Recovery of Phosphorus using a Low-grade Magnesium Oxide (industrial by-product) as an alternative Magnesium Source. The MAGNYFOS Project

A.Lopez[1], J. Gomez[1], V. Aguilar[2], S. Astals[2] , J.M Chimenos [2], K. Olaciregui-Arizmendi[3], B. Elduayen-Echave[3], E., Ayesa[3], M. Guembe[4] and I. Garcia[4]

[1] NILSA, Navarra de Infraestructuras Locales S.A., Av. Barañáin 22, 31008 Pamplona, Spain
[2] Universidad de Barcelona, C/ Martí i Franqués 1, 08028 Barcelona, Spain.
[3] CEIT-BRTA, Manuel Lardizabal 15, 20018 Donostia / San Sebastián, Spain
[4] MAGNA, Zubiri, Spain

Abstract:

The MAGNYFOS project aims to use magnesium by-products for the recovery of phosphorus in wastewater treatment plants (WWTPs) through the precipitation of struvite. This national project has developed and optimised laboratory-scale operating conditions for the precipitation of struvite. Afterwards, the scaling was carried out on two pilot-plants, where the experimental phase was done to improve hydraulic and design conditions. The process modelling is being adjusted and validated with the experimental results. The three phases have been essential to understand and validate the struvite precipitation process, using a by-product that is 10 times cheaper than $MgCl_2$. Furthermore, agricultural application trials are also being carried out with some of the products obtained. The main results show that it is possible to achieve up to 80% of phosphorus recovery with a P:Mg molar rate of 1:2. The formation of phosphorus as struvite is favoured when the calcium concentration is low and the pH values are 8.2-8.5. The struvite content in the precipitate is greater than 75%; its formation in a fluidized bed reactor was not influenced by the recirculation flow rate.

Keywords: Low-grade Magnesium oxide; Struvite; circular economy

1. INTRODUCTION

The European Union has classified phosphorus (P) as a critical raw material due to its scarcity and price. The need to recover P shows that wastewater treatment plants (WWTP) could provide 15-20% of global demand (Peng et al.,2018) and reduce the discharge of high P concentrations. Struvite precipitation needs the addition of a source of magnesium (Mg) and an alkali reagent. Magnesium chloride ($MgCl_2$) or magnesium oxide (MgO) are the most common Mg sources used, but their high prices limit the process economically.

The use of a cheap source of magnesium is presented in the MAGNYFOS project. Low-grade magnesium oxide (LG-MgO), obtained from the calcination process of natural magnesite was used for this purpose (Romero-Güiza et al., 2015) as a Mg source and an alkali reagent. The MAGNYFOS aims to design, develop and validate in a real environment technological solution that allows the efficient recovery of P while revaluing industrial by-products of MgO.

The main objective was to study the behaviour of different LG-MgO in the process of struvite precipitation related with the addition of these by-products. The results obtained at laboratory-scale and semi-industrial scales were combined to carry out the modelling and simulation tools.

2. MATERIALS AND METHODS

2.1 Laboratory-scale

The LG-MgO by-products used were provided by Magnesitas Navarras, S.A. Three LG-MgO were characterised by X-ray Fluorescence (XRF) X-ray diffraction (XRD) thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS), and reactivity was determined with the citric acid test.
Two supernatants of mesophilic anaerobic digestion were collected from two WWTP. The supernatants were obtained by centrifuging the effluent of the digesters. The pH and concentrations of Mg, P, ammoniacal nitrogen and calcium were measured.
The experimental steps include the study of the effect of the pH, P:Mg molar ratio and hydraulic conditions in struvite precipitation.

2.2 Pilot scale
The location of the semi-industrial plant is at the wastewater treatment plant of Tudela (Navarre). Two pilot plants have been used, one of 70L and another one of 4000L (figure 1).

Figure 1. Semi industrial plants a) 70L capacity; b) 4000L capacity

These two pilot plants have been used for over a year. Several experimental campaigns have been conducted, focused on the inlet water quality, the addition of the LG-MgO or the pH control of the process. LG-MgO was added once a day and pH was controlled and adjusted with NaOH in some tests. Physico-chemical parameters were measured in the influent and the effluent: concentration of ammonia (mg/l), phosphates (mg/l), magnesium (mg/l), calcium (mg/l) and pH. Some of the products obtained were characterised to determine the percentage of struvite.

