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Controlling struvite particles' size using the up-flow velocity

E. Tarragó, S. Puig *, M. Ruscalleda, M.D. Balaguer, J. Colprim

LEQUIA, Institute of the Environment, University of Girona, Campus Montilivi, E-17003 Girona, Catalonia, Spain

HIGHLIGHTS

- Up-flow velocity determines the minimum theoretical equivalent diameter recovered.
- Air-flow is the control variable to adjust the up-flow velocity.
- Particle size of the product recovered can be adjusted to customers' requirements.

GRAPHICAL ABSTRACT
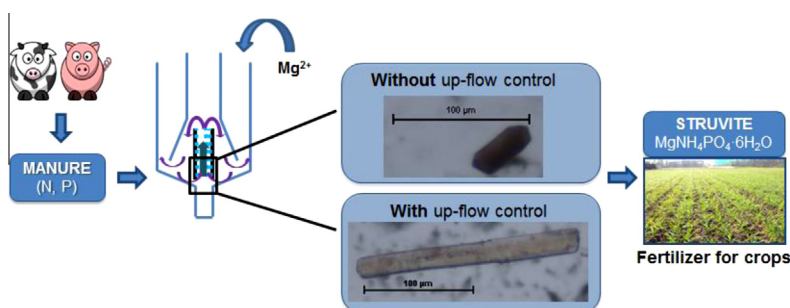
ARTICLE INFO

ABSTRACT

Struvite crystallization has been widely investigated, but little attention has been focused on particle size, an important characteristic in fertilizers that affects the agronomic response. Although there is no standard, it is an interesting parameter to be controlled as each crop and soil require a specific fertilizer size. Few attempts have been made to increase particle size. In air-lift reactors, the up-flow velocity could be used as a controlling parameter for particle size. It is hypothesized that the up-flow velocity determines the minimum theoretical equivalent diameter that can be recovered. Its effectiveness as a controlling parameter for particle size was evaluated in a combined air-lift reactor at different up-flow velocities (from 13.3 to 26.3 m h^{-1}). Particle size was found to be directly correlated with the up-flow velocity, and according to the theoretical approach about the minimum equivalent diameter. Moreover, particle growth was promoted by operating the crystallizer in continuous mode at the best up-flow velocity (22.6 m h^{-1}), having an increase of the mean particle size in time (138.6 h) from 201 μm to 314 μm, and recovering particles up to 800–1000 μm. The up-flow velocity control did not affect the phosphate recovery rates (>90%) and XRD confirmed that only pure struvite crystals were recovered. Therefore, this study shows that struvite can be recovered from a waste stream and control its particle size using the up-flow velocity to adjust to the customers' requirements.

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1. Introduction

Phosphorus recovery from waste streams is considered to be an essential and significant breakthrough for assuring long-term and economical phosphorus supply [1], as the reserves may be depleted within around 200 years [2]. For this reason, the actions for the coming 10–25 years must focus on its recovery, rather than its removal.

European cows and pigs jointly produce about 1.27 billion ton of manure each year. If this manure is directly applied to the soil, it can degrade water quality and represent an eutrophication threat in nitrate vulnerable zones [3]. Traditionally, these nutrients were removed before the application, to diminish the environmental impact and prevent contamination of agricultural soils.

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* Corresponding author.
  E-mail address: sebastia@lequia.udg.cat (S. Puig).

A new paradigm consists on the recovery of these nutrients, rather than its removal, to reduce the reliance on industrial fertilizers. Therefore, some European governments have been promoting new technologies to recycle P, a limited resource, from wastewater, sewage sludge and animal wastes [4].

Phosphorus can be recovered from waste streams via struvite crystallization. Struvite is an effective slow-release fertilizer. Struvite offers many advantages versus conventional fertilizers: presents low leach rates and slowly release of nutrients [5]; it is suitable in grasslands and forests where fertilizers are applied once in several years [6]; it does not damage growing plants when a single high dose is applied [7]; represents an alternative for those crops that require magnesium, such as sugar beets [8]; and, phosphorus uptake is higher in ryegrass when struvite is used as a fertilizer [9].

Particle size is an important characteristic in fertilizers, as bigger particles will have longer effects on soil, increasing the nutrient uptake of plants/crops. It also affects agronomic response, blending, storage, handling and application properties [10,11]. Although there is no standard for particle size, it is identified as the most important factor in producing a stable, high-quality, blended fertilizer [12]. Ahmed et al. [13] stated the need to focus future studies on determining the optimal placement and granule size to match the granule dissolution to the lifecycle of the plant.

Most probably, the product recovered from the waste streams will be used by the fertilizers producers as a green fertilizer blending, demanding for a stable particle size. Therefore, a methodology to control particle size could be helpful to adjust it in the range of customers' requirements.

How to increase particle size has been investigated in the literature. Two main methodologies were used: promote secondary nucleation or increase the reaction time. Seeding crystals or seeding inert materials can be used to promote secondary nucleation. Mehta and Batstone [14] recovered struvite crystals with a volume median size of 100 ± 5 μm by using struvite crystals of 35 ± 3 μm as seeds. Wang et al. [15] compared between seeded and unseeded experiments, and concluded that the production of large particles (350 ± 32 μm) is likely unfeasible in a reasonable operation time (1 h) without seeding. Suzuki et al. [16] assessed different inert materials (stainless steel, wood and rubber) for struvite accumulation on their surface at different reaction times (from 5 to 42 days). They showed that after 5 days in an aeration column, the 80% (weight) of struvite were under 1000 μm, whereas after 42 days, the 65% were over 2000 μm.

