 1.5 N at the beginning of the experiment to increase the initial pH to 9.2 was evaluated in Exp. 2. The N recovery in this case was designated as N2. In this experiment, the initial concentration of TAN in the digestate was 3419 $\pm$ 9 mg N L^{-1} and it decreased to a concentration of 270 $\pm$ 129 mg N L^{-1} after 10 days (Figure 2b). This implies a removal of 3149 $\pm$ 138 mg N L^{-1} (92%) and the mass of TAN removed was 4734 $\pm$ 198 mg N. In the case of the TAN concentration in the trapping solution, it rose to a value of 10,060 $\pm$ 292 mg N L^{-1} on day 10 (Figure 2b). As in the previous experiment, the volume of the trapping solution increased due to osmotic distillation, from an initial volume of 250 mL to a final value of 363.8 $\pm$ 5.7 mL. The total mass of TAN recovered in the trapping solution was 3652 $\pm$ 60 mg N, which implied a TAN recovery efficiency of 77% (Table 3). The TAN recovery rate was 13.9 g N m^{-2} d^{-1}.

In Exp. 1, the P recovery was designated as P1, and the initial concentration of P in the digestate was 473 $\pm$ 2 mg L^{-1}, which corresponds to a mass of P of 709 $\pm$ 3 mg. The mass balances are presented in Table 3, from which the average amount of P present in the liquid fraction at the end of the experiment was 266 $\pm$ 6 mg P, and in the solid fraction or precipitate was 451 $\pm$ 30 mg P. The P recovered is considered to be the total P precipitated in the solid fraction; therefore, the recovery efficiency in this experiment was 64% (Table 3).

Regarding the P recovery in Exp. 2 (P2), the initial concentration and mass of P were 426 $\pm$ 2 mg P L^{-1} and 639 $\pm$ 3 mg P, respectively. The mass of P in the liquid fraction at the end of the experiment was 139 $\pm$ 8 mg P and in the solid fraction was 512 $\pm$ 3 mg P. Therefore, the average P recovery in this experiment was 80% (Table 3).

3.2. Nitrogen Recovery and P Precipitation in Experiments 3 and 4 (Set 2)

In Exp. 3, the N recovery was designated as N3 and a 100 g TAN:m^2 membrane ratio was applied. In this experimental configuration, the initial TAN concentration in digestate was 3365 $\pm$ 25 mg N L^{-1} and it decreased to a value of 227 $\pm$ 0 mg N L^{-1} on day 9 (Figure 2c), which means a removal of 3076 $\pm$ 115 mg N L^{-1}. Taking this into account,

the mass of TAN removed was 4711 ± 37 mg N, which means a removal of 93%. The TAN concentration in the trapping solution increased from 0 to $10{,}654 \pm 643$ mg N L^{-1}, which implies an amount of TAN recovered from the digestate of 3986 ± 213 mg N, and thus a TAN recovery efficiency of 85% (Table 3). The TAN recovery rate was 9.7 g N m^{-2} d^{-1}. In this case, the trapping solution increased its volume from 250 mL to a final value of 380.7 ± 5.9 mL due to the water vapor that passed through the membrane (i.e., osmotic distillation).

In Exp. 4, the N recovery (N4) was performed with a 100 g TAN:m^2 membrane ratio, and the addition of 31 mL NaOH to obtain a pH of 9.2 at the beginning of the experiment. The digestate initial TAN concentration was 3511 ± 20.5 mg N L^{-1} and it decreased to a value of 291.5 ± 0 mg N L^{-1} on day 9 (Figure 2d), which means a removal of 3220 ± 48 mg N L^{-1}. Therefore, the TAN removed was 4848 ± 66 mg N, which means a removal of 92%. The TAN concentration in the trapping solution increased from 0 to $10{,}970 \pm 151$ mg N L^{-1}, which implies an amount of TAN of 4376 ± 52 mg N recovered from the digestate, and therefore a TAN recovery efficiency of 90% (Table 3). The initial volume of the trapping solution (250 mL) increased to a total of 399 mL at the end of the experiment. The TAN recovery rate was 8.4 g N m^{-2} d^{-1}.

