

# Development of a liquid N fertilizer from an agro-industrial effluent

## Desarrollo de un fertilizante N líquido a partir de un efluente agro-industrial

B. Riaño<sup>1</sup>, C. Horta<sup>2,3,\*</sup>, F.-G. Walker<sup>4</sup> & M.C. García-González<sup>5</sup>

<sup>1</sup>Agricultural Technological Institute of Castilla y León, Ctra. Burgos, km 119, 47071 Valladolid, Spain

<sup>2</sup>Polytechnic Institute of Castelo Branco, School of Agriculture, Quinta da Sra. De Mércules, 6001-909 Castelo Branco, Portugal

<sup>3</sup>CERNAS-IPCB Research Centre for Natural Resources, Environment and Society, Polytechnic Institute of Castelo Branco, 6001-909 Castelo Branco, Portugal

<sup>4</sup>Universidade de Passo Fundo, Rio Grande do Sul, Brasil

<sup>5</sup>Universidad de Valladolid, Escuela Técnica Superior de Ingenierías Agrarias, Spain

(\*E-mail: [carmoh@ipcb.pt](mailto:carmoh@ipcb.pt))

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### ABSTRACT

Anaerobic digestion (AD) has been largely studied and it is widely applied for manure treatment in Europe, although its implementation is scarce in Spain and Portugal. The major benefit of AD is the production of renewable energy in the form of methane and digestate that is used as fertilizer, as it contains N, P and K. The aim of this work was to use gas-permeable membrane technology to capture N from slurry co-digested with orange peel residue, obtaining a liquid solution of ammonium sulfate that has been tested as a fertilizer in micropot trials. The data obtained show a recovery of 62% of the N from the digestate, and a recovery rate of N of  $43.0 \pm 6.6$  g N per m<sup>2</sup> of membrane and per day. The results of the micropot test showed that the liquid ammonium sulfate solution had a fertilizing effect similar to that of the mineral N fertilization.

**Keywords:** digestate, gas-permeable membranes, N recovery, fertirrigation, micropot trials

### RESUMEN

La codigestión anaerobia del purín y otros residuos agroindustriales es uno de los tratamientos de residuos más utilizados en Europa, aunque su implantación en España y Portugal es muy escasa. El mayor beneficio de este tratamiento es la producción de metano y digestado, que se utiliza como fertilizante debido a su contenido en nitrógeno, fósforo y potasio. El objetivo de este trabajo ha sido utilizar la tecnología de membranas permeables a los gases para capturar el N del digestado de purín codigerido con residuos de piel de naranja, obteniendo una solución líquida de sulfato de amonio que se ha testado como fertilizante en ensayos en micromacetas. Los datos obtenidos muestran una recuperación del 62% del N del digestado, y una tasa de recuperación de N de  $43.0 \pm 6.6$  g N por m<sup>2</sup> de membrana y por día. Los resultados del ensayo en micromacetas muestran que solución líquida de sulfato de amonio tuvo un efecto fertilizante similar al de la fertilización con nitrógeno mineral.

**Palabras clave:** digestado, membranas permeables a gases, recuperación de N, fertirrigación, cultivo en micromacetas

## INTRODUCTION

Nitrogen fertilizers are a key component in the production of field crops. In late 2021, fertilizer prices began to raise going from 216 €/t to 355.5 €/t in the case of ammonium sulfate 21%, according to data from the Spanish Ministry of Agriculture, Fisheries and Food (MAPA, 2022). In this scenario, recovery of nutrients, such as N are of special relevance, even more from N rich livestock waste as manure or treated manure as digestate.

Recently, the gas-permeable membrane technology has been identified as one of the most energy and cost-effective technology for recovering N from waste (Beckinghausen *et al.*, 2020).

The aim of this work was to use gas-permeable membrane technology to capture ammonia from digested slurry co-digested with orange peel residue, obtaining a liquid solution of ammonium sulfate that has been tested as a fertilizer in micropot trials, since it has been scarcely studied.