However, some authors stated that these methodologies may increase the operational costs, may end into materials interferences or low accumulation efficiencies depending on the seeding materials used [16] and decrease the purity of the struvite crystals [1].

On the other hand, Ronteltap et al. [17] assessed the effect of some operational factors (type of stirrer, pH and temperature) on struvite particle size recovered from urine in a CSTR. They found that the use of a magnetic stirrer increased the supersaturation of the solution, preferring nucleation over crystal growth, and therefore, recovering smaller crystal sizes. Nevertheless, some of the developed crystallizers (such as air-lift reactors) do not have/use mechanical agitation. Therefore, alternative approaches should be put in practice, such as using hydrodynamics to control struvite particle size.

As stated, many studies have investigated the parameters affecting crystal growth. But, none of them, under our concern, suggest a methodology to control particle size. In this study, the up-flow velocity is assessed as a control parameter for the growth of struvite particles, in a combined air-lift reactor. By modifying the air-flow rate applied, the up-flow velocity can be controlled. It is hypothesized that the up-flow velocity determined the minimum theoretical equivalent diameter that can be recovered. This

theoretical diameter was contrasted with the experimental results, promoting both struvite nucleation and growth. The performance of the designed crystallizer was evaluated in terms of particle size and characterization of the product recovered.

2. Materials and methods

2.1. Experimental set-up

A methacrylate crystallizer was designed as an air-lift reactor plus a settler (Fig. 1). Three differentiated zones could be distinguished in the crystallizer: riser, clarifier and collector. Supersaturated conditions were ensured in the riser zone. Struvite growth was promoted in this zone thanks to the recirculation and fluidization of small particles from zone 2. The clarifier consisted of a quiet zone to prevent particles loss as the up-flow velocity was kept constantly low (0.0177 m h^{-1}), even at higher air-flow rates (0.0179 m h^{-1}). The collector, where the particles settled once their settling velocity was higher than the up-flow velocity.

The total volume of the crystallizer was 14.6 L with an hydraulic retention time (HRT) of 3.5 h. The influent wastewater was heated up to 30.5 ± 1.0 °C, to simulate the temperature of the digester supernatant, and fed continuously (4.13 ± 0.04 L h^{-1}) into the crystallizer (riser zone). A magnesium solution was added to allow struvite precipitation at a ratio Mg^{2+}/PO_4^{3-} of 2.5. Aeration in the riser was controlled by means of a mass flow meter (Rotameter, 2100/INOX). pH was controlled in the riser at 8.5 using a control panel (Memograph; Endress+Hauser, RSG40), dosing NaOH 1 M. Struvite particles settled in the bottom part of the crystallizer (collector) and were recovered at the end of the experiments, while the effluent wastewater was continuously discharged by overflow.

2.2. Experimental procedure

Five tests of 1 h were carried out in duplicate at five up-flow velocities (13.3, 15.4, 17.0, 22.6, 24.9 and 26.3 m h^{-1}) to find out the influence of the up-flow velocity on struvite particles' size. The up-flow velocity was controlled by modifying the air-flow applied at 1, 1.5, 2, 5, 7.5 and 10 L min^{-1}, respectively.

Then, a continuous mode test at the up-flow velocity of 22.6 m h^{-1} was carried out, in duplicate, to study the influence of increasing the particle residence time to 138.6 h on particle size distribution. Samples were taken periodically (25.5, 48.5, 69.5 and 138.6 h) from the collector to determine particle size distribution through time.

In all tests, struvite crystal size, recovery efficiency and purity conditions were analyzed.

2.3. Influent wastewater

Effluent from the wastewater treatment plant of Girona (Spain) was used as media to prepare the influent wastewater. The concentrations of ammonium and phosphate were adjusted to 929.3 ± 26.9 mg NH_4^+ L^{-1} and 368.5 ± 14.9 mg PO_4^{3-} L^{-1}, respectively. Those concentrations simulated the characteristics of cow and pig manure samples from Spain and The Netherlands, previously characterized (digested manure after a solid/liquid separation unit). Table 1 presents the main physico-chemical characteristics of the influent.

