

# RE-LIVE WASTE project: Advancing pilot-scale nutrient recovery from livestock wastewater by struvite crystallization

M. G. Antoniou<sup>1</sup>, N. Kallikazarou<sup>1</sup>, E. Constantinide<sup>2</sup>, L. Koutsokeras<sup>3</sup>, G. Constantinides<sup>3</sup>, G. Armenis<sup>4</sup>

<sup>1</sup>Department of Chemical Engineering, Cyprus University of Technology, P.C 3036, Limassol, Cyprus

<sup>2</sup>Department of Environment, Ministry of Agriculture, Rural Development and Environment, P.C 2025, Strovolos, Nicosia, Cyprus

<sup>3</sup>Department of Mechanical Engineering and Materials Science and Engineering, Cyprus University of Technology, 3036, Limassol, Cyprus

<sup>4</sup>Nicos Armenis and Sons LTD, Monagroulli, 4524 Lemesos, Cyprus

Keywords: struvite, nutrient recovery, wastewater, phosphorus, pilot plants

Corresponding author email: [maria.antoniou@cut.ac.cy](mailto:maria.antoniou@cut.ac.cy)

## 1. Introduction

The Mediterranean region, is characterized by intensive cattle and pig livestock farming, producing large amounts of waste and generating greenhouse gases (GHGs) emitted into the atmosphere and nitrates leached in groundwater. Beyond the aforementioned environmental problems, the poor manure management also leads to eutrophication of surface water, leaching of pathogens into groundwater, buildups of excess nutrients and heavy metals in soil, and destruction of fragile ecosystems such as wetlands (Casasús et. al., 2012).

With agricultural production expected to increase by 60% till 2050 and phosphorus (an important nutrient for plant growth and component in fertilizers) resources constantly declining, it is imperative to find alternatives to industrial P-fertilizers so that food availability and security are sustained.

Nutrient recovery (N and P) from livestock wastewater through struvite crystallization/precipitation could be a sustainable solution to alleviate this problem. Struvite is a crystalline mineral, which constitutes a slow-release high-value organic fertilizer, containing equal molar concentrations (1:1:1) of magnesium, ammonium, and phosphate (struvite  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), that can be recovered from nutrient-rich wastewater streams (Le Corre et al., 2009).

The Interreg MED project RE-LIVE WASTE aims to examine innovative solutions for livestock waste management in Cyprus, Italy, Spain, and the Federation of Bosnia and Herzegovina. In order to do so, four demonstrative struvite precipitation plants were constructed and operated (one in each region) to convert livestock waste into high-value commercial organo-mineral fertilizers (struvite).

## 2. Materials and Methods

Each pilot plant applied different processes on different types of livestock waste for the precipitation of struvite. The final products from each pilot are currently being evaluated for their chemical characteristics and quality, environmental footprint (Life-cycle assessment analysis), and production cost (Cost benefit analysis). Specifically, each pilot investigated different effluents (treated and untreated, slurries from cow, pig, or mixed effluent), pre-treatments prior to struvite crystallization (SC), and operating conditions during struvite crystallization.

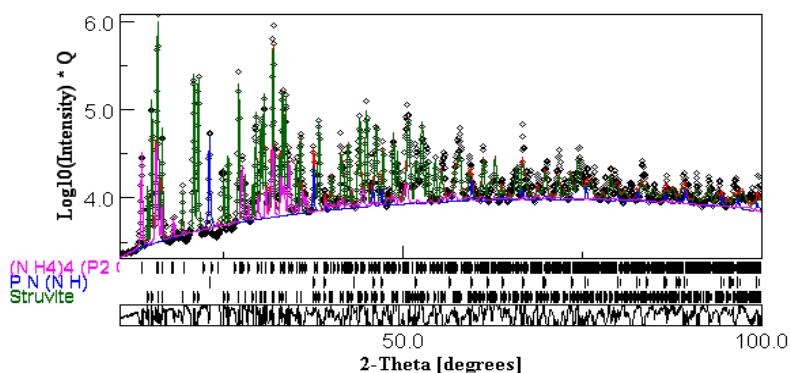
In the case of Cyprus, a pilot plant treating livestock waste was already constructed because of the LIFE Livestock Waste Project (LIFE12 ENV/CY/000544). The pilot was relocated to Monagroulli at Nicos Armenis and Sons Ltd farm, re-operated, and the struvite crystallization reactor was upgraded from 50 L to 250 L, while a phosphoric pump was added as well to achieve the optimal solution molar ratio of  $\text{Mg}^{2+}$ :  $\text{P-PO}_4^{3-}$ :  $\text{N-NH}_4^+$ .

The produced struvite in the pilot was analysed for its quality characteristics (TN,  $\text{NH}_4^+$ ,  $\text{P-PO}_4^{3-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , organic C, water content). Detection of heavy metals was performed through X-ray fluorescence (XRF), while its purity was assessed through X-ray diffraction (XRD). Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) was used to determine the morphology of the precipitate (size, shape), and its elemental composition. Finally, the precipitate was evaluated for its compliance with the EU legislative requirements for fertilizers (Regulation (EU) 2019/1009).