## MATERIALS AND METHODS

### *Nitrogen recovery*

A batch experiment was conducted in 2 L plastic jars (1.5 L digestate). The acid tank consisted of 500 mL Erlenmeyer flasks containing 100 mL of 0.5M H<sub>2</sub>SO<sub>4</sub> (Panreac). A peristaltic pump (Pumpdrive 5001, Heidolph, Schwabach, Germany) was used to continuously recirculate the acidic solution through tubular membranes inside the digestate jars and back into the acid tank using a constant flow rate of 12 L d<sup>-1</sup>. The acid pH was adjusted to keep it below 2. Gas-permeable tubular membrane (48 cm long, 5.2 mm outer diameter) made of expanded polytetrafluoroethylene (e-PTFE) (Zeus Industrial Products Inc., Orangeburg, SC, USA) was used for NH<sub>3</sub> capture. The membrane was submerged in the digestate. Low-rate aeration was used to increase digestate pH according to García-González *et al.* (2015). The airflow rate was 0.24 L<sub>air</sub> L digestate<sup>-1</sup> min<sup>-1</sup> in the first two days and 0.13 L<sub>air</sub> L digestate<sup>-1</sup> min<sup>-1</sup> to the end of the experiment and it was controlled using an airflow meter (Aalborg, Orangeburg, NY, USA). Ammonia was measured as total ammoniacal nitrogen (TAN).

### *Micropot trials*

A micropot experiment with two plants of triticale (*× Triticosecale* Wittmack) in each pot as crop test was performed in a growth chamber, during 34 days. The soil used was a dystric Cambisol derived from schist. The soil was sandy-loam (66.8% of sand, 20.1% of silt and 13.1% of clay), acidic (pH=5.0), high in organic matter (3.8%), low in available P (17 mg kg<sup>-1</sup>), high in available K (175 mg kg<sup>-1</sup>) and a level of soil total N of 1.75 g kg<sup>-1</sup>. The fertilization was done with a half-strength Hoagland solution with or without N, the last with the addition of the N recovered solution (Hoag and N-rec treatments respectively). These solutions were applied in every pots, according to the treatments, during the experiment (totaling 100 mg of N for each pot). A treatment without any fertilization was also done (W treatment). The N sources for the triticale were the mineral N from the Hoagland solution (Hoag) or the N recovered from the digestate (N-rec). After the end of the experiment, the plants of each treatment and repetition (four repetitions/treatment) were cut and weight (fresh matter) and then were dry at 65 °C and weight for dry matter. The total N was quantified in the triticale by the Kjeldahl procedure and the crop N uptake of each treatment was evaluated.

One-way ANOVA analyses were conducted to identify the effect of the treatments on the triticale biomass production and N uptake. Tukey's test was used to compare means at 0.05 probability level.

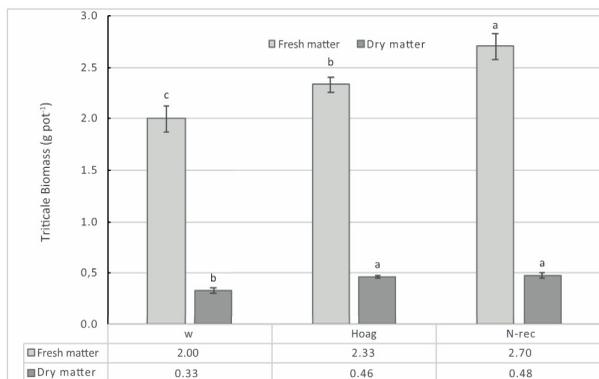
## RESULTS AND DISCUSSION

The aeration increased the pH of the digestate from 8.48 to up 9.48. The total ammoniacal nitrogen concentration in the digestate decreased from 2462 ± 24 to 1019 ± 12 mg N L<sup>-1</sup> in four days of the experiment. Simultaneously, TAN concentration in the acid solution increased up to 14889 ± 2324 mg N L<sup>-1</sup>, that was more than six-fold higher than in raw digestate. Sixty-two percent of TAN removed from digestate was recovered in the acid solution. This value was the same than this obtained by García-González *et al.* (2016) when recovering ammonia from anaerobically digestate manure using gas-permeable membranes in a 32-day experiment. A percentage of the TAN removed (37.7%) was

volatilized to the atmosphere as a consequence of the high pH achieved during the treatment.