The average $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio in the influent was 2.5:13.3:1.0. Mg^{2+}/PO_4^{3-} molar ratio was 2.5, similar to the ratios found in the literature for similar influents: Mg^{2+}/PO_4^{3-} of 1.79 from digested swine wastewater [18], 2.14 from synthetic swine wastewater [19], 3.29 (calculated) from anaerobic digested sludge [20] and 4.8 from anaerobically digested dairy manure [21].
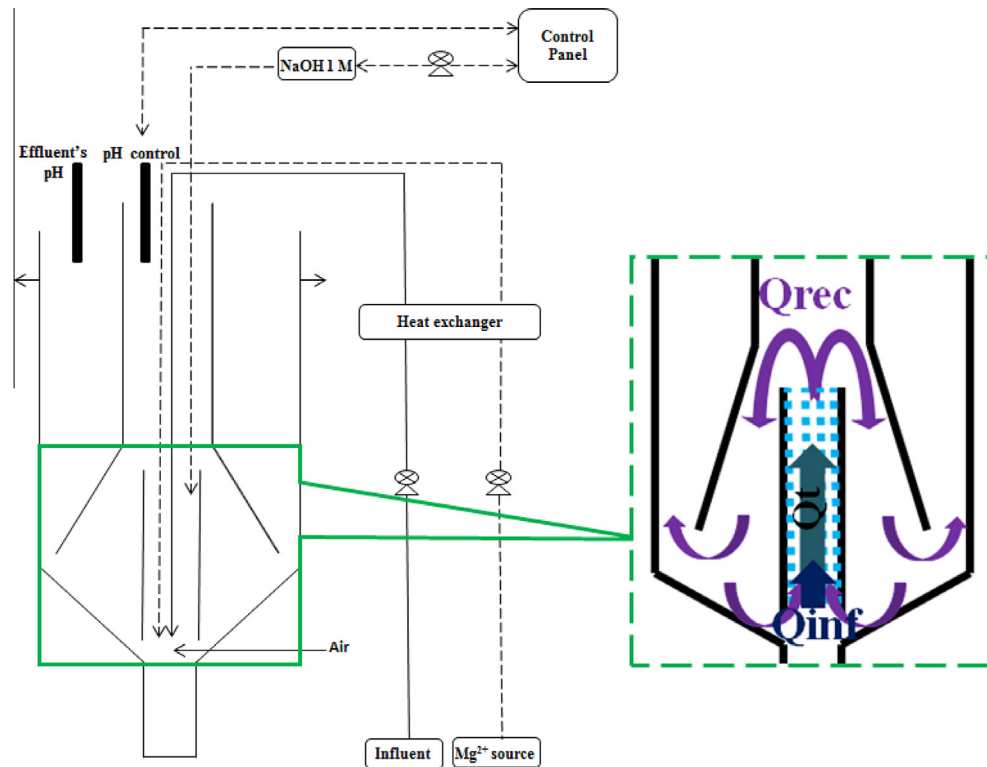
Fig. 1. Scheme of the crystallizer designed for struvite recovery. Crystallizer's parts: riser (1), clarifier (2) and collector (3). In the zoom, crystallizer's hydrodynamics in the riser: recirculation flow (Qrec), induced by the air-flow rate applied; influent flow (Qinf); and total flow (Qt) as the sum of Qrec and Qinf.

Table 1
Physico-chemical characteristics of the influent. The results are presented as mean ± standard deviation.

	Units	Influent
pH	–	8.45 ± 0.02
Conductivity	mS cm^{-1}	5.56 ± 2.95
Temperature	°C	30.5 ± 1.0
Total suspended solids (TSS)	mg TSS L^{-1}	167 ± 71
Volatile suspended solids (VSS)	mg VSS L^{-1}	83 ± 21
Magnesium	mg Mg^{2+} L^{-1}	236.9 ± 19.2
Ammonium	mg NH$_4^+$ L^{-1}	929.3 ± 26.9
Phosphate	mg PO$_4^{3-}$ L^{-1}	368.5 ± 14.9
Potassium	mg K$^+$ L^{-1}	21.8 ± 7.3
Calcium	mg Ca^{2+} L^{-1}	66.5 ± 19.9

2.4. Calculations

The up-flow velocity in the riser was calculated according to Eq. (1). This parameter was function of the total flow inside the riser and the section of the riser. In the designed crystallizer, the total flow (Qt) was the sum of the influent flow treated (Qinf) plus the recirculation flow (Qrec) induced by the aeration applied. The recirculation flow into the riser was calculated according to Merchuk and Gluz [22], taking into account the superficial gas velocity (J$_G$). By determining the recirculation and the influent flow, the total flow (Qt) was obtained, and the up-flow velocity was calculated according to Eq. (1).

$$\text{Up-flow velocity} = \frac{\text{Total flow}}{\text{Section}} \tag{1}$$

The up-flow velocity determines the minimum theoretical equivalent diameter (MTD) that can be recovered. The MTD was calculated according to Eq. (2). Particles smaller than the theoretical equivalent diameter remain in suspension, while bigger
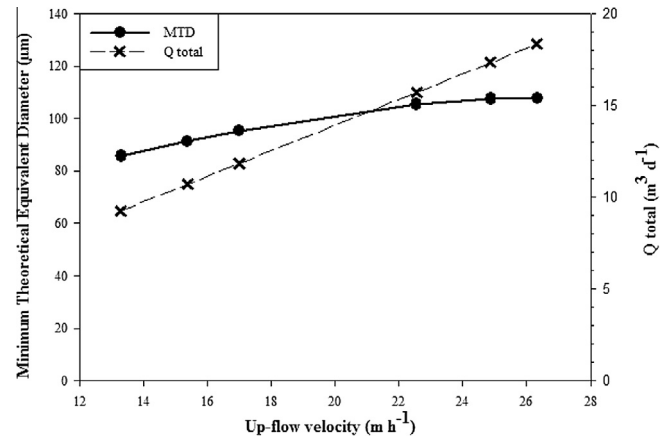

Fig. 2. Minimum theoretical equivalent diameter (MTD), in μm, that can be retained in the riser as a function of the up-flow velocity (m h^{-1}). The total flow (m^3 d^{-1}), as a sum of the recirculation (Qrec) and the influent flow (Qinf), is represented as Q total.

particles settle in the collector. The MTD that can be retained in the riser is determined as a function of the up-flow velocity applied (Fig. 2).

$$\text{MTD} = \sqrt{\frac{v \cdot 18 \cdot \mu}{(\rho_p - \rho_L) \cdot g}} \tag{2}$$

where the critical settling velocity (v) was assumed to be the up-flow velocity, ρ_p and ρ_L were the density of the particle and the fluid density (995.65 kg m^{-3}); g was the standard acceleration due to gravity and μ was the fluid viscosity (0.7978 mPa s^{-1}). The fluid density in the riser was also influenced by the air-flow according to Eq. (3).

$$\rho_L = (\rho_{air} \cdot \varphi_{riser}) + (\rho_{fluid} \cdot (1 - \varphi_{riser})) \tag{3}$$

where ρ_{air} is the density of the air at 26.5 °C (temperature of the air entrance), φ_{riser} is the gas holdup in internal air-lift reactors [22] and ρ_{fluid} is the fluid density at 30.5 °C (average temperature inside the crystallizer).