2.3 Modelling
The precipitation model was developed in WEST-DHI simulation platform. The model was constructed following Plant Wide Model (PWM) methodology. Therefore, it is compatible with the simulation of the rest of the unit processes in a WWTP. In the model, nine different solid compounds and different transformations were considered. The model incorporates saturation index (SI) calculations for each solid compound in each time step, which were the driving force of the precipitation and kinetics, including nucleation and growth. Results of laboratory-scale were considered to adjust and validate the model.

3. RESULTS AND DISCUSSION

3.1 Laboratory-scale
The MgO content in the LG-MgO varied from 42% to 56%. The LG-MgO provided magnesium ions and increased the pH. The P:Mg molar ratios of 1:1 and 1:2 favoured struvite precipitation (Fig. 2). The percentage of phosphate precipitated was between 89-97% at a P:Mg molar ratio of 1:2 (Fig. 3), depending on the LG-MgO reactivity. The struvite content in the precipitated

solid depended mainly on the added molar ratio and not on the recirculation flow rate or feed position.

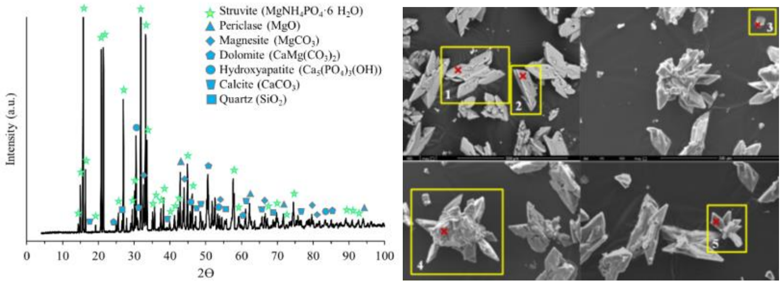

Figure 2. XRD of the precipitate obtained using LG-MgO_A and a P:Mg molar ratio of 1:2. And Scanning electron micrograph (1) hopper, (2) polyhedral, (3) partly-dissolved LG-MgO particle, (4) agglomeration of polyhedral on LG-MgO particles, and (5) agglomeration of polyhedral.

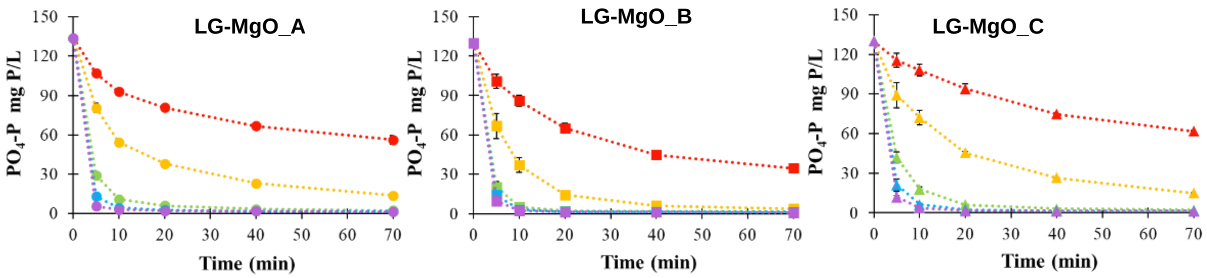

Figure 3. Phosphorus precipitation in the anaerobic digestion supernatant. P:Mg molar ratio of (■) 1:1, (■) 1:2, (■) 1:4, (■) 1:6, (■) 1:8.

Some of the results obtained during the experimental campaign have been published recently (Aguilar-Pozo et al., 2023).

3.2 Pilot scale

The results show a recovery more of than 80% with the supernatant of the sludge line of the treatment plant with a P:Mg ratio of 1:2 and 1:3 and with pH adjustment. However, the high concentration of calcium in the treated stream interferes with the struvite precipitation process, although it does not reduce the phosphorous recovery rate. In addition, nutrient release tests are being carried out at the laboratory-scale and in agricultural fields. Finally, the results have made it possible to determine the implementation of this technology on a real scale in the next expansion of the wastewater treatment plant.

3.3 Precipitation model

Some of the preliminary results of the model that is being validated with the experimental test at the laboratory-scale are shown in Figure 4. On the other hand, after calibration, the model is being validated at the global level of the WWTP. At the moment, the biological model of the plant and the precipitation model are not linked, but as both are developed using the PWM methodology, this will be done soon. To date, the water line of the WWTP has been calibrated (Fig. 5).

