

## The determination of fertiliser quality of the formed struvite from a WWTP

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### ABSTRACT

Struvite from nutrient-rich wastewaters has been identified as a potential substitute for commercial mineral fertilisers, with the added benefit of reducing threats to global food security by prolonging phosphate rock reserves. A fertilisation test using grass (*Brachiaria brizantha Marandú*) and a sand column leaching test was conducted to determine the agronomic effectiveness of struvite precipitates produced from the supernatant of dewatered sewage sludge (centrate) from a municipal Wastewater Treatment Plant (WWTP). The performance of this struvite as a fertiliser was compared with biosolids and commercial fertilisers (Urea and Triple15). The results show that the concentration of heavy metals in struvite was lower than in biosolids and below the limits of Colombia and European fertiliser regulations. Struvite increased the uptake of N and P in grass, resulting in crop yields similar to other treatments tested. Struvite use as an effective slow-release fertiliser is highly dependent on the size of crystal particles, particularly in achieving low P losses, but resulted in high N loss in the sand columns tested; N losses from struvite were higher than in the commercial fertilisers due to the struvite small particle size. Therefore, struvite represents a suitable opportunity to recover and recycle nutrients from municipal sewage sludge, facilitating the effective reuse of P and N in agriculture and uptake by plants.

**Key words** | biosolid, centrate, crop yield, nutrients recovery, struvite

### HIGHLIGHTS

- Heavy metal concentrations of the struvite from the studied centrate of a WWTP were below the threshold limits.
- P uptake and apparent P recovery efficiency by the grass were significantly higher in two struvite treatments than in the commercial fertilised tested.
- N and P leaching depend on particle size. Smaller crystals can produce greater N uptake by the grass but at the same time more significant N losses by leaching.

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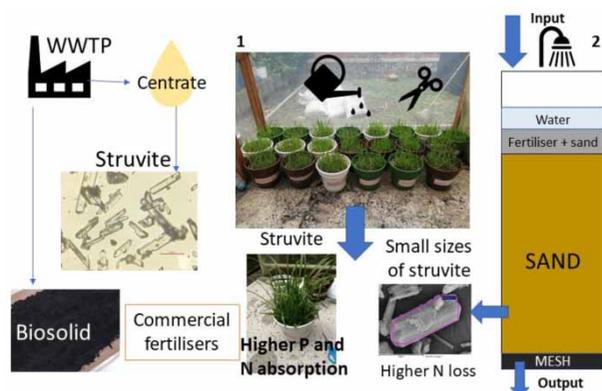
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## GRAPHICAL ABSTRACT



## INTRODUCTION

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) recovered from wastewaters, as a secondary phosphate source, has the potential to reduce the pressure on phosphate rock mining and contribute to a more sustainable fertiliser production (Talboys *et al.* 2016). In fact, struvite is considered an eco-friendly fertiliser because nutrients are released at a slower rate compared to other fertilisers; plants can take up the nutrients before they are rapidly leached, and less frequent application is therefore required, while phosphorus ( $\text{PO}_4^{3-}$ ), nitrogen ( $\text{NH}_4^+$ ) and magnesium (Mg) can be absorbed simultaneously without using any other artificial components. Also, struvite has 2–3 times lower heavy metals impurities than commercial fertilisers (Hall *et al.* 2020) and can help to reduce greenhouse gas emissions from agriculture because plants take up most of the N after its application, avoiding other biological transformations of N leading to nitrous oxide formation and release from the soil (Lee *et al.* 2009).

However, the use of struvite as a fertiliser can be highly dependent on the size of the crystal particles (Warmadewanthi *et al.* 2019): an increase in size ( $>1$  mm) leads to a slower fertiliser release rate due to a lower surface to volume ratio. Additionally, struvite with a larger size is easier to handle, transport, and apply (Li *et al.* 2019).

Many studies have evaluated the potential of struvite as a fertiliser using synthetic struvite produced in the laboratory or granular struvite commercially produced with high particles sizes (e.g. Crystal Green™) (Degryse *et al.* 2017), but only few works have compared the agronomic effectiveness of resulting struvites from nutrient recovery units at WWTPs.

The characteristics of struvite precipitates (morphology, size and quality) rely on the nature of the crystallisation

process used, mainly the hydrodynamic behaviour and operational conditions in crystallisers (Le Corre *et al.* 2009). To date, different reactors have been examined for efficient phosphorus recovery by struvite crystallisation, such as the continuous stirred tank (CSTR) or fluidised bed reactors (FBR) (Rahman *et al.* 2013), both with high recovery efficiencies ( $>60\%$ ) depending on the P source (type of wastewater used).

Therefore, this research aims to assess the agronomic efficiency of struvites obtained in a laboratory-scale CSTR and FBR reactors, using the supernatant of dewatered sewage sludge (centrate) from an existing municipal WWTP, and to compare them with the corresponding agronomic efficiency of biosolids (dried digestate sludge obtained from the same WWTP, currently disposed on land) and common commercial fertilisers (urea and Triple 15 fertilisers). For that purpose, key performance parameters like apparent recovery efficiency (ARE; %) and nutrient (N or P) uptake, determined in fertilisation trials, were used for comparison between all fertilisers tested. The total nutrient loss and nutrient loss rates were also determined in parallel leaching tests.

## METHODS

### Fertiliser products

Struvite precipitates were produced using a centrate from the sludge dewatering unit at San Fernando WWTP (Itagui, Colombia); centrate samples were stored at  $4^\circ\text{C}$

and characterised in the lab for ammonium, phosphate, calcium and potassium with initial mean concentration of 1,176 mgN-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>, 106 mgP-PO<sub>4</sub><sup>3-</sup> L<sup>-1</sup>, 60 mg Ca L<sup>-1</sup> and 125 mg K L<sup>-1</sup>. Two types of struvite precipitates were produced: (a) SR1, produced in a CSTR-type reactor (5 L of working volume); and (b) SR2, produced in a FBR-type reactor (6.5 L of working volume). The crystallisation time in CSTR and FBR reactors was 7 hours and 5 days, respectively; both operating at pH 9 (NaOH 1M added). The mean nutrient removal efficiency achieved in both reactors was similar (i.e. 26% N-NH<sub>4</sub><sup>+</sup> and 91% P-PO<sub>4</sub><sup>3-</sup>).

Synthetic struvite (SS) was precipitated in distilled water using a Jar tester (6 × 2 L beakers), at a fixed stirring speed of 120 rpm during 3 hours of reaction time, and at constant pH of 9 (NaOH 1M added). The reactants used to adjust nutrient concentrations were NH<sub>4</sub>Cl, NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O, all reactive grade (EMSURE<sup>®</sup> and JT Baker).

All struvite precipitates (including synthetic struvite) were collected by filtering (cellulose filter, 20 μm; Stilotex S.A), dried for 24 hours at room temperature (22 °C) and

stored in a desiccator before characterisation including X-ray diffraction (XRD) analysis.