For Exp. 3, the P recovery was designated as P3. In this case, the initial concentration of Pt was 466 ± 1 mg L^{-1}, which represented an amount of Pt of 700 ± 1 mg P. The mass of Pt in the liquid fraction accounted for 243 ± 4 mg P and, in the solid fraction, this was 523 ± 77 mg P. Therefore, the P recovery efficiency in this experiment was 75% (Table 3).

In Exp. 4, the initial concentration and mass of P were 409 ± 22 mg P L^{-1} and 614 ± 33 mg P (Table 2), respectively. In this configuration, the P in the solid fraction accounted for 537 ± 4 mg P, so the average P recovery efficiency was 88% (Table 3).

4. Discussion

4.1. N Recovery

The main differences found between configurations N1 and N2 were related to the duration of the experiments and the TAN recovery rates. This can be attributed to the differences in the FA content. The FA content in the digestate is one of the main factors affecting TAN recovery when using the GPM technology and is determined by pH and temperature Equation (4). The pH affects the acid-based chemical balance between the ammonia and the ammonium (NH_4^+/NH_3), and it has been stated that a pH value close to 9 shifts the chemical equilibrium favoring the release of NH_3. An increase in the FA concentration on the first day with respect to the initial value of FA of the digestate was observed in both experiments. This is due to an increase in the pH (Figure 3a,b; Figure 4) caused by the aeration alone for N1 (up to 262 mg L^{-1}), and the aeration plus the addition of alkali for N2 (up to 811 mg L^{-1}).

The average FA for N1 configuration was 94 mg L^{-1}, while for the N2 configuration it was 325 mg L^{-1}. This difference is due to a higher pH in the N2 configuration (up to 9.28) (Figure 4). Most of the TAN recovered for the N1 configuration occurred in the first five days, then remained almost constant until the end of the experiment (Figure 3). This agrees with Riaño et al. [14], who determined that the TAN recovery rate decreases when the FA content available in the digestate is lower than 95 mg N L^{-1}. As for the N2 configuration, most of the TAN recovery occurred in the first six days (Figure 3) and, in this case, a higher availability of FA favored the TAN recovery, the TAN recovery rate being approximately 21% higher than for the N1 configuration.