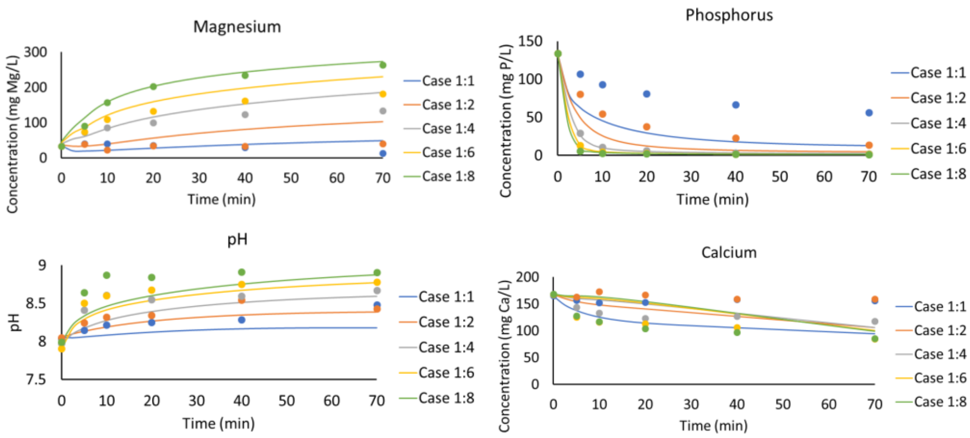

Figure 4. Evolution of physico-chemical parameters at experimental test at laboratory-scale and with the model

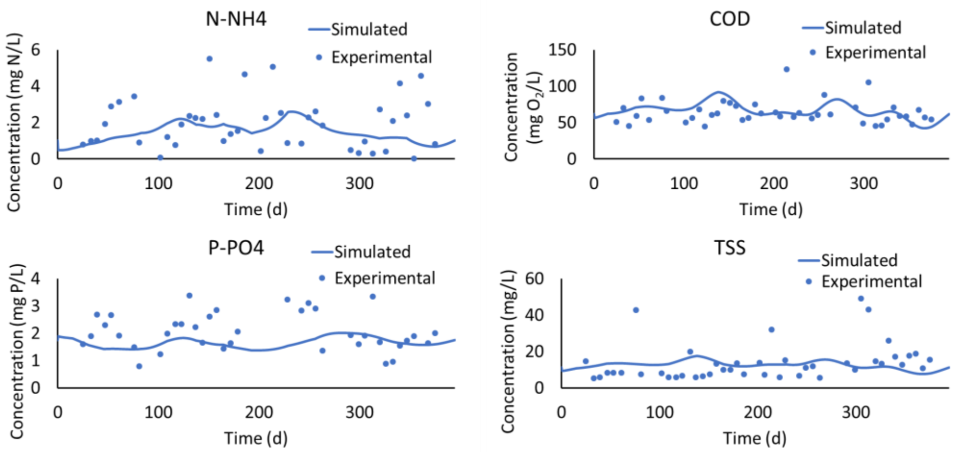

Figure 5. Calibration of the water line of the WWTP

CONCLUSIONS

-The LG-MgO in addition to providing magnesium raises the pH in the reactor, which means lower reagent costs for P recovery to take place.

-The reactor designed with recirculation allows recoveries of more than 80% when LG-MgO was dosed once a day.

-The developed precipitation model can reproduce correctly the data obtained in the laboratory experiments.

The next steps of the project involve the technical-economic evaluation and the study of the possibility of continuous dosing of LG-MgO in suspension.

References

Aguilar-Pozo, V.B., Chimenos, J.M., Elduayen-Echave, B., Olaciregui-Arizmendi, K., López, A., Gómez, J., Guembe, M., García, I., Ayesa, E., Astals, S., 2023. Struvite precipitation in wastewater treatment plants anaerobic digestion supernatants using a magnesium oxide by-product. Sci Total Environ **890**, https://doi.org/10.1016/j.scitotenv.2023.164084

Romero-Güiza, M.S., Tait, S., Astals, S., del Valle-Zermeño, R., Martínez, M., Mata-Alvarez, J., Chimenos, J.M., 2015. Reagent use efficiency with removal of nitrogen from pig slurry via struvite: A study on magnesium oxide and related by-products. Water Res **84**, 286–294. https://doi.org/10.1016/j.watres.2015.07.043

Peng L., Dai H., Wu Y., Peng Y., Lu X., 2018. A comprehensive review of phosphorus recovery from wastewater by crystallization processes. Chemosphere **197**, https://doi.org/10.1016/j.chemosphere.2018.01.098