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Recovery of Potassium-Rich Struvite in a Pig Farm Downstream a Nitrogen Removal Treatment Plant: Technological, Agricultural and Economic Assessment

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Abstract

Simultaneous recovery of phosphorus (P), potassium (K), and magnesium (Mg) as precipitated phosphate salt (PPS) was assessed (K-struvite and hazenite included) in a pig farm downstream a nitrification-denitrification unit. The precipitation process was addressed using denitrified effluent (DE) and waste sludge (WS) purged from the bioreactor. For DE, the inherent unbalanced Mg:K:P molar ratio (1.4:9.5:1.0; 1.6 g K/L) led to poor K recovery ($\leq 15\%$) if considering P as the limiting element. By considering K as limiting, the supply of external sources of Mg and P (final Mg:K:P as 1.0:0.5:1.0) allowed the recovery of most of the K available. For WS, a selective pretreatment with oxalic acid resulted in an available Mg:K:P ratio of 0.8:1.2:1.0. Risk of interference by free calcium will exist if the operational parameters are not optimized, thus constraining the recovery of K ($\leq 51\%$). A fertilization field trial demonstrated the fertilizing value of the recovered PPS with respect to a mineral fertilizer, and the increased risk of soil salinization under a reiterative application of processed DE. Scenarios without extra addition of nutrients will introduce an enhanced handling in the current nutrient management planning of the pig farm. On the contrary, the trade of the PPS formed becomes essential when external sources of Mg and P were added.

Highlights

- Precipitation of P, K and Mg downstream an N-removal plant was assessed in a farm.
- The precipitation process was addressed using denitrified effluent and waste sludge.
- The precipitated phosphate salt (PPS) was evaluated as a fertilizer in a field test.
- Nutrient export out of the farm's productive system is needed when dosing $MgO-H_3PO_4$.
- The trading of the recovered PPS is essential to recover the expense in reagents.

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Graphical Abstract
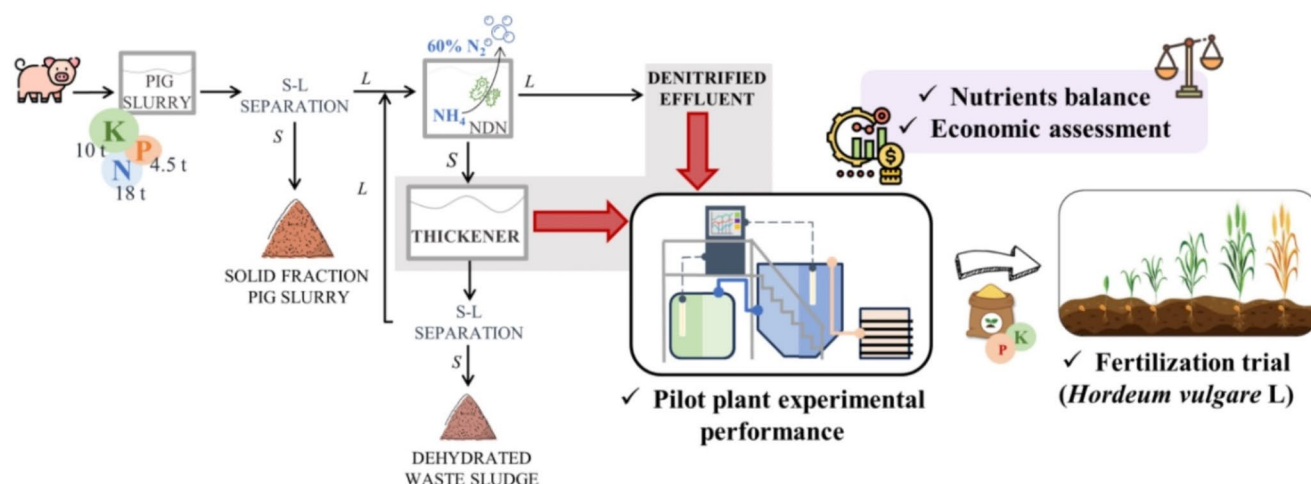
Introduction

Phosphorus (P) and potassium (K) are two essential nutrients in agrifood producing systems. Currently, the fertilizer producers mostly obtain these macronutrients from the mining industry as non-renewable resources. The reserves of phosphate rock, as the typical source of P [1], and potash, as the typical source of K [2], are unevenly distributed across the planet. This uneven distribution leads to geopolitical instabilities and large environmental impacts. According to the circular economy paradigm, using new productive methods for these nutrients based on recovery strategies from wastewater and organic by-products such as livestock manure [3, 4], can facilitate the implementation of more sustainable productive processes at the local scale, while simultaneously protecting human health and the environment. In this context, the availability of P has received considerable attention. As an example, the European Union [5] has classified P as a critical raw material, whereas precipitated phosphate salts (PPSs) recovered from secondary sources are typified following the fertilizing products regulation (EU) 2019/1009 [6, 7]. In contrast, K availability has received much less attention than that accorded to P, despite the small number of existing producers. The need for new sources beyond those derived from conventional mines will become increasingly apparent in the near future [8, 9]. So far, K has been considered, basically, as not recoverable from wastewater or similar sources.