The anaerobically digested sewage sludge (sewage digestate), with an initial humidity of 67%weight, was also collected at San Fernando WWTP. Sewage digestate samples were dried at room temperature (22 °C) for one week; the resulting solids or biosolids (Bio) from here on, were crushed in a crushing machine before application to pots in the fertilisation trials. Also, a mixture (Mix) 90:10 (in % weight) of Bio and SR1 was prepared as fertiliser. Finally, two commercial fertilisers for grass were used: Urea (U) and Triple 15 fertiliser (T15), both provided in solid form by Abonamos S.A.S (Colombia). Table 1 summarizes the main characteristics of all fertilisers tested.

### Fertilisation test

Grass (*Brachiaria brizantha Marandú*) was cultivated for 90 days in plastic pots (13 cm surface diameter; 0.01327 m<sup>2</sup> surface area; 10 cm of working depth) filled with sand

**Table 1** | Characteristics of struvites, biosolid and commercial fertilisers (Urea and Triple 15)

| Parameter (units)*                               | SR1    | SR2   | SS     | Bio    | U     | T15    |
|--|--------|-------|--------|--------|-------|--------|
| Struvite purity (%)                              | 86.1   | 78.7  | 77.7   | –      | –     | –      |
| Mean particle size (μm)                          | 112.88 | 26.90 | 89.20  | > 200  | NM    | NM     |
| Min. Particle size (μm)                          | 39.27  | 10.89 | 15.60  |        |       |        |
| Max. particle size (μm)                          | 271.49 | 60.31 | 350.20 |        |       |        |
| Density (g cm <sup>-3</sup> )                    | 1.60   | NM    | 1.90   | 0.64   | 0.77  | NM     |
| Conductivity (dS m <sup>-1</sup> )**             | 0.65   | NM    | –      | 0.18   | NM    | 0.0078 |
| DM (%)   | 98     | 98    | 98     | 95     | 98    | 98     |
| TN (%)*  | 6.07   | –     | –      | 2.81   | 46.94 | 15     |
| NH <sub>4</sub> -N (%)*                          | 5.02   | 4.59  | 4.53   | 2.81   | 46.94 | 7.08   |
| TP-P (%)*  | 11.11  | 10.35 | 15.6   | 1.32   | 0     | 6.68   |
| K (%)*   | 0.05   | 0.49  | NQ     | 0.06   | 0     | 12.45  |
| Mg (%)*  | 5.77   | 6.86  | 7.79   | 0.79   | 0     | 2.14   |
| Ca (%)*  | 1.12   | 2.1   | 0.01   | 0.16   | 0.01  | 1.66   |
| Al (%)*  | NQ     | 0.22  | 0      | 3.71   | 0     | 0.07   |
| Mn (%)*  | NQ     | NQ    | NQ     | 0.01   | NQ    | 0.01   |
| Na (%)*  | 0.06   | 1.56  | 0.05   | NQ     | 0.04  | NQ     |
| Fe (%)*  | 0.09   | 0.1   | NQ     | 0.15   | 0     | 0.15   |
| C-org (%)*                                       | 1.52   | 1.46  | NM     | 19.68  | NM    | 5.1    |
| <i>Salmonella</i> genus (presence- absence/25 g) | Absent | NM    | NM     | Absent | NM    | Absent |
| <i>Enterobacteriaceae</i> family (cfu g-1)       | 0      | NM    | NM     | 0      | NM    | NQ     |

Abbreviations: NQ, not quantifiable; DM, dry matter; NM, not measured; TN, total nitrogen; TP, total phosphorus; cfu, colony forming units.

Note: \*All percentages are reported on dried weight basis. \*\*Conductivity of a liquid extract (1/200).

(river sand supplied by Depósitos Chagualo, Colombia). Sand is well suited for fertilisation tests as it drains well and has a minimum organic matter content that reduces biological activity, which might interfere with N analyses. Pot trial tests were performed at room temperature, inside a greenhouse facility (University of Antioquia; Medellín, Colombia).

In each pot, 1.5 g of grass seeds (150 seeds per pot) were planted within the top 1.0 cm of sand (day 0). All fertilisers were applied in their solid form directly on the soil at day 15, after sowing seeds (Figure 1(a)). The experiment was arranged as a completely randomised design with 3 replicates per fertiliser: synthetic struvite (SS), struvite precipitates (SR1, SR2), biosolids (Bio), a 90:10 mix of Bio and SR1 (Mix), and the commercial fertilizers urea (U) and Triple 15 (T15). For a medium to high production of grass, the fertiliser Bio is usually applied with a dose of  $5.64 \text{ gP m}^{-2}$  (Bernal & Espinosa 2003). Therefore, this P dose was selected to calculate the amount to be applied for all other fertilisers tested, apart from T15. T15 was applied with a dose of  $2.46 \text{ gP m}^{-2}$  due to a calculation mistake (i.e. Phosphorus content in T15 was initially assumed at 15% as TP; however, its actual P content is 15% reported as  $\text{P}_2\text{O}_5\text{-P}$ , which is equivalent to 6.54% as TP). For Urea fertiliser dosage, which has no phosphorus, the criteria was to match the N dose of struvite SR1. Table 2 summarizes the dose used per fertiliser. A control treatment or pot without N and/or P fertilisation was included; therefore, 8 sets of 3 pots each were prepared. Tap water (60 mL per pot) was added every two days. At day 27, plants were harvested for the first time and weighed before and after being dried (at

$105^\circ\text{C}$  for 24 hours) to determine their fresh and dry weight. Later, at day 32, the same fertiliser dosage per pot was applied. Finally, at day 76, all plants were harvested again and weighed to estimate fresh and dry weight.

The agronomic efficiency ( $AE$ ;  $\text{kg kg}^{-1}$ ) is defined as the dry mass of crop produced obtained per mass of nutrient applied (N or P). It can be calculated by using Equation (1) below (Fageria 2009). Agronomic efficiency was calculated for P (AEP) and for N (AEN). The apparent recovery efficiency ( $ARE$ ; %) is defined as the quantity of nutrient uptake per unit of nutrient applied. It was calculated by using Equation (2a) (Fageria 2009). This parameter was calculated to assess both P (APR) and N (APN) recovery efficiencies. The N or P uptake ( $G$ ) was also calculated by multiplying the dry matter yield of the biomass by the respective P or N content ( $C$ ) of the biomass (Equation (2b)).

$$AE(\text{kg kg}^{-1}) = \frac{((DMY)_T - (DMY)_C)}{Na} \quad (1)$$

$$ARE(\%) = \frac{((G)_T - (G)_C)}{Na} \times 100 \quad (2a)$$

$$G = DMY \times C \quad (2b)$$

where, dry matter yield ( $DMY$ ) is the amount of total dry matter (DM) per pot ( $\text{kgDM pot}^{-1}$ );  $Na$  is the quantity of nutrient (P or N) applied per pot;  $G$  is the nutrient (N or P) uptake into leaves per pot (kg); subscripts  $T$  and  $C$  denote 'treatment' and 'control' (without fertiliser), respectively.