The driving force for struvite formation, and for all crystallization processes, is the supersaturation [23]. The relative supersaturation (Sr) was calculated based on the methodology followed by Bergmans (2011) [2] (Eq. (4)). The relative supersaturation is a function of the dimensionless supersaturation ratio (Sc), which in turn depends on the analytical molar concentration (Pso) and the solution properties (Pcs). Pcs is a function of the minimum struvite solubility product (Kso), as well as the ionization fraction (α_i) and the activity coefficients (γ_i) of each struvite compound (Eq. (5)). The activity coefficients were calculated from the extended form of the Debye-Hückel equation proposed by Davies, 1962 [24]. According to this, the solution is supersaturated for Sr > 0 and undersaturated for Sr < 0.

$$Sr = Sc - 1 \tag{4}$$

$$Sc = \left(\frac{Pso}{Pcs}\right)^{1/3} \tag{5}$$

The induction time was determined by monitoring on-line pH. Mehta and Batstone [14] defined the induction time as the period time between the achievement of supersaturation and the appearance of crystal nuclei, which can be measured as the time for the first pH drop after the initial setting.

2.5. Analytical methods

Influent and effluent liquid samples were taken periodically and analyzed to determine the nutrient recovery efficiency of the process. The concentrations of ammonium, phosphate, magnesium, potassium and calcium in the liquid phase were determined by Ion Chromatography (Dionex, IC5000). Total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to standard methods [25]. pH (EC-Meter BASIC 20+, Crison, Spain) and conductivity (EC-Meter BASIC 30+, Crison, Spain) were measured on-line and periodically, respectively. The product (precipitate) obtained was characterized by X-ray diffraction analysis (X-ray Diffractometer, Bruker, D8 Advance) to determine crystal's structure. Laser diffraction (Beckman Coulter, LS 13320 MW Optical Bench) and optical counting (Nikon, Eclipse E2000) were used to determine the size distribution of the crystals.

3. Results and discussion

3.1. MTD as a function of the up-flow velocity

The up-flow velocity determines the minimum theoretical equivalent struvite diameter that can be recovered. Fig. 2 presents the MTD versus the up-flow velocity. The MTD increased at the highest up-flow velocities. By increasing the air-flow rate (so the up-flow velocity), the density of the liquid is decreased and a higher recirculation flow is induced, increasing the minimum theoretical equivalent diameter that can be recovered. Therefore, only particles with the minimum diameter could settle in the collector, whereas smaller particles were recirculated into the riser and maintained in fluidization, while growing until the critical diameter was reached.

The methodology used, based on Merchuk and Gluz [22] calculation for the recirculation flow induced in an air-lift reactor, allowed to determine the minimum theoretical equivalent diameter that could be recovered. It was a useful tool, both for

operational conditions and product recovery. This theoretical approach was confirmed with the experimental results for the different up-flow velocities tested, as only bigger particles than the minimum theoretical equivalent diameter were recovered.

3.2. Struvite recovery performance at different up-flow velocities

Table 2 compares the struvite recovery performance at different up-flow velocities. Its recovery performance was not influenced in any of the up-flow velocities applied, in terms of supersaturation, phosphate recovery and struvite production.

The design of the crystallizer as an air-lift reactor plus a settler was proved to be effective for P-recovery as struvite from simulated digested manure after a solid/liquid separation. High P-recovery efficiency (94.4 ± 1.3%, on average) was achieved by minimizing the reagents consumption (Mg^{2+}/PO_4^{3-} ratio of 2.5). Phosphate was recovered as struvite in the collector, achieving an average struvite production of 1.63 ± 0.21 g L^{-1} treated. These results are in agreement with Stumpf et al. [26] that recovered struvite from a synthetic solution, in a similar air-lift reactor (with a diameter of 30 cm) at different air-flow rates (from 1.7 to 8.3 L min^{-1}). They established that P-recovery was dependent on the amount of the stripped CO_2, increasing at higher air-flow rates (from 58% of P-recovery in 1 h at 1.7 L min^{-1}, to 90% at 8.3 L min^{-1}). In the present study, P-recovery efficiency at all the up-flow velocities studied, and consequently, in all the air-flow rates applied, was approximately 95% in 1 h.

X-ray diffraction (XRD) analysis confirmed that the crystals recovered in the collector were pure struvite. Fig. 3A presents a representative XRD diffractogram of the particles recovered at the up-flow velocity of 22.6 m h^{-1}. These results confirmed that the quality of the struvite recovered was not affected by the presence of suspended solids (83 ± 21 mg L^{-1}) or calcium concentration (66.5 ± 19.9 mg Ca^{2+} L^{-1}) in the influent (Ca/Mg ratio of 0.17). The suspended solids in the influent were mainly colloidal (as it would be expected after a solid/liquid separation unit) and just passed through the system without being settled in the collector nor captured into the crystals. Thus, the effluent VSS concentration was similar (75 ± 23 mg L^{-1}), except in the lowest up-flow velocity of 13.3 m h^{-1} (Table 2). The concentration of calcium was around 66.5 mg Ca^{2+} L^{-1}, which came from the treated effluent from Girona's WWTP, used as a media to prepare the synthetic swine wastewater. The product obtained in all the studies was characterized by X-ray diffraction (XRD) analysis as pure struvite crystals, showing no presence of amorphous substances, contrasted with optic microscope observations. Our results are in concordance with Crutchik and Garrido, Hwang and Choi, Le Corre et al. and Stratful et al. [27–30], in which struvite formation was enhanced by having a Ca^{2+}/Mg^{2+} molar ratio below 1 [27–29] (0.17 in our study), and/or a high ammonium concentration in the influent, in a NH_4^+/PO_4^{3-} ratio of 9.4 [30] (13.3 in our study). Therefore, nutrients were always recovered as pure struvite crystals, without any interference of influent's colloidal suspended solids or the presence of calcium in the influent used.