Struvite (MgNH$_4$PO$_4$·6H$_2$O; magnesium-ammonium-phosphate hexahydrate, MAP) precipitation for the simultaneous recovery of NH$_4^+$-nitrogen (N) and orthophosphate-P

(PO$_4$-P: H$_3$PO$_4$ + H$_2$PO$_4^-$ + HPO$_4^{2-}$ + PO$_4^{3-}$) from liquid waste streams, as well as its subsequent use as slow-release fertilizer, has been proposed profusely in the literature [10–13]. However, references to the K-rich struvite "relatives" K-struvite (MgKPO$_4$·6H$_2$O; magnesium-potassium-phosphate hexahydrate, MPP) [14, 15] and K,Na-struvite (Mg$_2$KNa(PO$_4$)$_2$·14H$_2$O; hazenite) [16] are less common. K-struvite contains 11.6% P, 14.7% K, and 9.1% Mg on a weight basis whereas hazenite contains 11.2% P, 7.1% K, 4.2% sodium (Na), and 8.8% Mg. Although these phosphate salts can be found as high-purity precipitates [17, 18], treating wastewater and organic by-products they normally occur within a multi-nutrient product [19, 20]. Thus, the simultaneous formation of other amorphous/crystalline calcium phosphates (Ca-P) and magnesium phosphates (Mg-P) tends to occur [21, 22], negatively affecting the recovery of K. The need to reduce the ammonium and inorganic carbon contents before crystallizing K-rich struvites determines its downstream implementation concerning biological treatment for N removal [23]. With the exception of a few studies [24, 25], most of the trials conducted on the crystallization and subsequent utilization of K-rich struvites have been conducted in lab-scale setups [26–28], and a comprehensive evaluation of the fertilizing value of the recovered products at field-scale is lacking.

To recover K-rich struvites directly from liquid streams it is necessary to work at high pH values (i.e., 9.0–12.0) [29], which is typically achieved by the addition of an alkali (e.g., sodium hydroxide (NaOH)). Otherwise, in the case of solid-rich streams, it is first necessary to apply an acidification step to mobilize P, Mg (and calcium (Ca)) [30]. The

addition of an acidifying agent to decrease the pH disrupts bonds in mineral and organic compounds. If such acidifying agents release Ca-chelating or -binding substances such as they do ethylenediaminetetraacetic acid (EDTA) or oxalic acid ($H_2C_2O_4$) [31–33] the Ca interference will no longer exist when raising the pH.

The aim of this work is to characterize the production of K-rich struvite in a pilot plant (TRL-5) installed in a pig farm, downstream of a nitrification-denitrification (NDN) treatment unit, using the denitrified effluent (DE) and the waste sludge (WS, sludge removed from the NDN bioreactor to control the solids retention time (SRT)). The experimental performance of the pilot plant is reported. The process is characterized by considering P as limiting element (pH adjustment) and K as limiting element (magnesium oxide + phosphoric acid addition plus pH adjustment) when treating DE and by considering Mg as limiting element (oxalic acid addition plus pH adjustment of the liquid supernatant) when treating WS. Furthermore, a mass balance and an economic assessment are conducted at the farm level. Finally, the fertilizing value of the K-rich struvite produced is evaluated in a fertilization field trial with a barley (*Hordeum vulgare* L.) crop.

Materials and Methods

### Pig Farm, Onsite Slurry Treatment, and Characterization of the Resulting Streams

The treatment plant under consideration serves an industrial pig farm (Granges Terragrisa SL) located in the Catalan county of Osona. This region is characterized by a high level of pig production, where manure production exceeds crop demand. The farm has capacity for rearing aprox. 1300 sows and 3600 post-weaning pigs, resulting in an estimated yearly production of 5900 t of slurry (roughly equivalent to 18 t of N, 4.5 t of P, and 10 t of K). Regarding slurry treatment, it is initially separated into solid and liquid fractions using a screw press. The liquid fraction is subsequently treated biologically in a sequencing batch reactor (SBR) under intermittent aeration aiming to remove N through NDN. The bioreactor is operated according to a hydraulic residence time (HRT) of approximately 70 days, SRT of 58 days and cycles lasting 8 h under 43% time of aeration. The DE obtained after sludge settling is stored in an uncovered pool before being used for irrigating nearby field crops. Otherwise, the excess sludge wasted from the bioreactor is stored in a thickening tank before mechanical dewatering using a filter press (Depurdisc, Depurtech SL, Spain) running with a cationic polyelectrolyte (Demfloc-1002-C). According to this description, the slurry originally produced

on the farm is currently transformed into three different processed streams: slurry solid fraction, dewatered WS and DE (Fig. 1).

The typical characteristics of the streams exiting the biological treatment (i.e., DE and WS) are given in Company et al. [26]. The DE has a pH of approximately 8.0, with ammonium under detection limits, low alkalinity, but a notable electrical conductivity (EC) due to the presence of soluble ions (7.2 ± 0.3 dS/m). The K^+ content (1.6 ± 0.3 g K/L) is high concerning PO_4-P and Mg^{2+}, resulting in an average Mg^{2+}:K^+:PO_4-P molar ratio of 1.4:9.5:1.0. Additionally, the Na^+ content is also significant, with an average K^+:Na^+ molar ratio of 1.4. Conversely, the concentration of Ca^{2+} is low (Ca^{2+}:Mg^{2+} molar ratio averaging 0.2), which is favorable for the formation of struvites. Regarding the WS in the thickener, the solids content typically ranges from 25 to 30 g TS/L (TS, total solids), influencing the concentration of other elements, especially those less soluble. Therefore, in the case of TK, the concentration reaches a similar value to that of the DE. However, in the case of TP, the measured range is much wider (0.6–1.4 g P/L). A low volatile-to-total solids ratio of the sludge (0.53 ± 0.03) indicates a high degree of mineralization. The concentration of TCa is also much higher than that for the DE (ca. 77 ± 20 mg Ca/g TS), with an average TMg: TCa molar ratio of 0.5. Thus, the TMg:TK: TP molar ratio of the WS averaged 0.7:1.2:1.0, which is a much more balanced ratio than in the case of the DE, but still not equimolar.