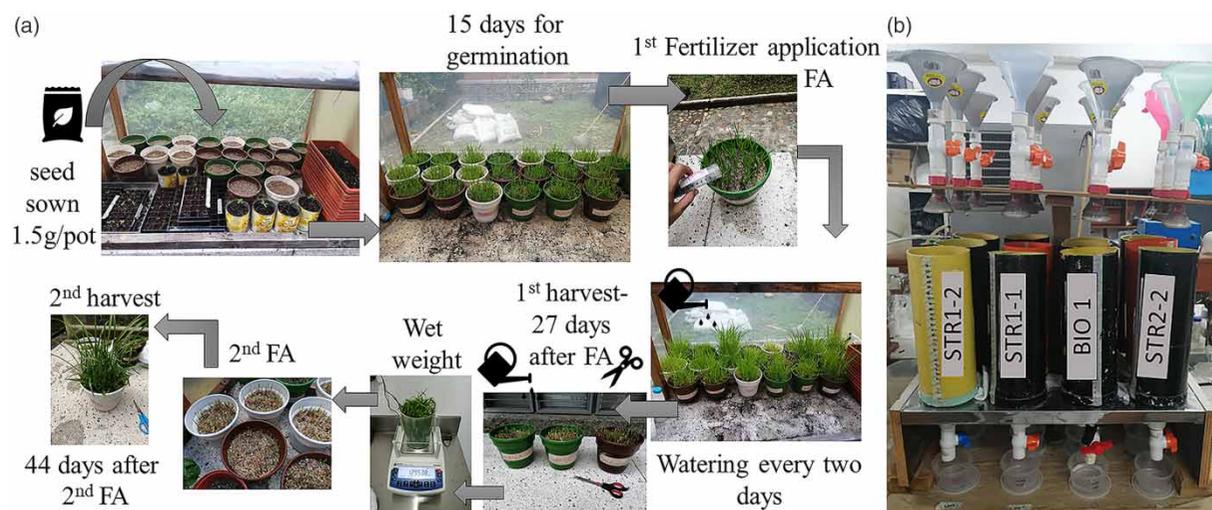


Figure 1 | Experimental set-up. (a) Steps of the fertilisation test (pot experiment). (b) Image of the leaching test experimental set-up.

**Table 2** | Experimental conditions for fertilisation trials (FT) and leaching tests (LT): quantity added per fertiliser and equivalent P and N doses, based on a 5.64 gP m<sup>-2</sup> criterion

| Test fertiliser | FT Product tons. ha <sup>-1</sup> | FT P dose g TP m <sup>-2</sup> | FT N dose g N-NH <sub>4</sub> <sup>+</sup> m <sup>-2</sup> | LT Product g per column | LT (3) P dose gTP m <sup>-2</sup> | LT (3) N dose g N-NH <sub>4</sub> <sup>+</sup> m <sup>-2</sup> |
|-----------------|-----------------------------------|--------------------------------|--|-------------------------|-----------------------------------|--|
| SR1             | 0.52                              | 5.64                           | 2.55   | 0.42                    | 5.64                              | 2.55   |
| SR2             | 0.56                              | 5.64                           | 2.50   | 0.45                    | 5.64                              | 2.50   |
| SS (2)          | 0.37                              | 5.64                           | 1.62   | –                       | –                                 | –  |
| Bio             | 4.5                               | 5.64                           | 12.02  | 3.66                    | 5.64                              | 12.05  |
| Mix (1)(2)      | 2.57                              | 5.64                           | 7.34   | –                       | –                                 | –  |
| U               | 0.06                              | 0.00                           | 2.55   | 0.05                    | –                                 | 2.55   |
| T15             | 0.38                              | 2.46                           | 2.64   | 0.7                     | 5.64                              | 6.00   |

Notes: (1) For fertilisation with Mix product, 0.25 t-SR1 ha<sup>-1</sup> and 2.3 t-Bio ha<sup>-1</sup> were applied per pot. (2) These products were not assayed in LT. (3) In LT, the applied TP per column was 45.75 mgP, and TN ranged 20–98 mg N-NH<sub>4</sub><sup>+</sup>.

## Leaching test

The N and P losses from SR1, SR2, Bio, U and T15 in pot trials were determined by performing a leaching test at room temperature (25 °C). Ten testing columns (two per fertiliser) packed with sand (river sand supplied by Depósitos Chagualo, Colombia) were used, see Figure 1(b). Each column comprised a PVC tube (0.3 m height; 0.10 m of internal diameter; 0.008 m<sup>2</sup> of cross-sectional area), equipped with a metal mesh to support sand media and an outlet stop valve at the bottom for leachate collection. Firstly, the sand media was washed with HCl and rinsed with tap water to remove nutrient traces, organic matter and acid residual until the pH of the leachate was 6.8 (tap water pH). This cleaned sand media was distributed between all columns and saturated with distilled water before the experiment started. At day 0, the sand was mixed with the corresponding fertiliser dose in the superficial layer (0–0.03 m), to achieve a value of 5.64 g-TP m<sup>-2</sup>. In the case of the column with Urea (that has no P), the dose was 2.54 g-TN m<sup>-2</sup> (same N-dose as in the column with SR1). Irrigation with distilled water was done with a shower system, installed at the top of each column, which allowed a slow and uniform water flow (100 mL per column, twice per week for 4 weeks; 29 days in total). Leachate sampling was also done twice a week, always 24 hours after irrigation, by opening the stop valve at the bottom of each column. Nine leachate samples were collected per column during the experiment. The collected volume of leachate and its corresponding TN and TP concentrations were

periodically measured to calculate the cumulative nutrient mass loss. The cumulative nutrient mass (TN or TP) loss in leachates was calculated as the sum of the masses of N and P found in each individual leachate sample collected during the experiment. The total loss of N and P was calculated according to Equation (3), and the N or P loss rate was calculated according to Equation (4).

$$\text{Total lost N or P (\%)} = \frac{\sum_{i=1}^9 \text{nutrient mass}}{\text{Applied mass of N or P}} * 100 \quad (3)$$

N or P loss rate (mg.g<sup>-1</sup>.d<sup>-1</sup>)

$$= \frac{\sum_{i=1}^{n=9} (\text{nutrient mass } i / \Delta T)}{(\text{Applied mass of N or P}) * n} \quad (4)$$

where  $i$  is the number of irrigations ( $i$  varies from 1 to 9),  $\Delta T$  is the days between irrigations ( $\Delta T = T_{i+1} - T_i$ ) and  $n$  is the total number of irrigations ( $n = 9$ ).

## Analytical procedures

All fertilisers tested were characterised for heavy metal content using microwave-assisted digestion (EPA Method 3052) followed by flame ionisation atomic absorption spectrophotometry (ThermoScientific iCE 300 SERIES spectrophotometer) in accordance to Standard Methods (SM 3111B, SM 3112, SM 3114C) (APHA 2017). Ammonium concentration in struvite precipitates and bio-solid samples was determined using Kjeldahl method (SM 4500), while total nitrogen (TN) and total phosphorus (TP) analyses were conducted according to the Colombian technical standard methods for fertiliser characterisation (NTC 234 and NTC 370, respectively) (ICONTEC 2011). The microbiological analysis of SR1 and the biosolid was carried out following the NTC 4574 Colombian standard. The microbiological analysis was not performed in SR2 due to the small sample available to perform the fertilisation and leaching tests.