The air-lift configuration allowed the recirculation of small particles into the riser, promoting heterogeneous nucleation and crystal growth due to the recirculation flow induced by the air-flow applied in the riser. The crystallizer configuration promoted supersaturated conditions in the riser, where the influent wastewater was fed, the magnesium solution dosed and pH was adjusted. Consequently, struvite's nuclei were formed in the riser, where it had the highest availability of nutrients and supersaturation conditions (Sr of 0.21 ± 0.06, on average). The values of relative supersaturation obtained in this study were similar to the ones obtained by Kofina and Koutsoukos [31] in their study of spontaneous precipitation of struvite, as similar operational conditions were used, such

Table 2
Relative supersaturation, induction time, struvite production and phosphate recovery efficiency for each up-flow velocity studied. Also, volatile suspended solids (VSS) in the effluent of each test are presented.

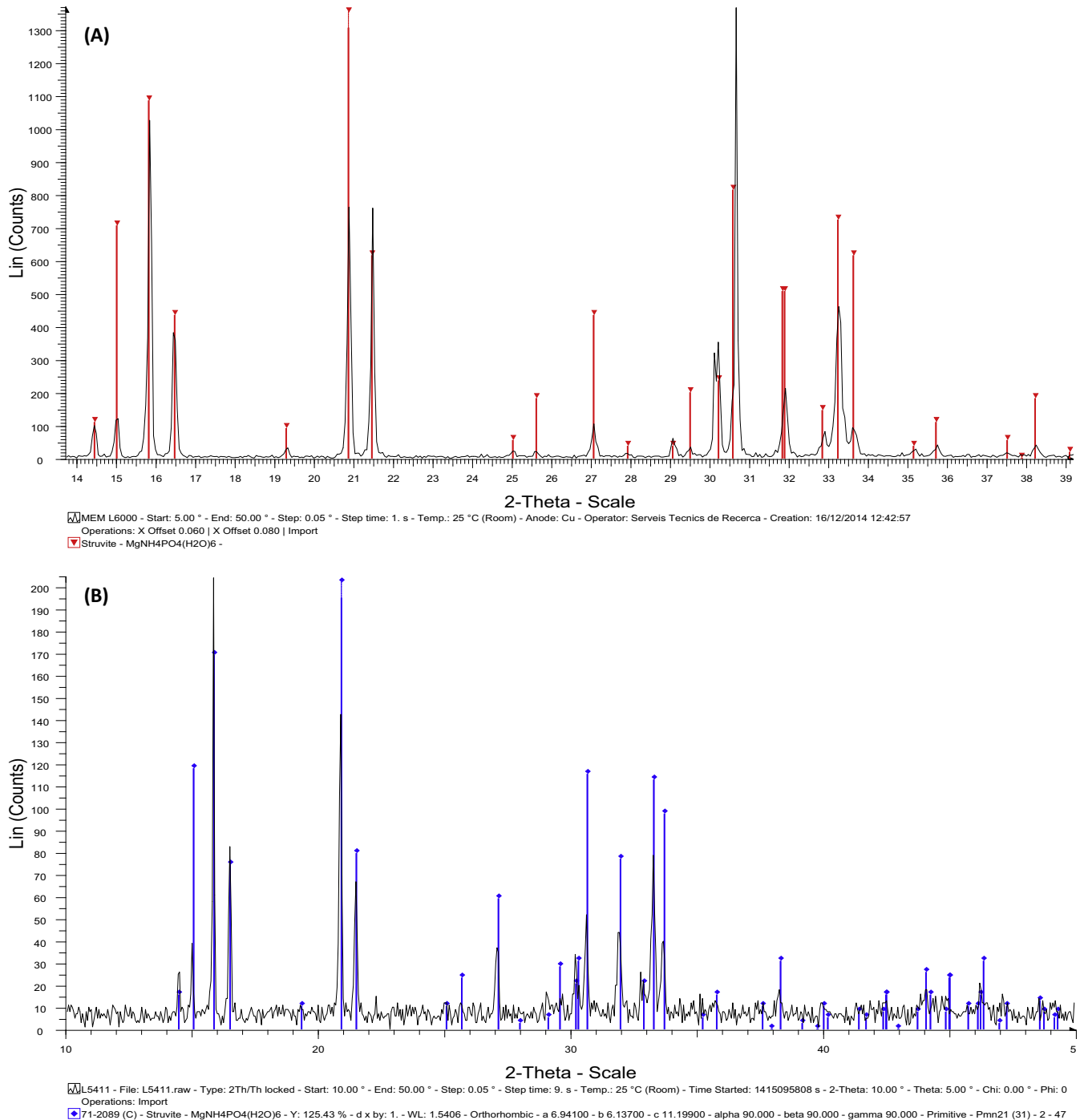| Up-flow velocity (m h⁻¹)	Air-flow (L min⁻¹)	Sr (mol L⁻¹)	Induction time (min)	Struvite production (g L⁻¹ treated)	PO₄³⁻ recovery efficiency (%)	VSS in the effluent (mg VSS L⁻¹)
13.3	1	0.25	2.17	1.26	92.3	35
15.4	1.5	0.12	2.33	1.74	94.5	68
17.0	2	0.22	0.67	1.76	94.6	54
22.6	5	0.22	0.34	1.67	95.4	108
24.9	7.5	0.27	0.54	1.55	95.0	93
26.3	10	0.27	0.67	1.70	95.4	71

Fig. 3. XRD diffractograms of the precipitates settled in the collector of the crystallizer at the up-flow velocity of 22.55 m h⁻¹. (A) Test for struvite recovery at different up-flow velocities (1 h tests); (B) continuous mode tests.

as pH, temperature and concentrations of the influent (considering the phosphate, the limiting compound in our study).