Downstream Crystallization Pilot-Plant and Analytical Methods

A remotely controllable crystallization plant was installed downstream the NDN-SBR process (Fig. 2). This plant basically consisted of a perfectly mixed stirred reactor (volume: 3 m^3; influent flowrate 1.5 m^3/h) running in continuous/batch where sodium hydroxide (e.g., NaOH solution at 25% on weight basis) was added to raise the pH value as needed (pH controller installed). Subsequently, the crystals formed were agglomerated with a cationic polyelectrolyte (Demfloc-1002-C) and separated from the liquid stream with a filter press (Depurdisc). The polyelectrolyte solution was prepared in-situ prior to its dosage. The liquid stream resulting after solid-liquid separation was neutralized with sulfuric acid (H_2SO_4 solution at 50% on weight basis) before being transferred to the final storage pond. Concerning the DE, when the crystallization plant was operated considering P as the limiting element, the crystallizer ran in continuous (HRT of 2 h; mixing speed set to 100 rpm), and NaOH was the only reagent added aiming to reach the targeted pH-value (11.0–11.5). When the crystallization plant was operated considering K as the limiting element,
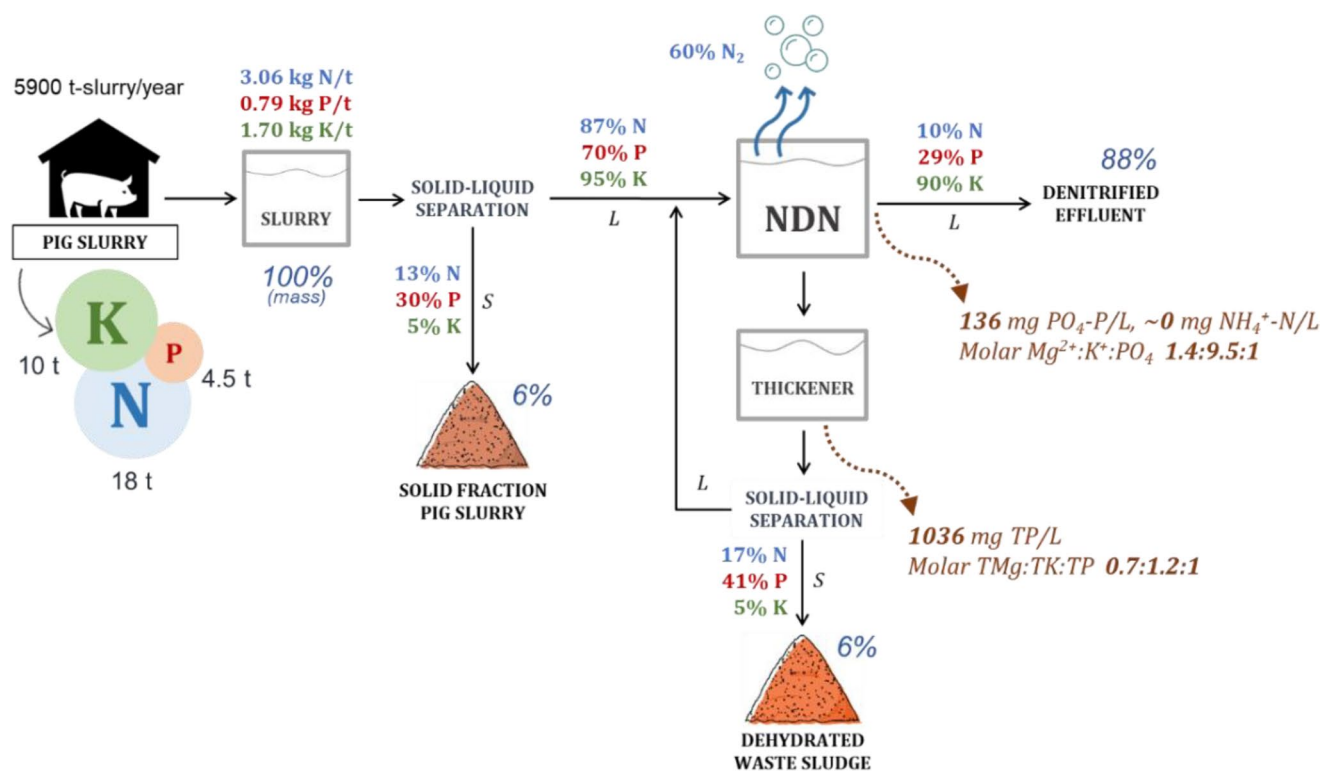
Fig. 1 Slurry production and nutrient mass balance in the pig farm under evaluation (Granges Terragrisa SL) [26]. PO_4-P concentration in the denitrified effluent (DE) ranged from 130 to 146 mg/L (136 ± 8 mg PO_4-P/L) and TP concentration in the waste sludge (WS) -thickener- ranged from 563 to 1420 mg/L (1036 ± 436 mg TP/L). The Mg^{2+}:K^+:PO_4 molar ratio in the DE ranged 1.2–1.5:8.6–11.0:1.0 (mean: 1.4:9.5:1.0). The TMg:TK:TP molar ratio in the WS ranged 0.7–0.9:0.9–2.1:1.0 (mean: 0.7:1.2:1.0)
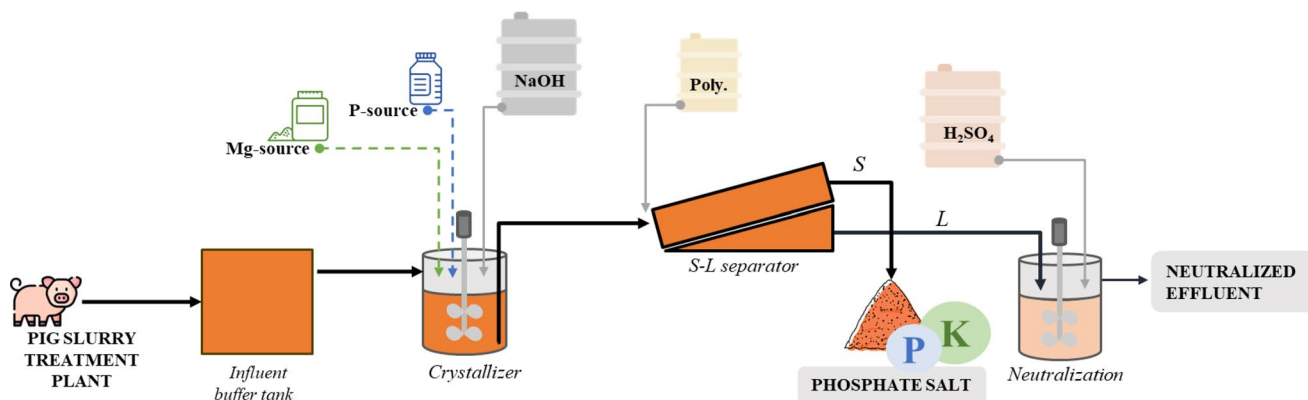
Fig. 2 Pilot-plant installed in the farm, downstream the NDN-SBR process, for the recovery of phosphate salts

