K-EcoFeRtilizer – Development of a new potassium struvite recovery process for use as a fertiliser for pig slurry treatment

Summary

At the European level, sustainability, circular economy and bioeconomy paradigms are a priority to boost competitiveness, create jobs and generate sustainable growth. These approaches apply mainly to the management and treatment of wastewater and organic waste, including livestock manure. The European Commission has recently published a reference document on Best Available Techniques (BAT) for intensive poultry and pig farming, which identifies BAT applicable to the treatment of pig slurry at farm level and describes struvite precipitation as an interesting emerging treatment. On the other hand, it is also specified that there is still a lack of knowledge and successful experiences in-situ to consider it as a consolidated technology. Along the same lines, the Generalitat de Catalunya does not consider the precipitation of struvite-K a consolidated treatment of livestock manure. Thus, this project is seen as an opportunity for the development of an innovative treatment that requires the definition of specific application guidelines within the livestock sector. The project should serve to promote the implementation of a slurry treatment system aimed at nutrient recovery.

The interest of the process lies in producing a material rich in phosphorus (P) and potassium (K) in order to be able to use it as a fertiliser in agriculture. In this context, within the K-EcoFeRtilizer project, the struvite-K precipitation process is intended to be applied to the treatment of effluents from nitrification-denitrification (NDN) systems, which have a low N concentration but a significant K content (a major nutrient in relation to N and P), as well as a rather low buffer capacity compared to the initial slurry (due to biological treatment). Precipitation also produces treated water with reduced salinity (and a corrected P and K composition), suitable for reuse for irrigation of adjacent crops.

In the field of pig slurry liquid fraction treatment, the integration of biological N removal (BNR) with the recovery of MPP-type phosphoric precipitates (containing P and K) has proven to be technically feasible. In order to study it, a series of precipitation tests were carried out on a laboratory scale. In these trials, synthetic media or denitrified effluent and purified sludge obtained at the outlet of the Mas Monellots NDN bioreactor were used.

This project involved the design, construction and installation in situ of a prototype crystalliser at the Mas Monellots farm, owned by Granges Terragrisa, for the recovery of struvite-K from the denitrified effluent from the NDN reactor (SBR technology). On this farm there are about 1,400 sows and about 25m^3/day of slurry is generated. Following completion of the laboratory work, piloting work began.

The struvite-K fertiliser obtained was applied in field trials carried out on experimental crops and/or crops of the Sant Martí de Tous Agricultural Cooperative. With the application of struvite-K or mixtures of this product with compost and sludge as fertiliser for a spring barley crop, similar or slightly higher yields are achieved than with the reference Mineral treatment. The crop fertilised with struvite-K achieves a grain protein content as high as that of the Mineral treatment, although this is probably not directly related to the application of this material, but may be due to the higher N supply in mineral form in the cover crop in this treatment, and in the Mineral treatment.
When applying NDN Effluent, with nitrogen criterion, in a single crop cycle, an increase in electrical conductivity (EC) is observed, as well as in the levels of assimilable sodium and potassium in the soil. Repeated applications of this material, in the medium to long term, can lead to an increase in these

parameters above the recommended levels and have marked effects on soil quality, increasing the risk of salinisation-sodification. This is an aspect that is expected to be improved in the fertiliser material obtained by optimising the operating procedure of the Monellots pilot plant crystalliser.

Objectives

This project seeks to develop a recovery process for a little-studied mineral, such as potassium struvite, in the field of pig slurry treatment, in order to make possible the recovery of nutrients (P and K) and their subsequent recovery as a slow-release fertiliser in the agricultural framework, in accordance with the concepts of environmental sustainability, circular economy and bioeconomy.