The induction time (the time lapse until the first pH drop of 0.05 is detected) was always short, between 0.34 and 2.33 min (Table 2). However, the induction time was reduced when the up-flow velocity was increased, meaning that first nuclei were formed faster at higher up-flow velocities. Hence, the induction time depended on the air-flow rate applied in the riser. Higher up-flow velocities led to lower induction times, as the mixing energy, one of the parameters affecting induction time [1], was supposed to be higher and favored nucleation.

The applicability of the designed crystallizer is proved, showing good performance results, both in batch and continuous mode, without affecting the production and the quality of the product recovered. The results obtained in this study were compared to the performance of similar reactors, in terms of P-recovery, operation conditions (HRT) and the average particle size of the product recovered (Table 3). High P-recoveries were achieved, both in batch and continuous mode tests, in comparison with other studies [2,26,32]. The system was able to operate at low HRT, compared to Ueno and Fuji [33], without affecting the system performance. The air-lift configuration allowed the possibility of controlling particle size, which will be further analyzed in the following sections.

3.3. Experimental size of struvite particles

The design of the crystallizer allowed the control of the up-flow velocity in the riser, by applying a specific air-flow rate. The up-flow velocity could have an influence in the size of the particles' recovered in the collector. As stated in Fig. 2, only bigger particles with a settling velocity equal or higher than the up-flow velocity can settle at the collector. Different up-flow velocities were tested (from 13.3 to 26.3 m h^{-1}) by increasing the air-flow rate from 1 to 10 L min^{-1}.

Table 4 presents both the theoretical approach about the MTD that can be recovered and the experimental results of particle size (mean equivalent diameter recovered). In all tests, the theoretical approach was confirmed experimentally, recovering a mean equivalent diameter (Mean Deq) bigger than the MTD calculated by Eq. (2).

The results obtained showed that the up-flow velocity in the riser is directly correlated with the particle size of the struvite recovered. Fig. 4 shows the experimental particle size recovered as a function of the up-flow velocity, including 95% confidence

Table 4
Comparison between the MTD and the experimental mean equivalent diameter recovered (Mean D$_{eq}$) for each up-flow velocity studied.

Up-flow velocity (m h^{-1})	MTD (µm)	Mean D$_{eq}$ (µm)
13.3	85.7	112.2 ± 0.6
15.4	91.4	126.5 ± 7.3
17.0	95.4	136.9 ± 4.9
22.6	105.5	148.5 ± 6.4
24.9	107.5	201.9 ± 7.0
26.3	107.8	244.0 ± 2.0

and prediction bands. All particle sizes recovered are in the zone of 95% confidence, except for the particle size recovered at the up-flow velocity of 22.6 m h^{-1}, which differs slightly. This up-flow velocity is enclosed in the 95% prediction band, due to the standard deviation between duplicates.

Therefore, by increasing the up-flow velocity from 13.3 to 26.3 m h^{-1} (air-flow rate from 1 to 10 L min^{-1}), the average diameter of the crystals recovered increased from 112.6 to 242.6 µm (46%). Besides, the increase of the up-flow velocity in the riser resulted in an increase of the recirculation flow, promoting heterogeneous nucleation and crystal growth.

A wide range of struvite particles' sizes were recovered in the literature, from 0.5 mm to 6.5 mm [34]. Nevertheless, few studies have been able to deal with the production of fines and growing large pellets, mainly by using fines as seeding material and increasing the retention time (longer periods of time). For example, Ueno and Fujii [33] recovered particles up to 500–1000 µm in a fluidized bed reactor treating dewatered filtrate from anaerobic sludge digestion and using the fines produced as seeding materials, at a retention time of 10 days. In comparison with our results, as the designed crystallizer allowed the recirculation of small particles, and therefore, enhanced struvite growth, a mean particle size of 250 µm (mean equivalent diameter) was recovered in a retention time of 3.5 h. The low retention time applied can be a key point for the application of the technology, having a compact system which can treat bigger flow volumes (e.g. 100 L day^{-1}), without affecting the growth phase. Then, the results presented in this paper prove that particle size can be increased in the designed crystallizer at lower retention times and without seeding, by controlling the up-flow velocity applied and thanks to the design.

Soare et al. [35] introduced the effect of the air-flow to the final crystal size and shape, in an air-lift reactor, applying different air-flow rates (from 1.6 to 13.3 L min^{-1}) and seeding loads, and obtaining a narrower distribution size at the lowest up-flow veloc-

Table 3
Comparison between performances of the designed crystallizer and similar reactors available in the literature cited.