besides modifying the pH, magnesium oxide (MgO) and phosphoric acid (H_3PO_4) were added as a source of Mg and P, respectively, targeting a final Mg:K:P molar ratio of 1.0:0.5:1.0. The MgO was added first, allowing its hydration for 15 min before H_3PO_4 dosage (the crystallizer ran in batches of 2.5 h; mixing speed set to 100 rpm). Concerning the WS, it was first pretreated with oxalic acid in the thickening tank to solubilize PO_4-P and Mg^{2+} while immobilizing Ca^{2+}. The oxalic acid was dosed at a rate near 1 mol per mol TCa. Sulfuric acid was eventually dosed to further

decrease the pH down to 4. The WS was then separated in solid and liquid fractions using the filter press and the liquid fraction was subsequently processed in the crystallization pilot-plant (working in continuous with an HRT of 2 h; mixing speed set to 100 rpm). All experiments were carried out in triplicates.

Total solids (TS) were determined gravimetrically, after sample drying to constant weight at 105 °C. The pH (offline) and electrical conductivity (EC) referred to 25 °C were measured with pH-meter (mod. sensION + PH3, Hach,

Germany) and conductimeter (mod. EC-Meter Basic 30+, Crison Instruments SA, Spain), respectively. The concentration of the soluble cations (i.e., ammonium (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+})), as well as the concentration of the soluble anions (i.e., phosphate (PO_4)), were determined using ion chromatography (mod. ICS-5000, Dionex, USA), after filtering samples with 0.2-µm nylon filters. Total C (TC) and total N (TN) were determined by elemental analysis (mod. 2400 Series II Elemental Analyzer, Perkin Elmer, USA). The total content of other elements (i.e., TP, TK, TNa, TMg, and TCa) was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES) (mod. 5100, Agilent Technologies, USA). Crystal structure was analyzed using powder X-ray diffraction (XRD) (mod. D8 Advance, Bruker). The morphology of the crystals was qualitatively observed with an optical microscope (mod. Eclipse E200, Nikon, Japan).

Fertilization Field Trial

A field trial was conducted from December 2021 to June 2022 in an agricultural commercial field located in Baix Empordà (Catalonia). The soil was uniform with a sandy loam texture, no gravels, and low fertility (Typic Xerofluvent) [34]. Top soil was sampled before starting the trial and at its end, and main soil chemical characteristics were analyzed in the samples. The trial had a randomized block design, with six treatments, three replications and an elementary plot size of 24 m^2 (8 m long x 3 m wide). A spring barley crop (var. Signora) was sown at a density of 235 kg/ha. The reference amount of nutrients to be supplied (100 kg N/ha, 50 kg P_2O_5/ha and 100 kg K_2O/ha) was estimated based on an expectable grain yield of 4 t/ha. The treatments finally applied (Table S1) were as follows: (T1) control (without fertilization); (T2) N-P-K mineral fertilizer; (T3) PPS obtained from the DE when processed considering P as the limiting element; (T4) PPS + composted slurry solid fraction (70% + 30% on wet weight basis); (T5) PPS + dehydrated waste sludge (70% + 30% on wet weight basis); and (T6) DE exiting the crystallization plant. For treatments T2–T5, the application rates at pre-sowing for the different products aimed to cover K_2O needs of the crop. When needed, mineral fertilizer was supplied at top dressing to cover total crop N needs. In treatment T6, processed DE was split applied at pre-sowing and top dressing to jointly cover the total N needs of the crop. Moreover, for T6, mineral superphosphate was applied at pre-sowing to equalize the total P applied in treatments T2–T5. At the time of application, the materials to be applied in each plot were weighted and blended as needed. All the (blended) materials considered, including the mineral fertilizer, were applied homogeneously by hand to the total surface of the corresponding plots. At the end of the barley crop cycle, grain yield was determined for each elementary plot. Immediately after harvesting, different grain quality parameters were determined: humidity, specific weight, protein content, and nutrient (N-P-K) content. The gathered data was analyzed with the statistical package SAS (SAS Institute Inc., USA). An analysis of variance and the Tukey's test were performed to study the separation of means at a significance level of 5%.

