New insights into phosphorus recovery from mixed waste through struvite crystallization

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1. Introduction

Phosphorus (P) is an essential nutrient for crop development and is thus commonly applied as fertilizer to maintain agricultural production. However, P-mineral fertilizers are manufactured using phosphate rocks which are limited, non-renewable resources. Furthermore, large amounts of organic waste are still inefficiently treated and are discharged as pollutants, resulting in eutrophication of surface waters, depletion of the quality of groundwater and air, as well as soil acidification.

Therefore, taking into account that the global demand for fertilizers is growing, phosphorus recovery from wastewater through struvite crystallization (SC) is a necessity to address future P-scarcity and food security, as well as to utilize unexploited organic waste as a valuable resource.

Struvite is a crystalline mineral, which constitutes a slow-release fertilizer, containing an equimolar amount (1:1:1) of magnesium, ammonium, and phosphate ($MgNH_4PO_4 \cdot 6H_2O$) that can be recovered from rich in nutrient effluents.

The aim of this study is to provide new insights into the synergistic effect of the optimum operational parameters for struvite crystallization from mixed livestock and cheese whey wastewater. To the best of our knowledge, this is the first study that investigates the utilization of anaerobically treated mixed livestock and cheese whey wastewater for nutrient recovery through struvite precipitation.

2. Materials and Methods

A series of bench-scale, batch, struvite crystallization experiments were performed by utilizing as starting material treated effluent from the CUT pilot unit installed at Monagroulli. The treated effluent was an anaerobically digested effluent (ADE) from mixed waste (50% pig slurry, 25% cheese whey, and 25% chicken manure, and rarely fruit waste and barley), that was filtered through filter bags (FB) and ultra-filtration ceramic membranes (UF).

Initially, an integrated multi-level single-factor evaluation was performed on the following factors: solution pH and molar ratio of Mg^{2+}:P-PO_4^{3-}: N-NH_4^+, magnesium source (pure and alternative), crystal retention time, temperature, and struvite seeds addition. Afterwards, a two- and three-factor evaluation of the optimum previously investigated single factors was carried out, to elucidate their synergistic effect on struvite precipitation and quality characteristics of the precipitate. Moreover, the effect of pre-treatment of the anaerobically treated and filtered effluent through filter bags, with oxalic acid and hydrogen peroxide (HP), was investigated. Finally, the effect of acidification (with nitric acid) on MgO slurry was assessed.

The produced struvite from each process was analysed for its quality characteristics (TN, NH_4^+, P-PO_4^{3-}, Ca^{2+}, Mg^{2+}, organic C, water content). Detection of heavy metals was performed though X-Ray Fluorescence (XRF), while its purity was assessed through X-Ray Diffraction (XRD). Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM-EDX) 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

Two different types of matrices were utilized in the bench-scale experiments for struvite precipitation/crystallization. Both matrices were obtained following anaerobic digestion of livestock waste. In the first one, the anaerobically treated effluent was filtered through filter bags (matrix 1), while in the second one the effluent was passed through ultra-filtration ceramic membranes as well (matrix 2). The quality characteristics of both effluents are summarized in Table 1. Filtration through filter bags and ultra-filtration ceramic membranes drastically changed the quality characteristics of matrix 2, resulting in approximately 50% reduction of COD and

95% of TSS. This is an extremely important finding, as their initial values (matrix 1) have been reported in the literature that can greatly inhibit struvite precipitation and crystallization (Capdevielle et al., 2015; Ping et al., 2016; Wang et al., 2016).

In addition, matrix 2 was analysed for its content to carcinogenic compounds that belong to the groups of polyaromatic hydrocarbons and polychlorinated biphenyls, and all tested congeners were below the method detection limit. Based on the above, though P-PO_4^{3-} and N-NH_3 were reduced as well after the effluent went through the ceramic membranes, it was decided to use matrix 2 primarily for our experiments. The optimum operational conditions (in terms of molar ratios, pH, and contact time) defined for matrix 2 were applied to matrix 1 for comparison. In addition, alternative treatments to UF were applied in matrix 1 including oxidation with oxalic acid and hydrogen peroxide.

The obtained precipitates from all experiments were analysed for their chemical characteristics, struvite purity (XRD), morphology and elemental composition (SEM-EDX). Overall, high purity (more than 90%) struvite precipitates were obtained. XRD analysis using Reference Intensity Ratio (RIR) method, confirmed that struvite was the main phase in all the tested operational parameters. It is important to note, that compared with studies from the cited literature on struvite precipitation where raw swine effluents were used as matrix (Jordaan et al., 2010; Liu et al., 2011), pre-treatment of the livestock waste and the applied operational conditions resulted in higher efficiency on struvite precipitation. Finally, XRF analysis confirmed that heavy metals were within acceptable regulatory limits in most of the struvite precipitates, hence the struvite produced met the requirements listed for solid organo-mineral fertilizers of the Regulation EU 1009/2019.

Table 1: Compositions of FB ADE (matrix 1) and UF&FB ADE (matrix 2). Range and average from the different sampling dates, and percentage relative standard deviation from three replicate measurements.

Parameters	FB ADE (matrix 1)			UF&FB ADE (matrix 2)		
	Range	Average	RSD%	Range	Average	RSD%
pH (26.5)	8.78-8.80	8.8	1.1	8.80-8.85	8.83	1.2
Cond (mS/cm)	25-25.1	25	1.45	23.5-24.2	24	1.5
Mg^{2+} (mg/L)	214-225	218	1.65	124-168	144.5	1.6
P-PO_4^{3-}(mg/L)	82-90	85	0.8	30-38	33	0.5
N-NH_3 (mg/L)	2128-2300	2180	3.2	1092-1680	1265	4.3
Ca^{2+}(mg/L)	300-320	305	2.7	280-300	287	1.8
COD (mg/L)	6950-7080	7000	1.9	3090-3260	3150	2.0
TN (mg/L)	3000-3080	3020	2.0	2600-2740	2653	1.9
TP (mg/L)	170-181	172	4.3	32-40	35.5	4.8
TSS (mg/L)	2000-2150	2090	2.4	95-145	118	4.2

4. Conclusions

Preliminary data from our bench-scale studies indicated that the pretreatment of the anaerobically digested effluent (ADE) enhanced the quality and purity of the obtained struvite precipitates.

The next step will be to confirm the transferability of these results in the struvite crystallization reactor of the pilot and perform analyses on the pilot struvite for the presence of pathogens, and carcinogens (PAHs, PCBs) and agronomically evaluate them to prove that they comply with the requirements of the Directive 2008/98/EC, so that struvite precipitates are no longer perceived as waste.

Finally, most of the precipitates in this study complied with the requirements of the product function category PFC 1.B.I, i.e. solid organo-mineral fertilizer of the Regulation EU 1009/2019 for CE marked fertilisers, thus rendering them a valuable resource. In summary, our results unveiled that nutrients recovery from livestock wastewater through struvite crystallization is the key to sustainable growth and food security maintenance.

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6. References

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