| Reference	Type of crystallizer	Stream treated	HRT	P-recovery (%)	Induction time (min)	Sr	Seeding	Mean particle size recovered (µm)
Present study	Air-lift reactor combined with a settler	Synthetic wastewater (treated effluent of WWTP as a media)	3.5 h	>95%	0.34–2.33	0.24 ± 0.02	No	Batch: 112.6–242.6 µm Continuous: 314 µm
Bergmans [2]	Short-long column	WWTP's digested sludge	n.d.	70–90%	n.d.	n.d.	No	n.d.
Martí et al. [32]	Stirred tank reactor (reaction and Settling zone)	Rejected liquors of different strategies of the sludge treatment line	2.5 h (reaction zone)	70–90%	n.d.	n.d.	No	n.d.
Soare et al. [35]	Air-lift crystallizer	Synthetic saturated solution	n.d.	n.d.	n.d.	0.5–1	Yes (average seed size of 110 µm)	400–600 µm
Stumpf et al. [26]	Batch tests and Pilot reactor (air-lift)	WWTP's digested sludge	n.d.	Batch: 85% Pilot reactor: 58–90%	n.d.	n.d.	No	90–150 µm
Ueno and Fuji [33]	Fluidized Bed Reactor (FBR)	Dewatered filtrate from anaerobic digestion	10 days	90%	n.d.	n.d.	Yes	500–1000 µm
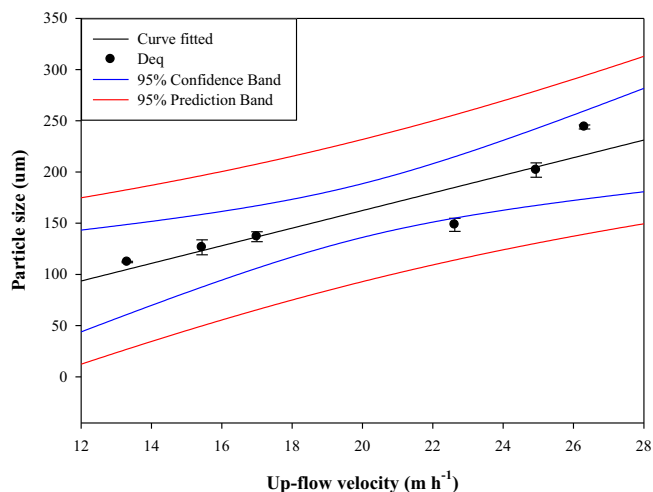
Fig. 4. Particle size recovered (Deq) as a function of the up-flow velocity. The curve fitted is showed in black, the 95% confidence band in blue, and the 95% prediction band in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ities (lowest air-flow rates). The differences remain in particle size distribution. Soare et al. [35] recovered largest particles at the lowest air-flow rates, as well as a better quality of the crystals; whereas the results presented in this study showed a narrower distribution (Fig. S1, Supplementary Material) and largest particles recovered at higher up-flow velocities, without affecting the quality. These differences can be explained by the superficial gas velocity of both systems. The gas velocity must be sufficient to generate an upward liquid velocity in the riser that is equal to the particle swarm velocity [35]. Low velocities might only fluidize a fraction of the crystals, depending of its size. In the present study, slightly higher gas velocities were obtained, allowing the recovery of bigger particles at higher air-flow rates (higher up-flow velocities).

In all the up-flow velocities tested, the crystals recovered in the collector zone had mainly rectangular type morphology (elongated crystals), with a minor fraction of coffin shaped (trapezoidal shape) crystals. The morphology observed in this study is in agreement with Le Corre et al. [29] which established that elongated crystals are the typical morphology for crystals recovered from synthetic wastewater using magnesium chloride as an additional chemical. Struvite crystals are rod-like, orthorhombic and ranging from X-shaped to flat trapezoidal [5], being the coffin, the needle and the trapezoidal shape the typical forms [17]. These differences in struvite morphology are due to some operational conditions, such as the initial concentration of the compounds [36] or the supersaturation ratio [37], among others. Shikazono, 2003 [38] stated that rectangular type precipitation form might be due to heterogeneous nucleation and growth of crystals on the surface of pre-existing crystals. This concurred with our results, as the design of the crystallizer allowed the recirculation of formed nuclei.

3.4. Promoting the growth of struvite particles by operating the crystallizer in continuous mode

The up-flow velocity determines the minimum theoretical equivalent diameter that can be recovered. Particle size can be increased enhancing growth phase, for example, by operating in continuous mode. For this reason, the system was switched from batch mode (experiments of few hours) to continuous mode operation to enhance growth phase (to reach metastable conditions) and test the implications for struvite particles' size.

Metastable zone can be defined as the period of time in which crystal growth preferably takes place over nucleation [2], being the area between supersolubility and solubility curves [39]. For continuous mode experiments, the up-flow velocity was kept at 22.6 m h^{-1} during 138.6 h, and particle size distribution was analyzed periodically.

Phosphate's concentration in the effluent was periodically analyzed (Fig. 5). An immediate phosphate removal was observed, remaining constant in time despite the continuous feeding. Despite the fact that the metastable zone was not determined experimentally, the results of the continuous mode experiments might proof that they were carried out close to the metastable zone. The immediate decrease of the concentration of phosphate (330 mg PO$_4^{3-}$ L^{-1} in 15 h) and the highest phosphate recovery rate at the end of the experiments (95.4 ± 0.3%) were due to the continuous mode operation, in which steady state was achieved, enhancing crystal growth. pH control at 8.5 ensured the optimal conditions for struvite formation. XRD confirmed that only pure struvite was recovered during continuous mode operation tests (Fig. 3B). Samples of the product obtained in the collector were taken at different times (25.5, 48.5, 69.5 and 138.6 h) and analyzed for particle size distribution. Fig. 6 depicts the particle size evolution over time. Fourteen particle size ranges (from 0–50 μm to 900–1000 μm) were obtained from an optical counting. The average crystal size increased in time: 201 μm at 25.5 h, 219 μm at 48.5 h, 237 μm at 69.5 h and 314 μm at 138.6 h (end of the study), meaning that struvite particle size increased in time (113 μm in 113 h) as growth phase was enhanced.

