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Optimum technical operating conditions and treatments for the production of high-purity struvite fertilizer from livestock wastewater.

KALLIKAZAROU N.I.[1], KOUTSOKERAS L.[2], CONSTANTINIDE E.[3], CONSTANTINIDES G.[2], and ANTONIOU M.G.[1,*]

[1]Department of Chemical Engineering, Cyprus University of Technology, P.C 3036, Limassol, Cyprus.
[2]Department of Mechanical Engineering and Materials Science and Engineering, Cyprus University of Technology, P.C 3036, Limassol, Cyprus.
[3]Department of Environment, Ministry of Agriculture, Rural Development and Environment, P.C 2025, Strovolos, Nicosia, Cyprus.

*corresponding author:
e-mail: maria.antoniou@cut.ac.cy

Abstract Inadequate treatment of nutrient-rich waste streams originating from human activities such as agriculture, animal breeding, urbanization, and industrialization causes an array of environmental problems. Among them are eutrophication of surface water, nutrients and pathogens leaching into groundwater, soil acidification, and destruction of fragile ecosystems. Moreover, food security will be jeopardized, since industrial P-fertilizers are manufactured using phosphate rocks which is non-renewable resource that is constantly depleting. Nutrient recovery (N and P) from wastewater matrices could be a sustainable solution to mitigate 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 $MgNH_4PO_4{\cdot}6H_2O$), that can be recovered from nutrient-rich wastewater streams. This presentation will focus on the optimum operating conditions that should be applied, in order to produce high-quality struvite fertilizer from livestock wastewater. The tested experimental conditions for struvite crystallization included: solution pH, molar ratio Mg^{2+}: $N\text{-}NH_4^+$: $P\text{-}PO_4^{3-}$, temperature, added Mg-sources, retention time, and seeding-material addition. Moreover, the effect of matrix composition is discussed. The produced struvite from each process was analyzed for its quality and purity, which was higher than 90%, and in most of the cases the precipitate was complying with the legislative requirements for fertilizers.

Keywords: recovery, wastewater, fertilizer, struvite, nutrient.

1. Introduction

Large amounts of livestock waste are generated in EU28 per year (around 1400 million tonnes), which are expected to increase due to the expected increase in world population and meat consumption (changes in consumer dietary preferences) (FAOSTAT, 2020). Unfortunately, more than 90% of the produced livestock waste is insufficiently treated. Most common practice is their disposal in agricultural land, with harmful effects on the environment such as aggravating soil fertility (EEA, 2019) and greenhouse gas emissions (EEA, 2021). Polluted soils can be a steady release source of toxic waste and leaching of contaminants including dust particles, bacteria, endotoxins, and organic contaminants (Mawdsley J.L. et al., 1995). These runoffs can then flow into water bodies resulting in pollution of surface (eutrophication) and groundwater, thus affecting biodiversity, and deteriorating water quality respectively (FAO, 2017).

Simultaneously, biowaste (food waste, agricultural waste, etc.) is the largest contributor (34%) to municipal waste in the EU. In 2017, the EU-28 generated 88 million tonnes of biowaste, of which 60% was food waste. Currently, only 19% of biowaste is anaerobically digested (EEA, 2020), while 60% of it is disposed in landfills and is incinerated, thus losing valuable nutrients (Chen C. et al., 2020; EEA, 2020), occupying and worsening a significant area of land (landfill leachates), attracting flies during decomposition, and emitting greenhouse gases (Slorach P.C. et al., 2020). Consequently, all these environmental problems may cause adverse health effects, i.e., cancer, respiratory problems, and birth defects.

In addition, annual world consumption of phosphorus fertilizers is expected to increase, to sustain the increased food demand and ensure food security. However, P-industrial fertilizers are manufactured using phosphate rocks which are non-renewable resources and are constantly depleting (USGS, 2020). It is noteworthy that phosphate rocks are on the EU list of the critical raw materials since 2014, and they are still on the new list of 2020.

Therefore, this nutrient imbalance is an emerging major environmental and socioeconomic global challenge. Nutrient recovery (N and P) from livestock and biowaste matrices, could be a sustainable solution to alleviate the abovementioned problems, aiming towards waste valorization, circular economy, and food security. 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 was to investigate the optimum experimental conditions that need to be applied for struvite crystallization from mixed livestock waste and bio-waste. To the best of our knowledge, this is the first study that explores the use of anaerobically treated mixed livestock (chicken manure and pig slurry) and bio-waste (cheese whey, fruit, and barley waste) for nutrient recovery through struvite precipitation.