Mass Balance and Economic Assessment

Mass balances were performed assuming five main potential scenarios: (S1) 100% P recovery from the DE as K-struvite; (S2) 100% Mg recovery from the non-dehydrated WS as hazenite (with the addition of oxalic acid); (S3) 100% K recovery from the DE as hazenite (with the addition of $MgO + H_3PO_4$); (S4) 100% K recovery from the non-dehydrated WS as hazenite (with the addition of oxalic acid and $MgO + H_3PO_4$); and (S5) 100% K recovery from the non-dehydrated WS (with the addition of oxalic acid and $MgO + H_3PO_4$) and DE (with the addition of $MgO + H_3PO_4$) as hazenite.

Regarding DE and WS supernatant, NaOH in the crystallization step (pH 11.5) was assumed to be dosed according to 1.5 kg/t in S1, 3 kg/t in S2, 3 kg/t in S3 (and S5), and 4.5 kg/t in S4 (and S5). H_2SO_4 in the neutralization step (pH 7.0) was assumed to be dosed according to Company et al. [26] (1.0 kg/t). $MgO + H_3PO_4$ were assumed to be dosed according to 3.2 + 7.9 kg/t-DE in S3 and S5 (equivalent to 14 kg of newberyite ($MgHPO_4 \cdot 3H_2O$ [35]) per ton of DE) and 2.3 + 5.6 kg/t-WS supernatant in S4 and S5 (equivalent to 10 kg of newberyite per ton of WS supernatant). Regarding non-dehydrated WS, oxalic acid was assumed to be dosed at a rate of 1 mol per mol TCa [31] (4.5 kg/t), and H_2SO_4 (pH 4) at a rate of 5 kg/t. Prices for NaOH, H_2SO_4, oxalic acid, H_3PO_4 (www.intratec.us; primary commodity prices in Europe (2018)), and MgO [36] were assumed as 217, 40, 1309, 591, and 306 €/t, respectively (1870 €/t-P and 507 €/t-Mg). The hypothetical price for synthetized newberyite ($MgO:H_3PO_4$ molar ratio of 1:1) was estimated as 403 €/t (2268 €/t-P). No information was found in the literature concerning the price for K-rich struvites. According to Muys et al. [12], common struvite is typically sold at prices ranging from 0 to 100 €/t, but also at considerably higher prices of 350–1000 €/t. The same authors estimated the market value of its macronutrients as 250–412 €/t. In this study, a reference price of 300 €/t was assumed for the K-rich struvites (2581–2677 €/t-P).

Results and Discussion

Recovery of K-Rich Struvite in the Pilot-Plant

Denitrified Effluent: Phosphorus as the Limiting Element (pH Adjustment)

By considering P as the limiting element, the reaction of precipitation occurred according to the availability of P in the DE, discarding the addition of P as an external reagent. The pH was adjusted to 11.0–11.5 by adding NaOH (roughly, 1.0–1.5 kg NaOH/t-DE [26]). The lack of P led to low K removal efficiencies from the liquid phase (no more than 15% of the total K^+) and low solids productivity. Removal efficiencies of $\geq 90\%$ for P and ca. 40% for Mg (remaining dissolved about 0.1 g Mg^{2+}/L) were obtained. Thus, the addition of an external Mg-source would not imply an improvement in the recovery of K. The presence of Na^+ in the liquid phase increased notably due to the pH control strategy applied, contributing to a slight increase of the EC of the treated water (about 10–20% increase). The presence of K-struvite/struvite in the PPS was identified by XRD (Fig. S1) under NH_4^+ availability in the liquid phase as previously in [26] (CC5) –it is thus advisable to operate the NDN SBR with a NH_4^+ removal efficiency slightly below 100%–. Hazenite was also present in the PPS. When the pH of the DE is raised, the presence of small amounts of NH_4^+ induces fast struvite nucleation. This struvite formed may act as an effective seed for the growth of other crystals with similar structure [26]. Co-precipitation of struvite and hazenite [37], or K-struvite and hazenite [38], has also been reported as feasible elsewhere. However, co-formation of other Mg-P products such as cattiite ($Mg_3(PO_4)_2 \cdot 22H_2O$; 9.4% P and 11.1% Mg) [22], or brucite ($Mg(OH)_2$) [20], was also feasible, which could lead to Mg: P molar removal ratios above 1.0 (Table 1). The presence of about 0.1 g Ca^{2+}/L in the DE may also interfere on the precipitation of P mostly resulting in amorphous Ca-P products (the precipitate formed contained $5.1 \pm 0.6\%$ TCa on dry weight basis

(Table 1)). The use of polymer in the S/L separator device resulted in a significant agglomeration of organic matter together with the PPS inducing a high TC content in the recovered salt (and eventually posing a collateral effect on cations). Because of this agglomeration, the level of TC in the PPS reached much higher values than in other similar experiences at lab scale (i.e., $13.6 \pm 1.3\%$ TC in the field vs. 1.6% TC in the lab [26], on a dry weight basis). This high C content ($> 3.0\%$) will constrain the sale of the recovered PPS as a struvite-like product in the framework of the fertilizing products regulation (EU) 2019/1009 [6, 7]. The PPS formed contained $2.3 \pm 0.3\%$ N, $5.9 \pm 0.2\%$ P and $3.9 \pm 0.4\%$ K on a dry weight basis (Table 1).