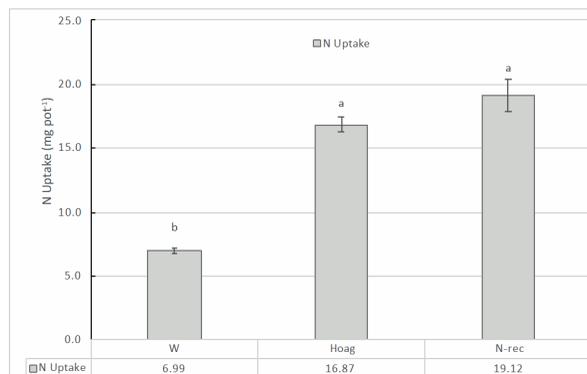
The TAN recovery was not linear and followed a 2nd-order curve, meaning that the TAN capture rate was higher during the first days, and decreased with time. The TAN recovery rate was  $43.0 \pm 6.6$  g N per m<sup>2</sup> of membrane and per day. This value is higher than the values obtained in previous batch studies with similar treatment time found in literature. For example, Vanotti *et al.* (2017) treated anaerobically digested swine wastewater containing 2350 mg N L<sup>-1</sup> using submerged membranes plus low-rate aeration to recover ammonia and reported a TAN recovery rate of 25.1 g TAN m<sup>-2</sup> d<sup>-1</sup>. Dube *et al.* (2016) tested the use of gas-permeable membranes for recovery ammonia from anaerobically digested swine manure and obtained TAN recovery efficiencies between 22.7 and 30.7 g N m<sup>-2</sup> d<sup>-1</sup>.

The data obtained showed a N recovery of 62% from the digestate in four days, and a N recovery rate of  $43.0 \pm 6.6$  g N per m<sup>2</sup> of membrane and per day.



**Figure 1** - Biomass production of the triticale in the different treatments. Different letters above the columns indicate statistical differences ( $p < 0.05$ ) between the treatments by the Tukey test (capital letters between fresh matter, lower cases letters between dry matter).

The results of the micropots trials testing the ammonium sulfate solution, showed that irrespective to the N source the fertilization with nitrogen increased significantly ( $p < 0.01$ ) compared with no N



**Figure 2** - N uptake by the triticale in the different treatments. Different letters above the columns indicate statistical differences ( $p < 0.05$ ) between the treatments by the Tukey test.

fertilization, being the N-rec the treatment with the highest biomass production (Fresh matter, Figure 1). However the triticale's dry matter showed no significant differences between the two N fertilized treatments (Hoag and N-rec). Similar results were obtained by Sigurnjak *et al.* (2019) in a comparison of the fertilizing value of recovered ammonium sulphate and ammonium nitrate compared with mineral fertilization of lettuce and maize, and also by Horta *et al.* (2022) with the same N-recovered solution used in a dystic Regosol derived from granite.

Regarding the N uptake (Figure 2), the N-rec treatment showed the highest value although without significant difference from the Hoag. Despite the experiment was conducted during a short period of time, the results pointed that at least the ammonium sulphate solution had a fertilizing effect similar to the mineral N fertilization.

## CONCLUSIONS

The biomass production together with the N uptake of the triticale fertilized with N recovered from the digestate, was similar to the treatment fertilized with the Hoagland solution. So, the gas-permeable membrane technology showed to be a promising technology to recover N from the effluents into a solution with crop fertilizing value.

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