2. Materials and Methods

The treated effluent used at the bench-scale struvite precipitation experiments was obtained from the CUT pilot unit, which is located at Monagroulli in Limassol, Cyprus. The obtained effluent resulted from anaerobically treating mixed waste comprising of 50% pig slurry, 25% cheese whey, and 25% chicken manure, and rarely fruit waste and barley; that was then filtered through filter bags (FB) and ultra-filtration ceramic membranes (UF).

Initially, multi-level single-factor experiments were carried out in triplicates, to evaluate the effect of the various parameters on the quality of the struvite precipitates. Among them were the solution pH, the molar ratio of Mg^{2+}:P-PO_4^{3-}: N-NH_4^+, magnesium sources (pure and from recycled materials), contact retention time, temperature, and struvite seeds addition.

Then, in order to demonstrate the combined effect of the optimal previously investigated single factors on struvite precipitation and on the quality characteristics of the precipitates, a two- and three-factor evaluation was performed.

The produced struvite precipitates from the experiments described above were analysed for their quality characteristics by measuring TN, NH_4^+, P-PO_4^{3-}, Ca^{2+}, Mg^{2+}, organic C, and water content. The levels of heavy metals in the struvite precipitates were also determined by X-Ray Fluorescence (XRF), while the crystallinity and purity of the precipitates was evaluated by X-Ray Diffraction (XRD). Finally, the precipitates were assessed for their compliance with the EU legislative requirements for fertilizers (Regulation (EU) 2019/1009).

3. Results and Discussion

A series of bench-scale batch struvite crystallization experiments were performed using two different matrix types. Both matrices used in the experiments were obtained after the anaerobic digestion of a mixture of livestock waste and bio-waste. Matrix 1 was the anaerobically digested effluent (ADE), which was then filtered through filter bags (FB), while for matrix 2, the effluent of matrix 1 was also passed through ultra-filtration ceramic membranes (UF). Table 1 displays the quality characteristics of both matrices. Filtration through filter bags and ultra-filtration ceramic membranes significantly reduced chemical oxygen demand (COD) by 50% and total suspended solids (TSS) by 95%. Application of the additional filtration step through ultra-filtration ceramic membranes, significantly reduced the concentration of a lot of components that are known to act as inhibitors in the precipitation and crystallization of struvite (Capdevielle A. et al., 2015; Ping Q.et al., 2016; Wang Y. et al., 2016;). Moreover, all the tested congeners of polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs), which are known carcinogenic compounds, were below the method detection limit in matrix 2. In view of the above, it was decided to use matrix 2 mainly for our experiments, although P-PO_4^{3-} and N-NH_3 were also reduced after the filtration through the UF ceramic membranes.

Quantitative XRD analysis using Reference Intensity Ratio (RIR) method, confirmed that struvite was the main phase in all the tested operational parameters. High struvite purity (more than 90%) was achieved in most of the precipitates. Moreover, the obtained precipitates from all the experiments were analysed for their chemical characteristics. In addition, XRF analysis showed that the detected heavy metals in most of the struvite precipitates, were within the acceptable regulatory limits. Therefore, the struvite produced met the requirements listed for solid organo-mineral fertilizers of the Regulation EU 1009/2019. It is noteworthy to state, that pre-treatment of the mixed waste and the applied operational conditions led to higher efficiency in the precipitation of struvite, compared with struvite precipitation studies where raw or anaerobically digested effluents of swine or mixed waste were used as matrix (Cerillo M. et al., 2015; Jordaan E.M. et al., 2010; Liu Y.H. et al., 2011).

Table 1: Compositions of FB ADE (matrix 1) and UF&FB ADE (matrix 2) 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)	
	Average	RSD%	Average	RSD%
TSS (mg/L)	2090	2.4	118	4.2
COD (mg/L)	7000	1.9	3150	2.0
N-NH_3 (mg/L)	2180	3.2	1265	4.3
TN (mg/L)	3020	2.0	2653	1.9
Mg^{2+} (mg/L)	218	1.65	144.5	1.6
P-PO_4^{3-}(mg/L)	85	0.8	33	0.5
Ca^{2+}(mg/L)	305	2.7	287	1.8
TP (mg/L)	172	4.3	35.5	4.8

4. Conclusions

Overall, the presented results from our bench-scale batch struvite crystallization studies indicated that the pretreatment of the effluent obtained from the anaerobically digested mixture of livestock waste and bio-waste, substantially enhanced the quality and purity of the obtained struvite precipitates.

Moreover, 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. Therefore, the valuable nutrients from the vast available amounts of mixed waste have the potential to be utilized to the maximum, turning them into useful products.

To sum up, our results provided insights into the potential of nutrients recovery from mixed livestock and bio-waste through struvite crystallization, thus closing the loop of mixed waste valorization and food security maintenance.

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