SR1 and SR2 were examined by X-ray diffraction (XRD) on an XPert PANalytical Empyrean Series II diffractometer with a PIXcel 3D detector 2012 model, using Cu K-alpha radiation, for struvite identification. Struvite particle sizes were determined by making at least 100 measurements of particles, observed under an inverted microscope (BOECO BIB100) and using the *ImageJ* program (<https://imagej.nih.gov/ij/index.html>; accessed on January 21, 2021). Struvite precipitates (SR1 and SR2) samples were also analysed

using an X-ray microscope-EDX (INCA PentaFETx3 Oxford Instruments) to observe their morphologies and verify their composition.

TN and TP content in grass leaves and leachates was determined using Kjeldahl and spectrophotometric methods, respectively. The gravimetry technique from the Colombian technical standard method used for the characterisation of products for the agriculture industry (NTC 5167; ICONTEC 2011) was conducted to determine humidity and ash content in harvested grass samples (% fresh and dried weight). Dry matter (DM) content was calculated considering humidity content and total wet weight of the samples tested.

### Statistical analysis

One-way analysis of variance (ANOVA) was carried out to determine statistically significant differences between treatments (at  $p < 0.05$ ). Fisher's least significant difference (LSD) multiple-comparison test determined homogeneous groups for the examined treatments. Statistical analyses were carried out using the Statgraphics v 4.1 software.

## RESULTS AND DISCUSSION

### Struvite and biosolid characteristics

Characterisation of struvite's precipitates showed a high concentration of N, P and Mg in SR1 and SR2, with a minimum presence of other nutrients and heavy metals (Tables 1 and 3). Considering that N only precipitates as struvite

during the struvite production, the precipitate's purity was determined by relating the moles of N to the moles of struvite (precipitate weigh/struvite molecular weight). Thus, the precipitate's purity was 86.1, 78.7 and 77.7% for SR1, SR2 and SS, respectively. EDX analysis (Figure 2) and the XRD analysis was also used to corroborate its composition. The XRD data indicated that all crystals of SR1, SR2 and SS were mainly composed of struvite, with a similarity to the struvite pattern (according to high score software) of 97, 90 and 59%, respectively.

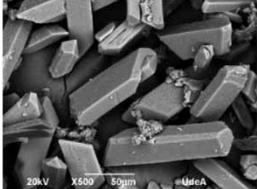
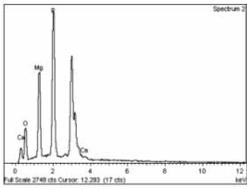
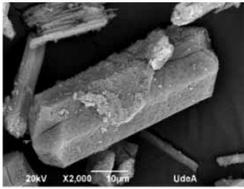
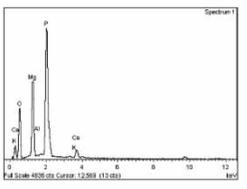
Struvite's precipitates, biosolids and commercial fertilisers were compared using the Colombian Technical Standards (NTC 5167) and European regulation (ICONTEC 2011; EU 2019) for fertilisers. It was found that the concentration of heavy metals in struvite precipitates was lower than in biosolids (Table 3). Thus, although heavy metals can be incorporated into the crystal lattice or adsorbed to the surface of the struvite and decrease the quality of struvite (Muhmood et al. 2019), the concentration of heavy metals was low in all precipitates, being lower than legal limits, except Cr in SR1. Biosolids fit the permissible limits for organic and organic-mineral fertilisers, except for Zn (19,000 mg kg<sup>-1</sup>) and Cr (87.2 mg kg<sup>-1</sup>), which were higher than the European Union limit (800 and 2 mg kg<sup>-1</sup>, respectively). SS, U and T15 presented minimum heavy metals concentration and below permissible limits, except for Cr in T15, which was higher than the European Union limit.

Particle sizes and struvite morphology were determined using inverted microscopy. The largest mean particle size of 112 µm was found in SR1, and the smallest mean particle size of 26 µm was found in SR2 (Table 1). According to

**Table 3** | Heavy metal concentrations in precipitates produced in this study (pH 9.0) and biosolid from San Fernando WWTP, as well as allowable limits for heavy metals in fertilisers (Colombia and European regulations)

| Component                 | Fertiliser |        |      |        |    |        | Legal limit (organic) |       | Legal limit (org-min) |       |
|---------------------------|------------|--------|------|--------|----|--------|-----------------------|-------|-----------------------|-------|
|                           | Biosolid   | STR1   | STR2 | SS     | U  | T15    | EU                    | Col   | EU                    | Col   |
| Cr (mg kg <sup>-1</sup> ) | 87.2       | 3      | 0.4  | NQ     | NQ | 33.61  | 2                     | 1,200 | 2                     | 1,200 |
| Ni (mg kg <sup>-1</sup> ) | 92.2       | 3.969  | 1.38 | NQ     | NQ | 10.97  | 50                    | 420   | 50                    | 420   |
| Pb (mg kg <sup>-1</sup> ) | 30.1       | NQ     | NQ   | NQ     | NQ | NQ     | 120                   | 300   | 120                   | 300   |
| Cd (mg kg <sup>-1</sup> ) | 1.751      | <0.003 | NM   | NQ     | NQ | NQ     | 1.5                   | 39    | -                     | 39    |
| Hg (mg kg <sup>-1</sup> ) | <0.01      | NQ     | NQ   | NQ     | NQ | NQ     | 1                     | 17    | 1                     | 17    |
| As (mg kg <sup>-1</sup> ) | <0.1       | NM     | NM   | NM     | NM | NM     | 40                    | 41    | 40                    | 41    |
| Zn (mg kg <sup>-1</sup> ) | 19,000     | 20     | 89   | NQ     | NQ | 695.87 | 800                   | -     | 1,500                 | -     |
| Cu (mg kg <sup>-1</sup> ) | 293.2      | 25.8   | 167  | 122.35 | NQ | NQ     | -                     | -     | 600                   | -     |

Abbreviations: NQ, not quantifiable; NM, not measured; EU, European Union; Col, Colombia.

| Struvite | SEM image (1)   | Element | Weight (%) (2) | Atoms (%) (3) | EDX  |
|----------|---|---------|----------------|---------------|--|
| SR1      |  | O       | 36.99          | 52.22         |  |
|          |   | Mg      | 20.56          | 18.69         |  |
|          |   | Al      | 0              | 0             |  |
|          |   | P       | 41.80          | 29.83         |  |
|          |   | K       | 0              | 0             |  |
|          |   | Ca      | 0.66           | 0.36          |  |
| SR2      |  | O       | 45.97          | 60.31         |  |
|          |   | Mg      | 18.99          | 16.40         |  |
|          |   | Al      | 0.31           | 0.24          |  |
|          |   | P       | 31.54          | 21.38         |  |
|          |   | K       | 0.37           | 0.20          |  |
|          |   | Ca      | 2.81           | 1.47          |  |

**Figure 2** | Characterisation of struvites obtained from real centrate SR1 (top) and SR2 (bottom) based on SEM image, compositional and EDX profiles. Notes: (1) SEM images at 500x and 2,000x for SR1 and SR2, respectively. (2) % weight refers to the weight of each element measured in the sample regarding the sum of weight of all elements of the sample. (3) % atomic is the number of atoms of each element with respect to the total number of atoms in the sample.