The percentages of N recovery in N1 and N2 were similar (79 and 77%, respectively, Table 3); nevertheless, the N2 configuration achieved this percentage in less time. It can be stated that the N2 configuration, with the addition of alkali, reduces the time of operation by two days to achieve an N recovery of 77% over an N removal of 90%.
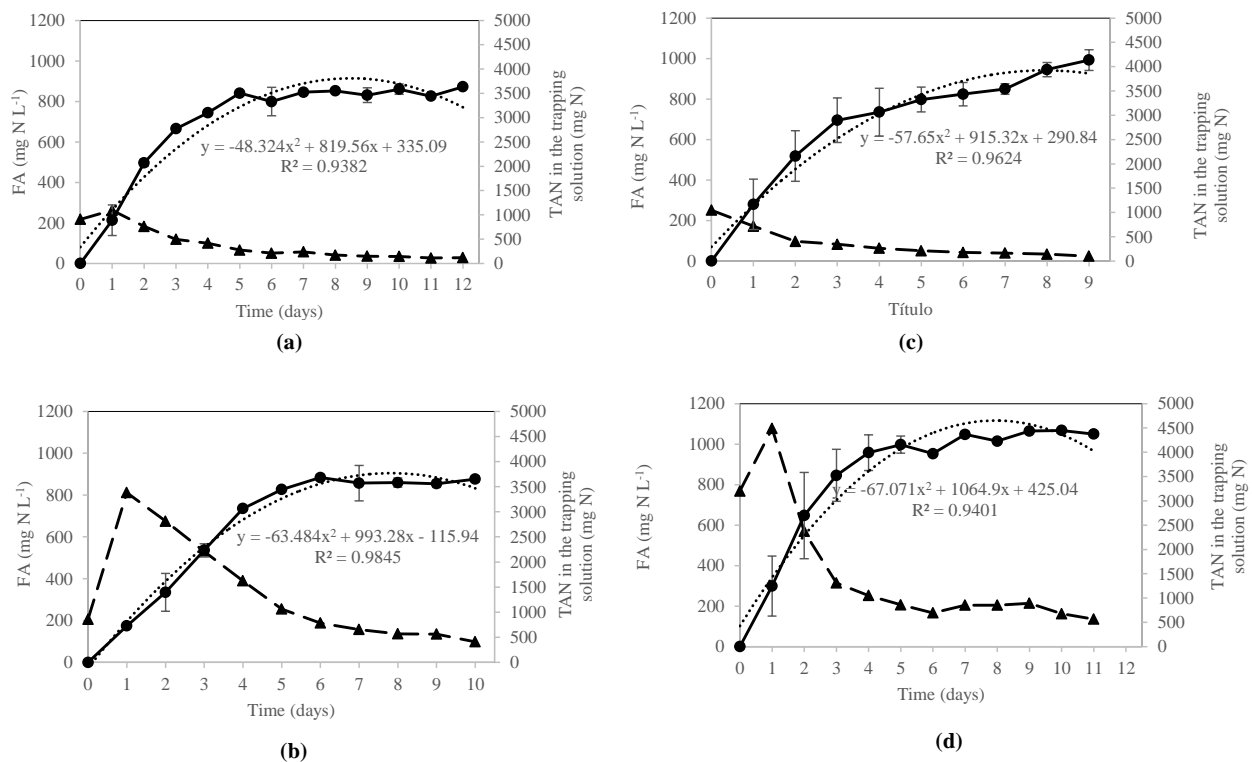
Figure 3. TAN recovery in the trapping solution (continuous line; mg N; secondary axis) with the polynomic equation and the R2 coefficient (dotted line) and free ammonia (FA) available in the digestate (discontinuous line; mg N L^{-1}; primary axis) for the four different configurations, where (**a**,**b**) correspond to a ratio 180 g TAN:1 m^2 of membrane, and (**c**,**d**) correspond to a ratio 100 g TAN:1 m^2 of membrane. Also, (**b**,**d**) correspond to the configurations with the addition of alkali.
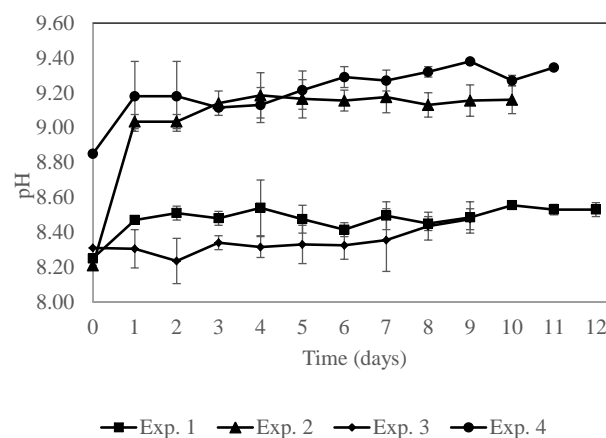
Figure 4. pH values for the four different experiments.

In the case of the N3 and N4 experimental configuration, with the 100 g TAN:m^2 membrane ratio, the main differences were due to the duration of the experiments and the FA content. Unlike the other configurations, N3 did not present an increase in the FA on day 1 (Figure 3c). This was due to the pH of the digestate, which remained close to 8 throughout the experiment. Despite this, the N3 configuration presented a TAN recovery rate of 9.7 g N m^{-2} d^{-1}, and a percentage of N recovery of 85% in nine days. The majority of the TAN recovery for N3 occurred in the first three days, and decreased on day four, when the FA presented values below 95 mg N L^{-1} (Figure 3c). In the case of configuration N4, the average FA concentration was 356.4 mg N L^{-1}, and the majority of the

N recovery occurred in the first four days of the experiment. Although there was a higher availability of N in the digestate, the TAN recovery rate was lower than in the previous configurations: 8.42 g N m^{-2} d^{-1}. Nevertheless, N4 presented the highest N recovery percentage (90%) in only two days more of experiment as compared to N3 (Figure 3d). The TAN recovery rate results agree with the results of García-González et al. [13], who obtained an average TAN recovery rate of 9.5 g m^{-2} d^{-1} when treating raw swine manure with GPM technology. Nevertheless, they were lower than those reported by Vanotti et al. [18] (up to 18.4 g m^{-2} d^{-1}). This could be explained by the difference in the membrane model.