Denitrified Effluent: Potassium as the Limiting Element ($MgO + H_3PO_4$ Addition and pH Adjustment)

By considering K as limiting (i.e., 1.6 ± 0.3 g K^+/L), it was necessary to add an external source of Mg and P to reach high K-removal efficiency from the liquid phase. To facilitate the addition of these nutrients to the crystallizer they were added individually as MgO and H_3PO_4, respectively, rather than simultaneously as on-site synthetized newberyite (i.e., a similar K-removal efficiency may be expected with this alternative procedure [39]). The main risk assumed by proceeding this way is that the concentration of P in the final effluent may reach values above the original DE. The removal efficiency finally obtained for K was high ($89 \pm 8\%$). The K^+:Na^+ molar ratio decreased significantly when considering K as the limiting element owing to the depletion of soluble K^+ or the additional demand for NaOH to adjust the pH (roughly, 3.0–3.5 kg NaOH/t-DE). Although it was expected that some Na-struvite crystallized [39], what was finally formed was hazenite, which must not be confused with a blend of the minerals K-struvite and Na-struvite. The formation of Na-rich struvite analogues is not the most interesting situation in the case study here described since it implies competition for the limiting ions Mg^{2+} and PO_4, which will negatively affect the recovery of K. The presence of hazenite was confirmed by XRD (Fig. S1) and the PPS formed contained $0.7 \pm 0.4\%$ N, $9.9 \pm 0.2\%$ P and $5.0 \pm 0.1\%$ K on a dry weight basis (Table 1).

Waste Sludge

The pretreatment of the WS with oxalic acid and H_2SO_4 (pH 4.0) resulted in 70–80% of the P and Mg initially present in the WS finally available in soluble form in the acidified supernatant, resulting in an average Mg^{2+}:K^+:PO_4-P molar ratio of 0.8:1.2:1.0 (Mg becoming the limiting element). Before acidification, only about 10–15% of the P and 10–20% of the Mg present in the WS were soluble. The

Table 1 Composition of the precipitates formed in the experiments conducted in the pilot plant[*, **]

Element	DE – P as limiting	DE – K as limiting	WS – Mg as limiting
Carbon (TC) (%)	13.6 (1.3)	3.3 (1.7)	3.0 (1.3)
Nitrogen (TN) (%)	2.3 (0.3)	0.7 (0.4)	0.5 (0.2)
Phosphorus (TP) (%)	5.9 (0.2)	9.9 (0.2)	9.7 (0.2)
Potassium (TK) (%)	3.9 (0.4)	5.0 (0.1)	4.4 (1.1)
Sodium (TNa) (%)	1.7 (0.2)	4.0 (0.2)	3.1 (1.1)
Magnesium (TMg) (%)	6.6 (0.2)	8.1 (0.7)	7.1 (1.2)
Calcium (TCa) (%)	5.1 (0.6)	1.9 (2.0)	3.9 (2.8)

[*] Values referred to dry weight at 35ºC

[**] Values are means (standard deviation in parentheses)

concentration of Ca^{2+} in the supernatant was still high (0.3–0.6 g Ca^{2+}/L) even though the dose of oxalic acid applied at least equaled the value theoretically needed (1 mol oxalic acid per mol TCa [31]). This fact could be caused by an ineffective mixing in the thickening tank (oxalic acid was dosed in solid form) and will impact on the recovery of K^+ owing to the competence exerted by Ca^{2+} for the combination with P. The solubilization of the oxalic acid in DE before its dosage to the WS tank is therefore advisable. In the conditions mentioned above, the removal efficiency from the liquid phase for K^+, Mg^{2+} and PO_4-P due to the crystallization process was up to 51%, 98% and 95%, respectively. Up to 98% of the available Ca^{2+} precipitated also. Lower P and Mg solubilization efficiencies were reached if no H_2SO_4 was added (final pH $\sim$ 6), but Ca^{2+} was better blocked. The presence of hazenite was confirmed by XRD (Fig. S1). The PPS formed contained 0.5 ± 0.2% N, 9.7 ± 0.2% P and 4.4 ± 1.1% K on dry weight basis (Table 1). The TC content was 3.0 ± 1.3%.

Fertilization Field Trial

Barley grain yield averaged 2454 kg/ha (13% humidity) (Table 2), which was below the value of 4000 kg/ha considered for fixing the fertilization needs. This low productivity can be explained by the lack of rain at the first stages of the crop development (19 L/m^2 from December to February with respect to an average value of 135 L/m^2) and at the end of the cropping cycle (23 L/m^2 from May to June with respect to an average value of 92 L/m^2). Significant differences among treatments were found in yield mainly occurring between the most productive treatments (T3 and T5) and the less productive one (T1; control without fertilization). The grain specific weigh averaged 58.5 kg/hL and no statistical differences were identified among treatments.