Shaddel *et al.* (2019), the size and morphology of the crystal are mainly influenced by the supersaturation (SI), but according to Tarragó *et al.* (2016), it is also influenced by the reaction time. Consequently, the mean size of SR1 was higher than SR2 size due to the high reaction time (5 days), despite presenting similar supersaturation levels (SI of 2.4 in both crystallisers).

Additionally, a microbiological analysis was performed on struvite SR1 and Biosolids. Enterobacteriaceae family (0 cfu g<sup>-1</sup>) and Salmonella genus (absent/in 25 g) were absent in both materials. This was expected because some pathogens, such as Enterobacteriaceae, are negatively charged; so owing to electrostatic repulsion, they will not be able to adsorb onto struvite particles at the alkaline pH 9 of the struvite crystallisation process (Muhmood *et al.* 2019). In the case of biosolid, Bedoya-Urrego *et al.* (2013) found a highly variable concentration of Enterobacteriaceae family (>3,000 cfu g<sup>-1</sup>) and the presence of Salmonella genus in all the samples in the biosolid of this WWTP, appointing that this material cannot be used as a fertiliser without a prior sanitation process. Therefore, the previous drying process of the biosolids (8 days in the open air) probably favoured the absence of these microorganisms in the tests' biosolids.

### Fertilisation test

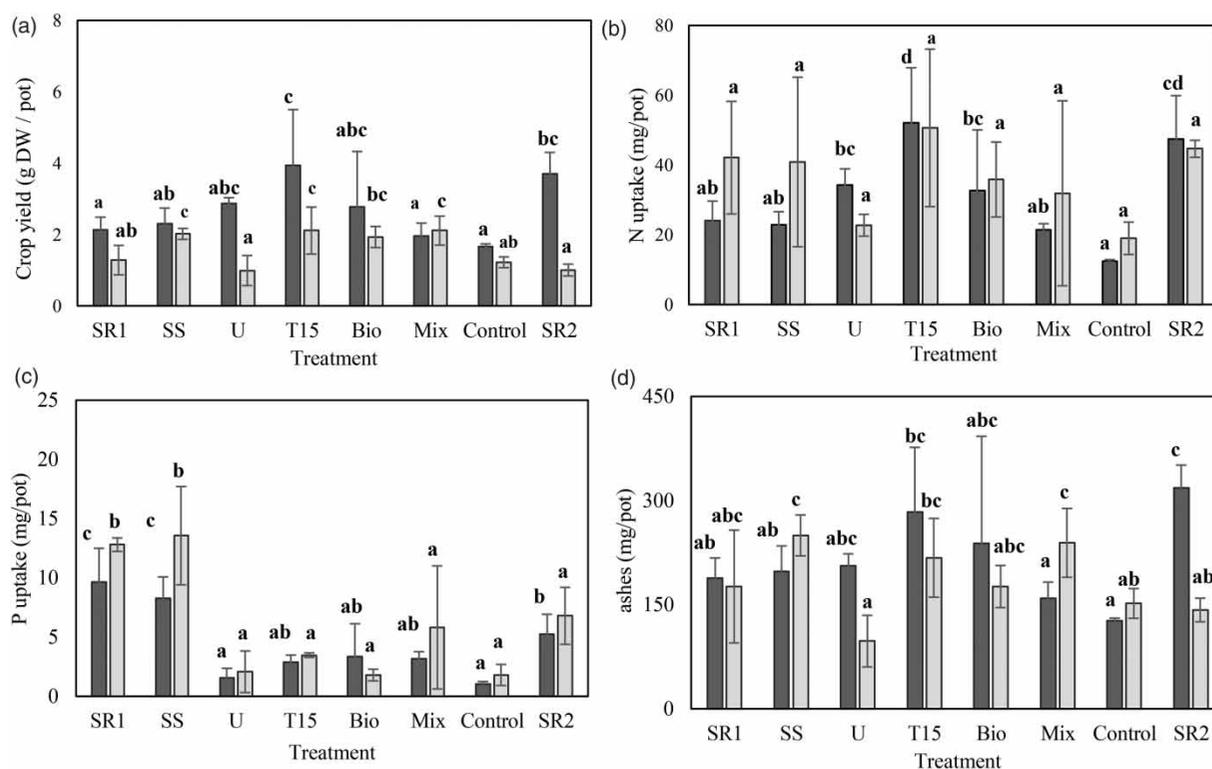
The highest and lowest crop yields after the first harvest (Figure 3(a)) of  $3.9 \pm 1.6$  and  $1.7 \pm 0.1$  gDW pot<sup>-1</sup> were obtained with T15 and in the control treatment, respectively ( $p < 0.05$ ). Despite this, in general, crop yields decreased after the second harvest, except in pots fertilised with Mix,

reaching again the highest crop yield in T15 treatment. This may be because the applied dose of N and K in T15 pots (Tables 1 and 3), as well as its accumulation (N uptake), was higher than in the other treatments ( $52 \pm 16$  mg N pot<sup>-1</sup>; Figure 3(b)). According to Fageria (2009), the N accumulation is one of the most critical factors for improving field crop yield.

The N uptake of SR2 treatment did not show statistically significant differences regarding T15, despite having a lower N content (Figure 3(b); Table 1). SR1 and SS presented lower N uptake (in the first harvest) than T15; this could be related to the particle size. Degryse *et al.* (2017) found that the rate of nutrient release from struvite is determined by the size of crystals. Also, Nelson (2000) showed an increase in N uptake of ryegrass as the size of the crystals decreased, after using struvite of different sizes. Therefore, it is possible that its low particle size can explain the highest N uptake in SR2 (mean size of 26.9 µm) in comparison with the others struvites tested (mean size >89 µm).

On the other hand, the P uptake by the grass was higher after SR1, SS and SR2 treatments than in the control and other treatments (Figure 3(c)). This proved that the P contained in struvites is highly available for plants. This might be due to the presence of Mg, which has a synergistic effect on P's dissolution in soils (González-Ponce *et al.* 2009). These results agree with those found by Ryu & Lee (2016), where the P and Mg concentration in the tissue of lettuces grown in struvite pots was much higher than that in commercial fertiliser pots.