Besides, there was a displacement of the particles' size ranges and the abundance of particles at higher ranges increased in time. As an example, the abundance of particles in the range of 300–400 μm was duplicated at the end of the experiment, and moreover, bigger particles (ranges from 500 to 1000 μm) only appeared at the end of the experiment, reaffirming the previous statement. This means that the small particles could grow in time and increase its size due to heterogeneous nucleation favored for the design of the crystallizer and the continuous mode operation. Nevertheless, small particles (range 0–50 μm and 50–100 μm) were found at the end, as they were the new nuclei formed that could settle in the collector either because they were attached to bigger particles (aggregation) or due to some part of the crystallizer with a velocity equals to zero. Soare et al. [35] also observed the presence of small particles at high air-flow rates, indicating nucleation at the end of the batch, which is in agreement of the results obtained in this study.
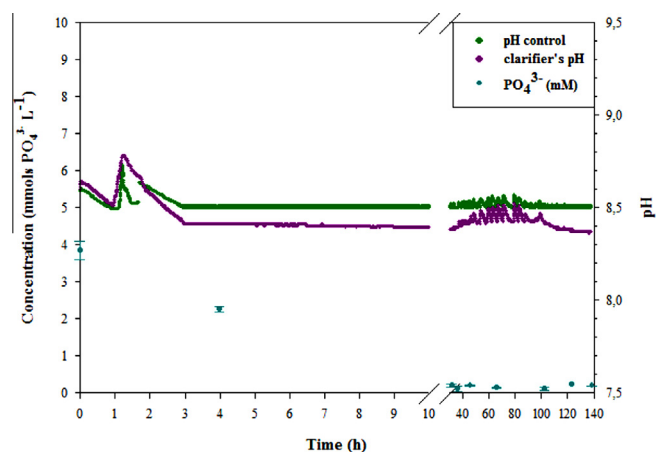

Fig. 5. Average phosphate's concentration during the tests of 138.6 h at the up-flow velocity of 22.6 m h^{-1}. pH control (pH in the riser) is presented in green and pH in the clarifier zone in pink, for one of the replicates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
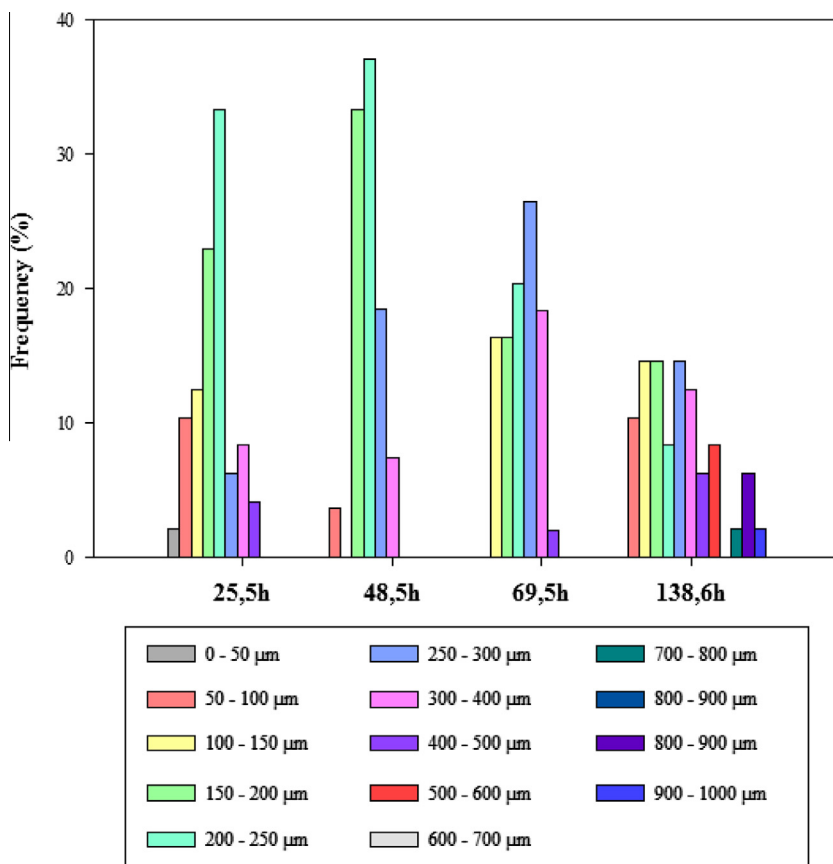
Fig. 6. Particle size distribution results over time in 14 particle size ranges (from 0–50 μm to 900–1000 μm), from the continuous mode experiments at the up-flow velocity of 22.6 m h^{-1}. The results presented are the average of replicates.

The results obtained from batch and continuous mode operation were consistent with those of Stratful et al. [40] and de-Bashan and Bashan [7], who reported that on increasing reaction time from 1 to 180 min, crystal size increased significantly. In our case, from 1 h to 6 days length tests, particle size increased from 150 μm to 300 μm.

4. Conclusions

This study proves that the up-flow velocity has a direct effect on the minimum theoretical equivalent struvite particle diameter that can be recovered. The theoretical approach was confirmed experimentally, recovering a mean equivalent diameter bigger than the theoretical.

By applying higher up-flow velocities, bigger struvite particles were recovered, without affecting recovery efficiency. Struvite particle size can be promoted up to 800–1000 μm by operating the crystallizer in continuous mode.

The excellent system performance, both in terms of process efficiency and quality of the harvested product, was confirmed, as high phosphate recovery rates were achieved. This study opens the door to use the up-flow velocity as a controlling parameter of particle size to the customers' requirements for fertilizer application (e.g. particle size).

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.06.036.

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