It can be stated that, between the configurations of Exp. 1 and Exp. 2, both with a 180 g TAN:m^2 membrane ratio, the second option (N2) with the addition of alkali presented a better performance, with a higher TAN recovery rate, a shorter time and a high percentage of recovery of N (77%). However, the N3 and N4 configurations (Set 2, with 100 g TAN:m^2 membrane ratio) presented 9% and 19% higher N recovery efficiency as compared to N2, although the TAN recovery rates for N3 and N4 as compared to N2 were approximately 30% and 40% lower (Figure 5). This is an important result because a high N recovery efficiency (average of 83% $\pm$ 3) and high N recovery rate using less membrane can be obtained with the N2 configuration.
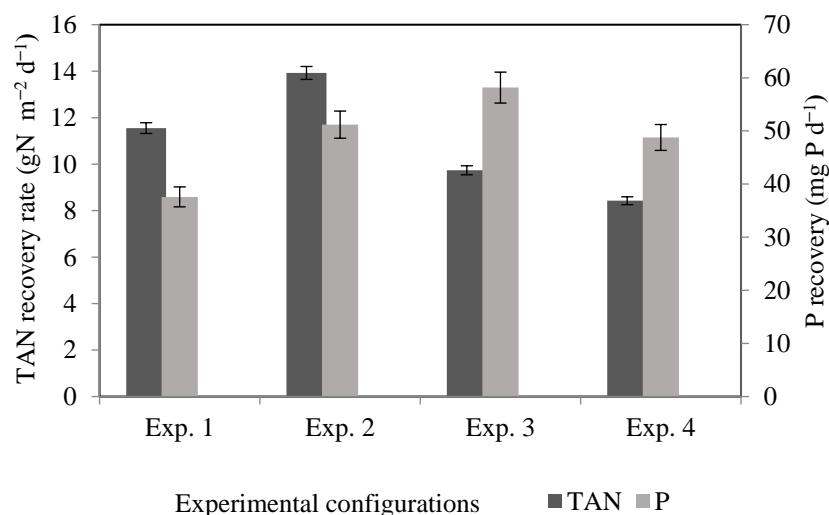

Figure 5. Comparison of the different experimental scenarios.

This implies a significant cost reduction when applying this technology for waste treatment and nutrient recovery.

4.2. P Recovery

The P recovery efficiencies were between 64% for P1 and 88% for P4 (Table 3). These results for P recovery are consistent with those reported by Brown et al. [23], who obtained 80% total P recovery from anaerobically digested manure, using stirred reactors for struvite precipitation, also with $MgCl_2 \cdot 6H_2O$ and at pH 8.7, and using NaOH to control the pH. The results obtained are also in agreement with those reported by Taddeo et al. [24], who obtained a P recovery efficiency of approximately 80% from co-digested and raw swine slurry, also using NaOH to obtain pH values of 10, but MgO as the Mg source. Vanotti et al. [18] reported recoveries of nearly 100% of the removed P from the liquid manure as solid precipitate, also using $MgCl_2$, $6H_2O$ and NaOH for pH control. This may be due to the influence of a higher pH (up to 9.7) for a quick elimination of the NH_4^+ ion, which may result in a more efficient P precipitation.

It was observed that configuration P2, with a ratio of 180 g TAN: m^2 membrane plus the addition of alkali, as compared to P1 with the same ratio but without alkali, showed an increase in P recovery of 16%. In the same way, P4, with a 100 g TAN: m^2 membrane and the addition of alkali, as compared to P3 with the same membrane ratio but without

NaOH addition, presented a P recovery 13% higher (Table 3). Nevertheless, the statistical analysis shows that no significant differences ($p > 0.05$) were found in the P recovery efficiencies between the different configurations, except between P2 and P4 ($p < 0.05$), where P4 presented 4% more recovery of P. This suggests that, with an increase in the membrane and the addition of alkali, a higher P recovery can be obtained via precipitation, as indicated by the initial premise. However, P4 had a duration of one more day compared to P2, which implies that the P recovery in mg per day for P4 is 5% less than P2 (Figure 5).