Table 2 Barley crop yield (kg/ha) and protein content in grain (%) for the different treatments in the fertilization field trial

Treatment	Description	Grain yield (13% humidity)* (kg/ha)	Protein in grain* (%)
T1	Control (without fertilization)	2045 b	10.0 c
T2	Mineral fertilizer	2421 ab	11.9 ab
T3	PPS	2644 a	12.7 a
T4	70% PPS + 30% compost	2515 ab	10.9 bc
T5	70% PPS + 30% dehydrated WS	2689 a	11.4 b
T6	Processed DE + mineral fertilizer	2409 ab	10.1 c
	p-value	*0.0358*	*0.0001*

DE, Denitrified effluent; PPS, precipitated phosphate salt; WS, waste sludge

*Means within a column with the same letter are not significantly different

The mean protein grain content (Table 2) was 11.2%. The protein content was significantly influenced by the treatment applied. Treatments T3 (12.7%) and T2 (11.9%) where those that presented the highest protein content, with significant differences to T1 (control) and T6, with ca. 10%. Probably, these differences were not caused by the kind of fertilizer used at pre-sowing but by the dose of mineral N applied at top dressing. The nutrient content in grain averaged 2.02% N, 0.48% P and 0.70% K. Significant differences were found for the N content (similar to the case of protein content) in grain, but not for the P and K content. At the end of the cropping cycle, in treatment T6 (processed DE), soil EC as well as the K and Na soil contents increased significantly as it could be expected considering the amount of K supplied in this treatment (Table S1). This fact is indicative of the risk of soil salinization under reiterative applications of the DE product.

Balance of Nutrients

To evaluate the potential amount of K-rich struvite material (K-struvite in S1 and hazenite in S2–S5; on a dry weight basis) recoverable in the pig farm under evaluation (Fig. 1), different scenarios were assessed through mass balance (Table 3). By processing the DE only raising the pH (S1), a yearly production as low as 6.1 t PPS was estimated (1.0 kg/t_{slurry}). This value can be increased by a factor of 2.6 when processing the non-dehydrated WS first with oxalic acid (S2) –although the corresponding mass flowrate is only 45% that of the DE–. The scenarios S1 and S2 could also be applied together, leading to a total recovery of 2.2 t P and 1.7 t K (about 47% of the total P and 17% of the total K available in the slurry). When targeting high efficiencies on the recovery of K (S3–S5), the preliminary addition of $MgO + H_3PO_4$ as external sources of Mg and P, respectively, becomes mandatory (this is why P-recovery is above 100% in Table 2). In this regard, most of the precipitate can be recovered from the DE (S3) (up to 120.6 t PPS). If assuming total K recovery from DE and WS (S5) (126.9 t PPS; 21.5 kg/t_{slurry}) 14.2 t P and 9.0 t K are managed in total.

In relation to the current nutrient management planning of the pig farm, scenarios S1 and S2 would allow mostly an enhanced handling of these nutrients in the arable land already considered in the fertilization plan. On the contrary, the trade of the material produced becomes essential in scenarios S3–S5 to export nutrients out of the farm's productive system due to the extra amount of P added during the precipitation process. When precipitating K-rich struvite, P and K are concentrated into a uniform, mineral, and solid material easily usable as slow-release fertilizer. Downstream processing of the DE before using it for irrigating nearby croplands may help to prevent excessive inputs of

Table 3 Estimation of precipitation potentials at the farm level through yearly mass balances according to different hypothetical scenarios (S1–S5). Total slurry production is $Q_0 = 5900$ t/year. Other mass flow rates are assumed as in Fig. 1, with the denitrified effluent (DE) as 54%·Q_0 (water line) + 34%·Q_0 (returns from the sludge line) and the non-dehydrated waste sludge (WS) as 40%·Q_0. Composition of the DE and WS assumed as in Company et al. [26]. Nutrient recovery percentages are referred to the maximum amount possible when accounting for DE + WS

Scenario	Description	Mg needs[*] (t)	P needs[*] (t)	P precipitated[**] (t)	K precipitated (t)	Precipitate produced[**] (t)	PO₄ recovered (%)	K⁺ recovered (%)
S1	100% P-recovery from DE	0	0	0.7	0.9	6.1	25	10
S2	100% Mg-recovery from WS	0	0	1.8	1.1	15.7	61	12
S3	100% K-recovery from DE	10.1	12.8	13.5	8.5	120.6	470	95
S4	100% K-recovery from WS	3.3	4.2	5.9	3.7	52.9	206	42
S5	100% K-recovery from WS + DE	9.4	8.3	14.2	9.0	126.9	494	100

[*] Stoichiometric (minimum) Mg and P needs as external reagents (supplied as MgO and H_3PO_4, respectively)

[**] The precipitate formed was assumed exclusively as K-struvite ($MgKPO_4 \cdot 6H_2O$) in S1 and as hazenite ($Mg_2KNa(PO_4)_2 \cdot 14H_2O$) in S2–S5, on dry weight basis

Table 4 Economic assessment according to different hypothetical scenarios (S1–S5). Total slurry production is $Q_0 = 5,900$ t/year. Other mass flow rates are assumed as in Fig. 1, with the denitrified effluent (DE) as 54%·Q_0 (water line) + 34%·Q_0 (returns from the sludge line) and the non-dehydrated waste sludge (WS) as 40%·Q_0. Composition of the DE and WS assumed as in Company et al. [26]

Scenario	Description	Cost €/year	€/t-slurry	€/t-PPS	Income €/year	€/t-slurry	€/t-PPS	Benefit €/year	€/t-slurry	€/t-PPS
S1	100% P-recovery from DE	1,898	0.32	312	1,822	0.31	300	-75	-0.01	-12
S2	100% Mg-recovery from WS	15,760	2.67	1,004	4,711	0.80	300	-11,049	-1.87	-704
S3	100% K-recovery from DE	32,878	5.57	273	36,186	6.13	300	3,308	0.56	27
S4	100% K-recovery from WS	24,496	4.15	463	15,858	2.69	300	-8,638	-1.46	-163
S5	100% K-recovery from WS + DE	44,671	7.57	352	38,063	6.45	300	-6,608	-1.12	-52