Therefore, the general objective of the project K-EcoFeRtilizer is **to generate new knowledge and experience for the development of a recovery process of magnesium potassium phosphate [$MgKPO_4 \cdot 6H_2O$], a mineral also known as potassium struvite or struvite-K, by chemically induced precipitation, and during the treatment of pig slurry.**

The following specific objectives were defined:

- Carry out an analysis applied to a pig farm including an NDN plant for the treatment of the slurry generated, and diagnosis of the interest of recovering struvite-K.
- Study experimentally in the laboratory the optimisation of the struvite-K precipitation process from the effluent of an NDN slurry treatment plant with batch and continuous tests.
- Characterise the effluent water from the treatment in order to study its recovery.
- Design, build and assemble in-situ (on a pig farm, downstream of an NDN reactor) a pilot struvite-K crystalliser.
- Operate and monitor for a sufficiently long period of time under field conditions (under winter and summer regime) a pilot plant (prototype) to evaluate its performance and to generate output streams (struvite-K and water).
- Carry out field studies on the diagnosis and valorisation of the products recovered at the crystalliser outlet.
- Carry out actions to disseminate the results obtained.

Description of the actions carried out in the project

This project focused on developing a process for the recovery of a mineral that has been little studied to date, potassium struvite, in the field of the treatment of pig slurry to recover nutrients, P and K, and its subsequent use as a slow-release fertiliser in agriculture, in accordance with the concepts of environmental sustainability, circular economy and bioeconomy.

Based on an initial conceptual study of its technical feasibility, an experimental study of the precipitation process has been carried out at two different scales: laboratory and pilot. The products resulting from the crystallisation process (struvite-K and water) have been used for agronomic purposes.

In the field of pig slurry liquid fraction treatment, the integration of biological N removal (BNR) with the recovery of MPP-type phosphate precipitates (containing P and K) has proven to be technically feasible. In order to study it, different precipitation tests have been carried out at laboratory scale, using beakers or an

air-lift type crystalliser (14.6 L volume), under continuous or batch operating conditions. In these trials, synthetic media or denitrified effluent and purified sludge obtained at the outlet of the Mas Monellots NDN bioreactor were used. Different operating conditions have been tested in relation to pH (range: 9.5-11.1, adjusted with NaOH dosage) and the addition of reagents (MgO, $H_2PO_4^{2-}$, NH_4^+, etc.).

A pilot plant has been installed and operated at the Mas Monellots farm for the recovery of struvite-K from the denitrified effluent from the NDN reactor. Once the crystalliser started to generate material suitable for the corresponding chemical analysis and agronomic tests relating to the quality of the material at the end of the treatment – struvite-K and water – three monitoring campaigns were carried out on the operation of the pilot plant: two without added phosphorus and one with added phosphorus. Additional monitoring of the plant with/without phosphorus dosing was also carried out. For each of the monitoring campaigns carried out, at least 3 liquid samples were analysed: denitrified effluent tank (TED), liquid outlet of the separator *Depurdisc* (SLD) and neutralisation tank where the acid is dosed (TDA) (e.g: pH_{ref} ~7.5 and $cond_{ref}$ ~7.8 mS/cm), and 1 solids tank sample (SSD).

Some of the products obtained in the treatment phase have been tested in the field as fertilisers for rain-fed winter crops. To this end, a field trial was carried out in an experimental plot in the town of La Tallada d'Empordà (Baix Empordà) and a demonstration plot in Sant Martí de Tous (Anoia), linked to the Sant Martí de Tous agricultural cooperative. In both cases, a spring barley crop has been planted and parameters of vegetative growth, production and harvest quality have been assessed.

The trial carried out on experimental plots in the Tallada d'Empordà had a randomised block design, with 6 treatments, 3 replications and an elementary plot size of 24 m^2 (3 m wide x 8 m long). The treatments established were as follows:

- Control: without fertiliser application.
- Treatments 2 to 5: Application of different products in the soil at doses that cover the K_2O needs and, when required, the application of nitrogenous mineral fertiliser in the mulch to cover the N needs.
- Treatment 6: Application of NDN treatment effluent, in which part of the potassium has also been extracted, in bottom and topsoil to cover, as a whole, the N needs of the crop. Mineral phosphorus fertiliser is also applied in the background to tend to equalise phosphorous inputs with the dose provided in treatments 2 to 5.

The commercial agricultural plot in Sant Martí de Tous was divided into three parts and the following three treatments were applied:

- Treatment with Struvite-K, supplemented with mineral nitrogen fertiliser (in pre-sowing and mulch) to cover the N needs and equalise the dose applied with respect to the other treatments.
- Treatment with sludge in the soil at a dose that covers the N needs of the crop.
- Treatment with a mixture of 50% struvite-K + 50% sludge, supplemented with mineral nitrogen fertiliser (as a mulch) to cover the N needs and equalise the dose applied with respect to the rest of the treatments.