The P uptake in SR1 and SS treatments was higher than in SR2 treatment. This could also be related to the particle



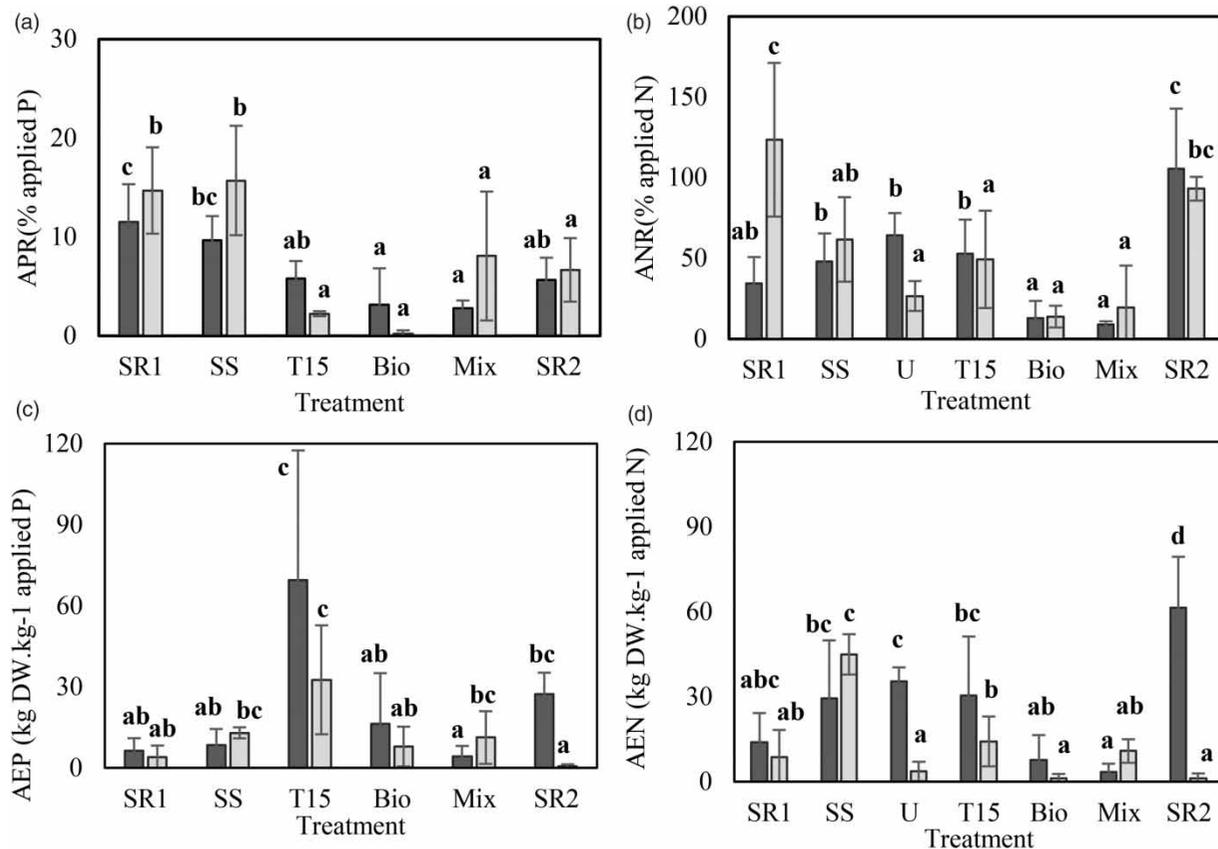
**Figure 3** | Crop yield, nutrients uptake and ash content, per harvest, in the fertilisation trial. (a) Grass yield (g DW per pot). (b) N uptake (mg per pot). (c) P uptake (mg per pot). (d) Ashes (mg per pot) in the grass. The standard deviation ( $n = 3$ ) within each treatment is indicated as the error bar. Letters (a–d) denote homogeneous groups; while within the same harvest, different letters indicate statistically significant differences according to Fisher's least significant difference (LSD) multiple-comparison test at the 0.05 level. Abbreviations: DW, dried weight; SR1, SR2, struvites produced in CSTR and FBR crystallizers, respectively; SS, synthetic struvite; U, commercial urea; T15, commercial fertiliser; Bio, digested WWTP sludge; Mix, mixture of biosolids and struvite; C control (without fertiliser). Colours: dark and light grey bars denote the mean values after the first and second harvest, respectively.

size. Guerrero (2013) found that the tomato P utilisation using triple-superphosphate increased sharply when the particle size increased from 0.5 to 6 mm (in diameter). So, it is possible that larger particle sizes in struvite increased the P accumulation during the grass fertilisation. The highest quantity of ashes after the first harvest was found in T15, SR2 and Bio treatments (Figure 3(d)). A high correlation was found between the amount of ash and the biomass (measured in dried weight), with a Pearson coefficient of 0.95 and 0.88 for data obtained after the first and second harvests respectively.

The agronomic efficiency (AEN, AEP) and the apparent recovery efficiency (APR, ANR) were calculated (Figure 4). The results show that the highest APR was attained after the first harvest in SR1 treatment and after the second harvest in SR1 and SS treatments:  $11.5 \pm 3.8$ ,  $14.7 \pm 4.4$  and  $15.7 \pm 5.5\%$ , respectively. Bio and Mix treatments reached the lowest APR ( $<3.14\%$  in the first harvest). The highest ANR was attained in the first harvest of SR2 treatment and in the second harvest of SR1 and SR2 treatments:  $100 \pm 37$ ,  $123 \pm 48$  and  $93 \pm 7\%$ , respectively. The lowest

ANR was also found in the first harvest of treatments Bio and Mix ( $<12.6\%$  Figure 4(b)). These results suggest that plants efficiently used the nitrogen and phosphorus contained in struvites based on their values of apparent recovery efficiency. The Mix product did not show favourable results concerning the N and P uptake or biomass production.

Regarding the agronomic efficiency, the T15 treatment reached the highest AEP of  $69 \pm 48$  and  $33 \pm 20 \text{ kg kg}^{-1}$  in the first and second harvests, respectively. The grass harvested firstly in the SR2 treatment also reached the highest AEN ( $61 \pm 18 \text{ kg kg}^{-1}$ ); however, grass of the second harvest in SR2 treatment was minimum. Crop yields depend on many factors, including climatic conditions and the presence of 17 essential nutrients for optimal growth and development (Fageria 2009). Therefore, the crop yield of grass in the T15 treatment could be positively affected by the small traces of nutrients (present in the sand used as substrate) and a higher contribution of K. However, struvite treatments presented an efficient use of N for biomass production, comparable or even higher than commercial



**Figure 4** | Phosphorus and nitrogen use efficiency, per harvest, in the fertilisation trial. Notes: The standard deviation ( $n = 3$ ) within each treatment is indicated as the error bar. Letters (a–d) denote homogeneous groups; while within the same harvest, different letters indicate statistically significant differences according to Fisher's least significant difference (LSD) multiple-comparison test at the 0.05 level. Abbreviations: APR and ANR, apparent fertiliser nutrient P and N recovery, respectively; AEP and AEN, agronomic efficiency of applied P or N, respectively; DW, dried weight. Colours: dark and light grey bars denote the mean values after the first and second harvest, respectively.