P and/or K to soil [40], nutrients which otherwise would accumulate in the soil or be lost through leaching and surface runoff, and may reach water bodies, thus contributing to eutrophication. Besides, the high alkaline conditions applied to induce precipitation are expected to reduce the level of pathogens in the water line [41]. Concerning WS, its further processing allows to recover P and K from the non-stabilized organic matrix making these nutrients more easily available for crops, especially in the case of P [42]. In case of commercializing the precipitate produced, a consolidated market for second-generation fertilizing products, in which struvite-type materials can unequivocally be valorized, is essential for guaranteeing economic viability.

Economic Assessment

Obtaining a positive economic balance will depend on the income (assumed as 300 €/t-PPS in Table 4) that can be obtained from the sale of the precipitated product. If no economic value can be given to the PPS it will be necessary to assume a treatment cost. This cost will be higher as far as more reagents have to be added, especially in the case of considering the addition of MgO + H_3PO_4 as external sources of Mg and P, or oxalic acid as a mobilizing agent in the WS. The cost of dosing base and acid agents in the precipitation process is quantified at a minimum of 0.32 €/t-slurry (S1). In all the other scenarios

(S2–S5), the costs will increase due to the addition of an extra amount of base/acid, MgO + H_3PO_4 or oxalic acid (2.67–7.57 €/t-slurry). The use of oxalic acid in WS leads to a substantial increase in the cost of treatment. The unitary price of releasing P from WS is estimated as 5879 €/t-P (assuming 100% release) while the price as a reagent for the subsequent eventual addition in the form of newberyite is estimated at 2268 €/t-P. Nutrient recovery based on the addition of reagents has a high cost (273–1004 €/t-PPS) but if the PPS can be valorized economically, then there is the opportunity to recover (partially) the expense. The use of by-products rich in Mg [43, 44] and P [44] instead of pure reagents may help to reduce the treatment cost.

The chemical precipitation of K-struvite/hazenite in a pig farm downstream of a biological N-removal plant makes it possible to separate a P-K rich material (which will be valorized as a bio-based fertilizer in distant croplands) from the nutrient depleted mainstream (which will be applied in croplands nearby the farm). This is particularly interesting in areas with a high livestock production. The introduction of new bio-based fertilizers into the market will potentially reduce dependence on mineral sources and promote circular economy and sustainability [4]. When estimating the price of a new bio-based fertilizer, it is important to consider not only its nutrient content, but also the social and political aspects involved in a fair way to ensure long-term

sustainability [45]. Some of the conventional mineral fertilizer producers have recently expressed interest in recovered nutrients, indicating a potential shift in their production lines [45]. Although mineral fertilizer producers point out a number of challenges most commonly associated with the quantities and consistency of recovered nutrients, there is a clear shift in perspective towards more circular sources. Consequently, the engineering approach based on calculating the price of a new fertilizer based on the nutrients it contains should be progressively replaced by a value-based pricing approach (i.e., pricing is based on the consumer's perception of value).

Conclusions

Experiments conducted at the farm level (pilot scale, TRL-5) demonstrated the technical feasibility for simultaneously recovering P, K, and Mg as a PPS (K-rich struvite may refer to K-struvite or hazenite depending on the operational conditions applied) downstream of a NDN treatment plant. The precipitation process could be managed using both outgoing streams (DE and WS). When dealing with the DE, the inherent unbalanced Mg^{2+}:K^+:PO_4 molar ratio (1.4:9.5:1.0; 1.6 g K^+/L) resulted in poor K recovery when P was considered to be the limiting element (no more than 15% of the total K^+ was recovered by only raising the pH). By considering K as the limiting element, the additional supply of external sources of Mg (MgO) and P (H_3PO_4), resulting in a Mg:K^+:PO_4-P molar ratio of 1.0:0.5:1.0, allowed the recovery of most of the K available. In the case of the WS, a selective mobilization pretreatment with oxalic acid led to a Mg^{2+}:K^+:PO_4 molar ratio of 0.8:1.2:1.0. If the operational parameters are not optimized, there is risk of interference by the presence of free Ca^{2+} (which promotes the formation of Ca-P), thus constraining the recovery of K (up to 51% K-recovery in this study). A fertilization field trial demonstrated the fertilizing value of the recovered PPS in comparison to a mineral fertilizer and highlighted the risk of soil salinization under a reiterative application of processed DE.

Concerning the current nutrient management planning of the pig farm, those scenarios that do not involve the addition of an extra amount of nutrients will open the door to an enhanced handling of these nutrients in the arable land that has already been considered in the fertilization plan. On the contrary, the sale of the material produced becomes essential in scenarios where external sources of Mg and P have been considered, in order to export nutrients out of the farm's productive system. In case of commercializing the PPSs produced, a consolidated market for second-generation fertilizing products, in which struvite-type materials can unequivocally be valorized, is essential for guaranteeing economic viability. The high C content in the PPSs linked to the use of polyelectrolyte in the separation device negatively impacts on the quality of the recovered product. The use of oxalic acid in WS processing leads to a substantial increase in the cost of treatment. Nutrient recovery based on the addition of reagents has a high cost but if the PPS can be valorized economically, the expense can be recovered (at least partially).

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Declarations

Competing Interests The authors declare that they have no conflict of interest.

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