To establish the nutrient doses to be applied, the needs of a spring grain barley with a target yield of 4 t/ha were considered. The application rates of the fertiliser products were calculated on the basis of their richness (estimated by the University of Girona UdG-LEQUIA and Granges Terragrisa).

In order to respond to the approach described above, the following activities of the project work plan have been carried out:

- ACTIVITY 1. Conceptual analysis applied to an NDN slurry treatment plant, and diagnosis of the interest of recovering struvite-K.
- ACTIVITY 2. Laboratory tests for struvite-K precipitation.
- ACTIVITY 3. Pilot plant trials (prototyping) for struvite-K precipitation.
- ACTIVITY 4. Study on the valorisation of products recovered under field conditions.
- ACTIVITY 5. Exploitation of the results obtained.

Final results and practical recommendations

In the field of pig slurry liquid fraction treatment, the integration of biological N removal (BNR) with the recovery of struvite-K phosphate precipitates has proven to be technically feasible. For their study, a series precipitation tests were carried out on a laboratory scale. In this sense, several operating conditions were tested in relation to pH and addition of reagents, using denitrified effluent and biological sludge. When P was the limiting element, the mismatched composition of the denitrified effluent (1.6 g K/L and molar ratio Mg^{2+}:K^{+}:PO_4 of 1.4:9.5:1) led to a low K recovery efficiency from the liquid phase (approx. 10%). In relation to biological sludge (1 g P/L and total Mg:K:P molar ratio of 0.7:1.2:1), higher K recovery efficiencies (27%) were obtained (the use of EDTA allowed selective chelation of Ca^{2+}, achieving high solubilisations of Mg^{2+} and PO_4). If K was considered as a limiting element, the addition of newberyite particles allowed K recovery efficiencies of up to 90%. The composition of the recovered mineral was not only struvite-K but also other phosphate salts were formed, resulting in a multi-nutrient product. As an example, the material formed contained 0-1% N, 10-17% P and 6-8% K (% dry weight). Further work is needed to optimise the process of co-precipitation of P and K for scaling up and implementation at farm level. The dosing of PO_4 is expected to be essential if high K recovery efficiencies are to be achieved.

A pilot plant for the recovery of struvite-K from the denitrified effluent from the NDN reactor has been installed and operated on Mas Monellots farm. The low availability of P-orthophosphoric acid in this effluent is the limiting factor in the crystallisation process. The dosing of polyelectrolyte in the separation equipment of the precipitate formed (*Depurdisc*) resulted in a higher organic C content of the solid produced than in the case of the product recovered in the laboratory, as the polyelectrolyte contributes to bind soluble organic compounds present in the denitrified effluent in the solid fraction. It is recommended to minimise the use of polyelectrolyte to that strictly necessary to form the filter plug of the *Depurdisc* (not always possible). The moisture content of the recovered product was also high. The addition of an external P source (*fosfodepur*) led to a higher solid production, contributing to a better formation of the filter plug in the *Depurdisc*. However, priority should be given to the use of an internal source of P (e.g. from biological sludge). It only makes sense to consider dosing an external source of P if the solid material generated is exported outside the current agricultural system. Alternatively, it could be evaluated whether the use of MgO as a source of magnesium would allow working without polyelectrolyte dosing and to what extent the P contained in the biological sludge could be mobilised to increase the efficiency of the MPP recovery process.

Some of the products obtained in the treatment phase have been tested in the field as fertilisers for rain-fed winter crops. In order to assess the effects of the application of organic fertiliser products on crop production and quality, it is necessary to have trials at different locations and/or in different seasons. Although data from one trial in one growing season and two locations are available in this work, with the data and results obtained, some general assessments can be made.

With the application of struvite-K or mixtures of this product with compost and sludge as fertiliser for a spring barley crop, similar or slightly higher yields are achieved than with the reference Mineral treatment. The crop

fertilised with struvite-K achieves a grain protein content as high as that of the Mineral treatment. These values differ significantly from the Control and the Effluent NDN treatment, which have the lowest protein content. The high grain protein value achieved in the struvite-K treatment is probably not directly related to the application of this material, but may be due to the higher N supply in mineral form in the cover crop in this treatment, and in the Mineral treatment. Both the Control treatment and the treatment where NDN effluent is applied have not received mineral nitrogen fertiliser in the top dressing.