In this sense, by taking into account the duration of the experiments to be compared, the TAN recovery rate together with the P recovery per day for each configuration can be observed in Figure 5. The configuration for Exp. 3 presented the highest P recovery (58.2 mg P d^{-1}); however, it has a low N recovery rate (9.7 g N m^{-2} d^{-1}).

Therefore, it can be stated that the configuration that presents the best performance is Exp. 2, with the highest N recovery rate (13.9 g N m^{-2}d^{-1}), and an N recovery efficiency of 77% and a P recovery of 51.2 mg P d^{-1}, which is only 7% lower than P3, and a P recovery efficiency of 80% (Table 3, Figure 5).

Regarding the foreign ions, their content was measured in the solid fraction of the digestate at the end of the four experiments as percentage of dry matter. The content of Ca^+ was in a range between 2.05% and 4.10%, and the content of K^+ was in a range from 0.31% to 0.38%. This indicates that any phosphates that may have been formed from these elements were not important contributors to the resultant precipitate. These results agree with those obtained by Vanotti et al. [18].

4.3. Future Perspectives of These Nutrient Recovery Technologies

In the case of N and P, it has been stated in the literature that membrane-based technologies and chemical precipitation are the two options for nutrient recovery with the highest technical and economic feasibility [8,25]. What is more, it has been reported that the combination of different recovery technologies could increase the quality and quantity of the recovered nutrients and that it would make them more viable in the future [26,26]. This makes this study especially relevant.

Specific technologies that recover such nutrients as N and P from wastes have experienced a great development in recent years due to the environmental limitations on organic fertilization, particularly with the continued increase in the prices of mineral fertilizers (30% more from early 2022) [27,28]. However, the question of whether these technologies could be economically viable is always related to this development.

The GPM technology and P recovery via precipitation present very high nutrient recovery rates (>90%), and the bio-based fertilizers obtained could be applied directly without further treatment in the soil. Furthermore, in the case of P recovery by precipitation, phosphate precipitates present good solubility in soils and have a high plant nutrient uptake (>76%), [29]. These characteristics make them economically attractive [25].

The GPM technology is one of those with the most efficient performance from an economic, energetic, and environmental point of view [8,17,30], and it is capable of a total benefit profit for products up to 0.32$ per kg [19]. P recovery via precipitation is an easy-to-operate process and can be used to meet low P discharge limits in the environment [31]. A market value has been calculated for P recovered as struvite of 2.9$ per kg of P produced, although the potential profits may vary depending on the conditions and the cost of chemicals in each case [32]. Even though there is not yet a precise market value for the recovery nutrients, these estimations can be very useful for future investments. It has been reported that mineral fertilizers are now more affordable for farmers [32], but their prices do not consider externalities, such as the environmental costs associated with their extraction. The negative environmental impacts related to the intense exploitation of mines and the greenhouse gas emissions associated with the mineral fertilizers' production must be added to the rapid consumption of phosphate-based rocks and costly ammonium production; therefore, investing in additional technologies may be necessary [3,25].

In addition to better environmental performances, nutrient recovery technologies can have other advantages, such as state incentives, as well as their capability to eliminate unwanted precipitates in waste streams, thereby facilitating management and reducing wastewater treatment costs [25,33].

In this context, this study showed the possibility of effectively combining GPM technology with P precipitation and obtaining high recovery rates, corresponding to the Exp. 2 configuration.

5. Conclusions

The combination of nutrient recovery technologies from agro-industrial residues is a field with great application potential. The combination of GPM technology to recover N together with chemical precipitation to recover P resulted in high recoveries of both nutrients. It has been seen that the ratio of 180 g of N per m^2 of membrane with the addition of alkali can achieve TAN recovery efficiencies of up to 77%, similar to those that can be obtained with a membrane ratio of 100 g of N per m^2. Also, the 180 g of N per m^2 of membrane presented the highest TAN recovery rate compared to the other scenarios with a larger membrane surface. This means lower capital costs. This configuration is also capable of obtaining recovery efficiencies of P of 80% and a P recovery of 51.2 mg per day. The comparisons performed and the proposed configuration could be particularly useful for agribusiness stakeholders when exploring the application of nutrient recovery techniques, especially when it comes to essential nutrients such as N and P.

Conflicts of Interest: The authors declare no conflict of interest.

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