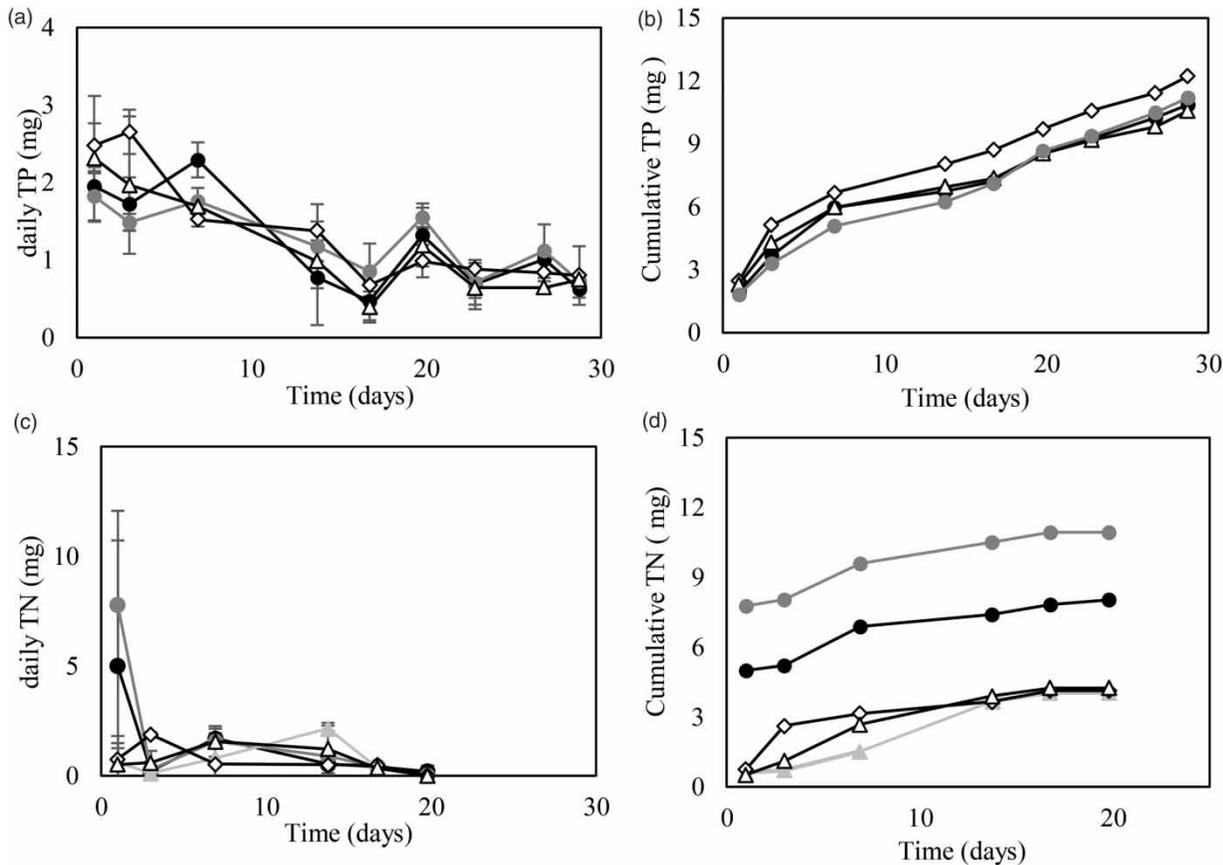
fertilisers (U and T15) (Figure 4(d)). The results indicate that struvite, although slightly soluble in water (solubility of  $0.18 \text{ g L}^{-1}$  at  $25^\circ\text{C}$ ; Le Corre *et al.* 2009), is as effective as commercial P fertilisers (solubility  $>950 \text{ g L}^{-1}$  at  $25^\circ\text{C}$  for Urea and T15; Nutrición de plantas SA) because of an increment of the available P concentration in soil and of the uptake of both P and N. These findings corroborate the usefulness of struvite obtained from real centrate as fertiliser, similarly to Talboys *et al.* (2016) and Hall *et al.* (2020).

### Leaching test

The daily and cumulative P loss in SR1, SR2, T15 and Bio, measured in leachates after irrigation (9 irrigations in 29 days), is shown in Figure 5(a) and 5(b). In the second irrigation (day 3), P leaching from T15 reached the maximum value of  $2.65 \text{ mg-P}$  ( $79.5 \text{ mg L}^{-1}$ ), equivalent to  $5.8\%$  applied-P. Meanwhile, the maximum P leaching value was attained in the third irrigation (day 7) in SR1 and SR2

columns, with values of  $2.29$  and  $1.76 \text{ mg-P}$ , respectively, being equivalent to  $5.0$  and  $3.8\%$  applied-P, respectively. The P leaching loss from Bio was slightly higher than struvites in the first two irrigations and presented its maximum release in the first irrigation (day 1). Therefore, SR1 and SR2 had better P slow-release properties than the other fertiliser tested because the maximum P release was attained after day 7. Although there is apparently an increase in the mass of P on day 20 in the tested fertilisers (Figure 5(a)), no statistically significant differences were found between the mass of P leached on days 17, 20 and 23 ( $p$ -value  $<0.05$ ; ANOVA analysis).

The N leaching loss in all treatments is shown in Figure 5(c) and 5(d). Nitrogen was rapidly washed out from the SR1 and SR2 treatment, whereas it was more slowly leached from T15, Bio and U treatments. The first irrigation N leaching from SR1 and SR2 reached the maximum value of  $5$  and  $7.8 \text{ mgN}$ , equivalent to  $24$  and  $46\%$  applied-N, respectively. In U treatment, the maximum N leaching loss



**Figure 5** | Nutrient loss in leachates during the leaching test. (a) Total P loss measured after each irrigation. (b) Mean cumulative P amount in leachates. (c) Total N loss measured after each irrigation. (d) Mean cumulative N amount in leachates. Note: After irrigation six (day 20), the content of N was not quantifiable. Symbols: ● SR1, ● SR2, ◇ T15 and ▲ Biosolid, ▲ U.

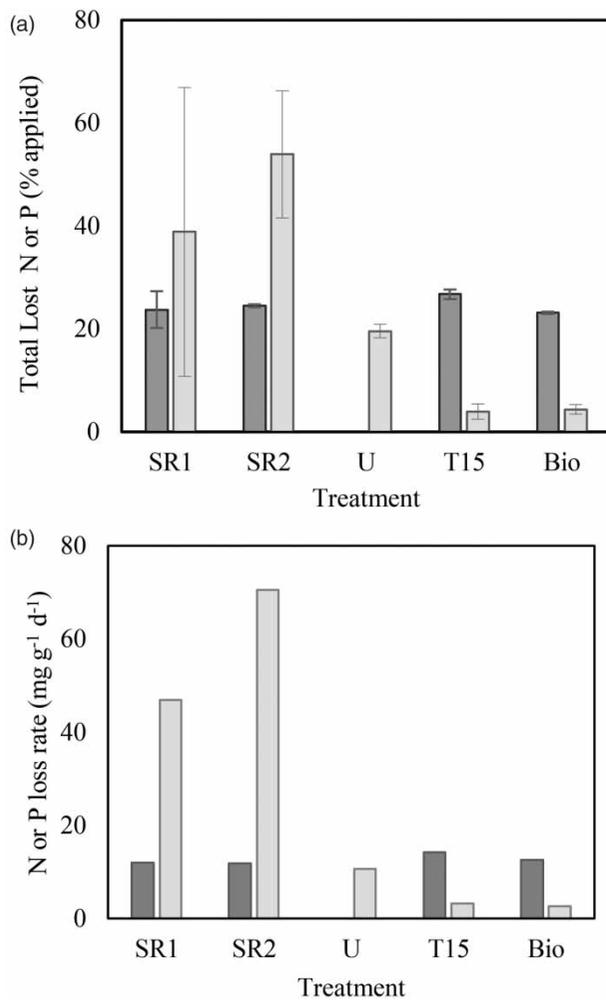
occurred in the third irrigation (day 7), equivalent to 3.9% applied-N. The maximum N leaching loss in the T15 and Bio columns occurred in the second and third irrigation, equivalent to 1.8 and 1.6% applied-N, respectively. Therefore, Bio had better N slow-release behaviour than the other fertilisers. The high N release in the first irrigation of SR1 and SR2 may be due to the small particle size of the struvite (<112  $\mu\text{m}$ ) tested in this research, similarly to Rahman *et al.* (2013).

