

Nitrogen and phosphorus recovery from swine manure

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Nutrient recovery has become one of the key points in agricultural policies related to sustainability in the EU. In particular, manure residues from the agri-food sector are the largest waste flow of nutrients and provide over 70% of the current total recovered N and P from all sources (Buckwell and Nadeu, 2016). Nevertheless, manure management and application results in large amounts of nutrient losses. With the application of different technologies to recover N and P, it is possible to improve the nutrient recovery process, and avoid the dependence on mineral fertilizers, therefore avoiding the associated impacts in their manufacture (such as GHG emissions and water pollution), and resulting in a practical application of the principles of the circular economy (Buckwell and Nadeu, 2016).

In this work, a set of experiments were designed and implemented for the N and P recovery in two phases, using two membrane technologies. In a first phase, an experiment for the N recovery was conducted using swine raw manure, with permeable-gas membranes. This gas-permeable membrane technology (GPMT) has been successfully used to recover N from swine manure (García-Gonzalez *et al.*, 2015). A polyethylene terephthalate (PET) vessel was used containing a manure volume of 700 mL, in which the tubular gas-permeable membrane was submerged. The gas-permeable membrane made of e-PTFE material, with a length of 50 cm. One magnetic stirrer was placed inside the vessel to keep the manure homogeneous, and it was used aeration as substitute of the use of alkali to increase pH (García-Gonzalez *et al.*, 2015). An acidic solution (150 mL of H₂SO₄ 1N) was continuously recirculated inside of the tubular membrane using a peristaltic pump. The acidic solution was used as a trapping solution to recover NH₃ as (NH₄)₂SO₄ solution, which can be used as a fertilizer. Daily samples of the acidic solution and the manure were taken to monitor pH and NH₄⁺ content. In addition, initial and final samples of raw manure were analysed for determination of pH, alkalinity, total solids (TS), volatile solids (VS), NH₄⁺, total Kjeldahl nitrogen (TKN) and total phosphorus (P_i).

In a second phase, the resultant manure of the N recovery process was used to recover P using an electro dialytic process (membrane technology). A cylindrical Plexiglas laboratorial cell was assembled with 3 compartments. In the central compartment (or compartment II) a volume of 230 mL of manure was placed. The manure was constantly agitated using an overhead stirrer (LBX OS20 series), at 470 rpm. Compartments I and III contained 0.01 NaNO₃ as electrolyte, to recover cations and anions respectively, and a platinum coated titanium bar (D=3 mm; L=5 cm) as electrode. Each compartment was separated by an ion-exchange membrane, (a cation exchange membrane CR67R, GE Water & Process Technology was placed between compartments I and II, and an anion exchange AR204R, GE Water & Process Technology was placed between compartment II and III). A voltage drop was applied across compartment II through two electrodes placed in compartments I and III. This membrane setup delays pH changes in the waste material in compartment II, while allowing P and heavy metals to migrate into the electrolytes (Oliveira *et al.*, 2018). The electrolyte solution was recirculated using a peristaltic pump between the compartment and an external reservoir (Erlenmeyer flask). A power supply (Hewlett Packard E3612A) was used to maintain a current of 50 mA. Samples of the manure and the electrolyte solution in each Erlenmeyer flask were taken daily to monitor the pH and conductivity and to analyse the amount of P. The voltage and the electric current were also monitored daily.

The first phase was carried out for 13 days. It was observed a decrease of NH₄⁺ in the manure, from the initial concentration of 3900 mg NH₄⁺ L⁻¹ to 1550 mg NH₄⁺ L⁻¹ (Table 1), where part of the ammonia was recovered and part volatilized. The TAN (total ammonia nitrogen) removal efficiency of was 60%. Although this result is consistent with previous studies, a high recovery rate is desirable. For that purpose, in further experiments, it would be necessary to make improvements for a better control of the pH to avoid NH₃ losses due to volatilization.

The second phase were conducted for 4 days, where the initial concentration of P of the manure was 1000 mg L⁻¹. During the experiment, the amount of P decreased reaching a final value of 110 mg L⁻¹, indicating an extraction of approximately 89% of the initial P and its recovery into the electrolytic solution (Table. 2).

Results showed the great potential of the use of the membrane technology to recover nutrients and the good results of combining different membrane technologies in consecutive settings.

Table 1. Concentration of total ammonium nitrogen (TAN) in the swine manure (SM) and in the trapping solution

| Day | TAN in SM (mg N L ⁻¹) | TAN in the trapping solution (mg N L ⁻¹) |
|-----|-----------------------------------|--|
| 0 | 3900 ± 301 | 0 ± 0 |
| 1 | 3808 ± 266 | 700 ± 188 |
| 2 | 3317 ± 119 | 1662 ± 272 |
| 3 | 2998 ± 372 | 2503 ± 1 |
| 6 | 1995 ± 196 | 4516 ± 100 |
| 7 | 1785 ± 356 | 4942 ± 174 |
| 8 | 1643 ± 158 | 5565 ± 63 |
| 9 | 1580 ± 246 | 6066 ± 137 |
| 10 | 1662 ± 10 | 6160 ± 164 |
| 13 | 1550 ± 102 | 7024 ± 92 |

Table 2. Concentration of total phosphorus (Pt) in the swine manure (SM) during the experiment for P recovery.

| Day | Pt (mg L ⁻¹) |
|-----|--------------------------|
| 0 | 1000 ± 135 |
| 1 | 727 ± 138 |
| 2 | 113 ± 33 |
| 3 | 69 ± 7 |
| 4 | 70 ± 2 |

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