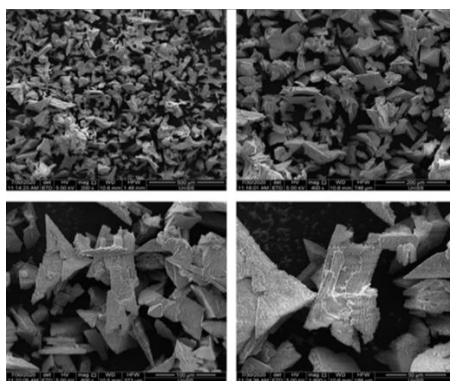
## 3. Results and Discussion

The pilot in Cyprus was treating anaerobically digested effluent (ADE) from mixed waste (50% pig slurry, 25% cheese whey, and 25% chicken manure, with small additions of fruit waste and barley), which was then filtered through filter bags (FB) and ultra-filtration ceramic membranes (UF), prior to struvite precipitation/crystallization. Bench scale experiment with the same matrix allowed to optimize the process in terms of added molar ratios of  $\text{Mg}^{2+}$ ,  $\text{P-PO}_4^{3-}$ , and  $\text{N-NH}_4^+$ , pH, and contact time. It was decided that the 1.2 to 1.5 molar ratio of  $\text{Mg}^{2+}$  to  $\text{P-PO}_4^{3-}$  and  $\text{N-NH}_4^+$  was the optimum for struvite precipitation. The obtained material was dried at 40°C (to avoid phase change) and was analyzed for its chemical characteristics, purity, and morphological properties.

XRD analysis on the struvite produced in the Cypriot plant had a purity over 90 wt % as indicated in Figure 1. Moreover, SEM images (Figure 2) exhibit the irregular shape of struvite crystals with their size ranging between 80 to 200  $\mu\text{m}$ . The internal side of these agglomerates is characterized by rectangular-shaped blocks of around 20  $\mu\text{m}$  x 5  $\mu\text{m}$ . Our results are similar with studies of the cited literature where struvite was produced from different matrices (Huang et al., 2011; Zhang et al., 2014; Xiao et al., 2018), though the struvite purity from our precipitates was higher. This proves that the conditions that we chose to apply were indeed the optimum and we were able to successfully transfer the operating conditions from bench-scale to pilot-scale. Finally, further analysis on struvite obtained from the Cyprus pilot, proved that it did not contain pathogens and carcinogens, and heavy metals were within the acceptable regulatory limits, hence making it safe for use in gardening and crops.



**Figure 1:** X-ray diffractogram of precipitates (struvite purity 92.5 wt%)



**Figure 2:** SEM images of the struvite precipitates.

#### 4. Conclusions

This study demonstrated the successful transfer of bench-scale operating conditions to the pilot unit with the subsequent production of high-quality struvite. It is important to note that the produced struvite was safe for use in crops since it did not contain pathogens, heavy metals, and carcinogens (possibly because of the filtering of the treated effluent through the UF ceramic membranes prior to struvite crystallization). Based on the above, it is safe to state that nutrient recovery from livestock wastewater through struvite crystallization, can play a key role in sustainable growth and food security maintenance.

#### 5. Acknowledgements

The authors are grateful to the Interreg Mediterranean project RE-LIVE WASTE which is co-financed by the ERDF. N.K. is thankful for the half tuition waiver from the internal funds of the CUT and the Cyprus State Scholarships Foundation for the full doctoral tuition scholarship. The authors are grateful to Dr. Sebastiano Garroni of the University of Sassari, Italy for the XRD and SEM-EDS analysis performed on the precipitate produced from the pilot.

#### 6. References

1. Casasús, I., Rogosić, J., Rosati, A., Stoković, I., Gabiña, D., 2012. Animal farming and environmental interactions in the Mediterranean region, *EAAP Scientific Series*, 131, pp. 276. Available at: <https://doi.org/10.3920/978-90-8686-741-7>. Last accessed: 25/02/2021.

2. Huang, H., Xu, C., Zhang, W., 2011. Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology. *Bioresour. Technol.*, 102, 3, pp. 2523–2528. Available at: <https://doi.org/10.1016/j.biortech.2010.11.054>. Last accessed: 25/02/2021.
3. Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S. A., 2009. Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Crit Rev Environ Sci Technol.*, 39, 6, pp. 433-477. Available at: <https://doi.org/10.1080/10643380701640573>. Last accessed: 25/02/2021.
4. Zhang, T., Fang, C., Li, P., Jiang, R.F., 2014. Application of struvite process for nutrient recovery from anaerobic digesters of livestock wastewater. *Environ. Prot. Eng.*, 40, 3, pp. 29-42. Available at: <https://www.infona.pl/resource/bwmeta1.element.baztech-6e9c15fd-af97-49d2-81a4-36f3651f535a>. Last accessed: 25/02/2021.
5. Xiao, D., Huang, H., Zhang, P., Gao, Z., Zhao, N., 2018. Utilizing the supernatant of waste sulfuric acid after dolomite neutralization to recover nutrients from swine wastewater. *Chem. Eng. J.*, 337, pp. 265–274. Available at: <https://doi.org/10.1016/j.cej.2017.12.097>. Last accessed: 25/02/2021.