The P leaching pattern in all treatments was very similar in all columns. However, the cumulative lost P in leachates was higher in T15 columns, with a mean value of  $12.22 \pm 0.42$  mgP, equivalent to  $26.7 \pm 0.92\%$  applied-P (Figure 5(b)). Nevertheless, the accumulated lost P in leachates was always higher in SR1 and SR2 columns (Figure 5(b)). The mean lost P in SR1, SR2 and Bio treatments was  $23.8 \pm 3.57$ ,  $24.5 \pm 0.29$ , and  $23.1 \pm 0.22\%$  applied-P, respectively. For the total nitrogen (TN), the average lost N for SR1, SR2, U, T15 and Bio treatments was  $38.8 \pm 28.1$ ,  $65.6 \pm$

$15.0$ ,  $19.6 \pm 1.3$ ,  $3.9 \pm 1.5$  and  $4.3 \pm 0.9\%$  applied-N, respectively (Figure 6(a)).

The average P leaching rate in this research was  $11.92 \pm 12.69$  and  $11.81 \pm 11.22$   $\text{mg-P g}^{-1} \text{d}^{-1}$  for STR1 and STR2, while it was  $14.23 \pm 16.94$  and  $12.51 \pm 15.87$   $\text{mg-P g}^{-1} \text{d}^{-1}$  for T15 and Bio, respectively. Meanwhile, the average N leaching rate was  $46.8 \pm 101$  and  $85.7 \pm 186$   $\text{mg-N g}^{-1} \text{d}^{-1}$  for SR1 and SR2, while it was  $10.87 \pm 15.86$ ,  $3.27 \pm 4.67$  and  $2.07 \pm 2.95$   $\text{mg-N g}^{-1} \text{d}^{-1}$  for U, T15 and Bio, respectively (Figure 6(b)).

The high variability of data occurred because the leaching rate was much higher in the first irrigations than in the last ones; additionally, also the high variability in the particles size of the struvites (Table 1) could have influenced this. Reza *et al.* (2019) also found higher P than N leaching rates in the fertilisers tested, finding an average P leaching rate of 1.78 and 2.07  $\text{mg-P g}^{-1} \text{d}^{-1}$  and an average N leaching rate of 4.88 and 5.59  $\text{mg-N g}^{-1} \text{d}^{-1}$  for struvite and fused superphosphate (FSP), respectively. The lower leaching



**Figure 6** | Nutrient loss and rate at the end of the leaching test. (a) Regarding the applied nutrient amount. (b) Mean nutrient loss rate ( $\text{mg N or P} \cdot \text{g}^{-1}$  applied-N or applied-P  $\text{d}^{-1}$ ). Colours: dark and light grey bars denote the mean values of P and N loss, respectively. Abbreviations: SR1, SR2, struvites produced in CSTR and FBR crystallizers, respectively; U, commercial urea; T15, commercial fertiliser; Bio, dried digested WWTP sludge.

values of N and P found by *Reza et al. (2019)* was explained by the irrigation frequency (once a week), the type of soil used (coarse sand and sandy soil) and the particle size of the struvite used. Additionally, other researchers have reported that low P leaching from fertilisers might be caused by the P molecule's binding capacity with clay particles and with other chemicals involved in P fixation in soils, such as Al, Fe and Ca (*Sharpley 1995*). However, the P with mineral or organic compounds' fixation may have been lower due to the inert sand soil used in this experiment.

Some researchers have reported that nutrient leaching from struvite is lower than chemical fertilisers. *Rahman et al. (2021)* observed in a test of 7 weeks (1 irrigation per week), a P leaching of 0.03–0.37% applied-P for struvite

and 0.23–0.25% applied-P for FSP. Also, *Rahman et al. (2021)* reported that leaching loss of N was higher in FSP-urea treatments (>6.47% applied-N) than in MAP-urea treatments (<2.05% applied-N). In this work, the total lost N showed an opposite trend: the highest total N lost was presented in the treatments with struvite (>39%) and the minimum in T15 (3.9%) and Bio treatments (4.3%).

According to *Degryse et al. (2017)*, struvite dissolution in soil depends on the particle size; the difference between granular or grounded struvite can be explained by the increasing soil-fertiliser contact with decreasing particle size. When struvite is in granular form, diffusion of dissolved P from the particle surface into the soil becomes the rate-limiting process. Therefore, although most research reported that leaching pattern of struvite is slow, and nutrients are released for a more extended period compared with mineral fertilisers that can be completely leached out in the first 1–3 days (*Ahmed et al. 2018*). In this research, we found that struvite with smaller particle size (<126  $\mu\text{m}$ ) presented similar P leaching rate to a commercial NPK fertiliser (T15) and higher N losses than the 2-commercial fertiliser tested (Urea and T15).

## CONCLUSIONS

This study shows the application of struvites (SR1, SR2), obtained from the centrate of a conventional WWTP containing high  $\text{NH}_4\text{-N}$  concentration using two types of reactors (CSTR and FBR), as fertiliser. These struvites were composed by N 4.5–4.9%, P 10.3–13.8%, Mg 5.6–7.6%, Ca 1.10–2.06%, and K 0.05–0.49%. Also, heavy metals were detected, but all were below the Colombian and European regulated limits for fertilisers, except slightly higher Cu content. Enterobacteriaceae family and *Salmonella* genus were not found in the precipitates.

In the fertilisation test, the maximum crop yield was attained by using the commercial fertiliser T15; however, it was found that P and N uptakes were higher in some of the evaluated struvites. The grass grown with the higher particle size struvite (89–113  $\mu\text{m}$ ) had the highest apparent P recovery efficiency ( $11.5 \pm 3.8$  and  $15.7 \pm 5.5\%$  in first and second harvests, respectively), meaning that the P of struvites is highly available to be used by plants, even more than commercial T15. Besides, the struvite with the smallest particle size (27  $\mu\text{m}$ ) presented the highest apparent N recovery efficiency in the first harvest ( $100 \pm 37\%$ ). Thus, struvites showed greater efficiencies in the grass absorption of N and P than the biosolid or the commercial fertilisers Urea and T15. Also, through the leaching tests, it was

found that P from struvites and biosolid was released slightly slower than that coming from commercial T15. Nevertheless, the N release was faster in struvite treatment than in Biosolid, T15 and Urea fertilisers; this effect was even increased in the case of the struvite with the smallest particle size ( $65 \pm 15\%$  N losses). Hence, struvites recovered from conventional WWTP are an effective alternative to commercial fertilisers as a readily available P and N source to plants. Although the Biosolid presented low nutrient recovery efficiency, further studies are required to ascertain the potential eco-friendly application of the combined use of Bio and struvites as this could also be another sustainable alternative for a WWTP.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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