In a single crop cycle, when NDN Effluent is applied with a nitrogen criterion, an increase in soil electrical conductivity (EC), as well as in the levels of assimilable sodium and potassium in the soil is observed. Repeated applications of this material, in the medium to long term, can lead to an increase in these parameters above the recommended levels and have marked effects on soil quality, increasing the risk of salinisation-sodification.

The low nutrient concentration of the NDN Effluent means that very high volumes (probably too high in practical terms) have to be applied to achieve the desired nutrient doses. This NDN Effluent had to be applied fractionally (several times in the bottom and several times in the topsoil) so that the soil could absorb the volume applied. The problem may be more serious in the case of agricultural plots with a certain relief and slope, which would cause the displacement of this effluent to the lower parts and, therefore, a high irregularity in the distribution of this effluent in the field.

The presentation of the struvite-K fertiliser supplied for the field trials made it difficult to handle, especially when making homogeneous applications on the plots. The fertiliser is solid, but the structure has a plastic-elastic component that does not allow the material to be broken down into separate particles. For future uses, it would be advisable to obtain a product with a more disaggregated texture.

The extraction of potassium from NDN treatment effluents, combined with an internal use of phosphorus from manure, allows the production of fertiliser products that can be easier to use sustainably (more balanced, more specific...). The results of a campaign, of its application in the field, give rise to good expectations in this respect. However, data from more seasons and soil and climatic situations are needed to draw more robust conclusions.

Leader of the Operational Group

ORGANISATION: GRANGES TERRAGRISA, SL

Coordinator of the Operational Group

ORGANISATION: GRANGES TERRAGRISA, SL

Other members of the Operational Group (grant recipients)

ORGANISATION: COOPERATIVA AGROPECUÀRIA SANT MARTÍ DE TOUS, SCCL

Other members of the Operational Group (not recipients of the grant)

ORGANISATION: University of Girona - LEQUIA

ORGANISATION: IRTA Mas Badia

ORGANISATION: Depuració i Tecnologia de l'aigua, SL (Depurtech)

Geographical area(s) of application

PROVINCE(S)	REGION(S)
Barcelona.	Osona and Anoia.

Girona.	Baix Empordà.

Dissemination of the project (publications, conferences, multimedia, etc.)

DIGITAL BROADCASTING CHANNELS
https://www.udg.edu/ca/udg/detall-noticies/eventid/13108#.X3RS4WAwDR8.twitter

https://www.retema.es/noticia/el-lequia-participa-en-el-desarrollo-de-un-novedoso-proceso-de-recuperacion-de-estruv-oXyAD

https://www.tecnoaqua.es/noticias/20200930/lequia-participa-desarrollo-proceso-recuperacion-estruvita-potasica-estacion-depuradora-aguas-residuales#.YDVReGH0m70

https://www.aguasresiduales.info/revista/noticias/lequia-participa-en-el-desarrollo-de-un-nuevo-proc-5XlMQ

SCIENTIFIC AND TECHNICAL DISSEMINATION ACTIVITIES OF THE PROJECT

The following specialised congresses and/or conferences have been attended:

Company, E.; Farrés, M.; Colprim, J.; Magrí, A. (2021). "Integration of biological treatment of swine manure with phosphorus and potassium recovery as K-struvite". *V Conference of Predoctoral Researchers of the UdG (JoDoc 2021)*. 14-17 June. University of Girona. *(ISBN pendiente)*.
https://twitter.com/JoDoc_UdG/status/1407733011928473603
https://www.youtube.com/watch?v=WLAk1ImY2Gg (minute 3:47:25)

Magrí, A. (2022). "Development of a new process for the recovery of potassium struvite for use as a fertiliser for the treatment of pig slurry". Challenges and Innovations for the Promotion of the Circular Bioeconomy: Information seminar and participatory workshop. 1 February, Webinar, University of Girona.
https://twitter.com/AlimentacioUdG/status/1488434161245429760
https://www.udg.edu/ca/Portals/76/UdGEventsNews/25646/Media/Document/Reptes_i_solucions_en_Bioeconomia_Resums.pdf

Magrí, A. (2021). "Nitrification-denitrification (NDN)". New Developments in Livestock Waste Treatment Technology. PATT Technical Seminar. 30 December, Generalitat de Catalunya, Lleida. https://www.youtube.com/watch?v=B8Qz9jqRQ2E (minute 2:32:00)

Farrés, M.; Company, E.; Colprim, J.; Magrí, A.; Ferrer, J.; González, E.; Domingo, F.; Vallbona, P. (2022). "K-EcoFertilizer: Development of a new process for the recovery of potassium struvite that can be used as a fertiliser for the treatment of pig slurry" PRO-AGRICLOSE: Nutrient management from the farm to the field, Lleida.
https://ruralcat.gencat.cat/documents/20181/9981573/09_k_Ecofertilizer.pdf/54d9f23d-00fa-4e8a-baa0-5051232e8d22

Magrí, A. (2021). "Nitrification-denitrification (NDN)". New Developments in Livestock Waste Treatment Technology. PATT Technical Seminar. 30 December, Generalitat de Catalunya, Lleida. https://www.youtube.com/watch?v=B8Qz9jqRQ2E (minute 2:32:00)

Farrés, M.; Company, E.; Colprim, J.; Magrí, A.; Ferrer, J.; González, E.; Domingo, F.; Vallbona, P. (2022). "K-EcoFertilizer: Development of a new process for the recovery of potassium struvite that can be used as a fertiliser for the treatment of pig slurry" PRO-AGRICLOSE: Nutrient management from the farm to the field, Lleida.
https://ruralcat.gencat.cat/documents/20181/9981573/09_k_Ecofertilizer.pdf/54d9f23d-00fa-4e8a-baa0-5051232e8d22

Technical visit "*Esperienze a confronto sulla produzione di ferlizzanti rinnovabili e loro utilizzo agronomico*". La Tallada d'Empordà, 26 and 27 April 2022

A group of about forty Italian (Emilia Romagna) producers, livestock farmers and technicians came on a technical trip to Catalonia where they visited different centres and farms in relation to the treatment of livestock manure and the agricultural use of effluents. A visit was made to IRTA-Mas Badia, where the K-EcoFeRtilizer Operational Group was explained, and to the trial plot at La Tallada d'Empordà (Baix Empordà). The following day, they visited the facilities of the struvite-K pilot plant in Sant Bartomeu del Grau (Osona).

Technical conference "RECOMEX. Results of trials and innovations in extensive winter crops". Calaf, 2 September 2022
At this annual event, innovations in the field of field crops and results of various activities and projects are presented. Within this framework, the conference documentation includes a poster with the objectives, tasks carried out and main results obtained in the K-EcoFeRtilizer Operational Group.

Five students from the UdG (academic years 2020-2021 and 2021-2022), will have completed their Bachelor's Degree Final Projects (Bachelor's degree in Biotechnology (2), Bachelor's degree in Environmental Sciences (1) and Double Bachelor's Degree in Biology and Environmental Sciences (1)) and one student has completed his Master's Degree Final Project (Master's Degree in Water Resources Science and Technology) within the framework of the K-EcoFeRtilizer project.

Project website

http://www.lequia.udg.edu/ca/difusio/noticies/item/2796-ecokferrtilizer.html

More information on the project

PROJECT DATES	TOTAL BUDGET
Start date (month-year): July 2020	Total budget: €190,429.00
Completion date (month-year): September 2022	DACC funding: €72,363.02
Current status: Completed	EU funding: €58,709.62
	Own funding: €53,895.00

With funding from:

Project funded through Operation 16.01.01 (Cooperation for Innovation) through the Catalan Rural Development Programme 2014-2022.

Order ARP/133/2017 of 21 June, approving the regulatory bases for grants for cooperation for innovation by promoting the creation of European Association for Innovation operational groups in the areas of agricultural productivity and

sustainability and the execution of innovative pilot projects by those groups, and Resolution ARP/1531/2019, of 28 May, announcing the call for the grant.

Generalitat de Catalunya
Departament d'Acció Climàtica, Alimentació i Agenda Rural

Fons Europeu Agrícola de Desenvolupament Rural:
Europa inverteix en les zones rurals