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P-recovery in a pilot-scale struvite crystallisation reactor for source separated urine systems using seawater and magnesium chloride as magnesium sources.

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Abstract

Practical recovery of a non-renewable nutrient, such as phosphorus (P), is essential to support modern agriculture in the near future. The high P content of urine, makes it an attractive source for practicing the recovery of this crucial nutrient. This paper presents the experimental results at pilot-plant scale of struvite crystallization from a source-separated urine stream using two different magnesium sources, namely magnesium chloride and seawater. The latter was chosen as sustainable option to perform P-recovery in coastal areas. Real seawater was used to assess in a more realistic way its efficiency to precipitate P as struvite, since its composition (with noticeable concentration of ions such as Ca^{2+}, SO_4^{2-}, Na^+,…) could lead to the formation of impurities and other precipitates. 0.99 grams of struvite were obtained per litre of urine irrespective of the operational conditions tested. In all tested conditions, precipitation efficiencies exceeded 90% and recovery efficiencies were higher than 87%, with an average struvite crystal size higher than 110 µm (and up to 320 µm, depending on the experimental conditions) in the harvested struvite samples. Almost pure struvite was obtained when $MgCl_2$ was used as precipitant, while amorphous calcium phosphate and other impurities appeared in the precipitates using seawater as magnesium source. However, the lower settling velocity of the amorphous precipitates in comparison with the struvite precipitates suggest that their separation at industrial scale could be relatively straightforward.

Keywords phosphorus recovery; struvite; urine; crystallization; seawater

1. INTRODUCTION

Spontaneous precipitation of P-precipitates on internal pipe walls and surface equipment of Wastewater Treatment Plants (WWTPs) is possible due to the phosphorus (P) content in wastewater (Ohlinger *et al.*, 1998; Barat *et al.*, 2009). This unexpected precipitation can lead to operational problems such as scale formation, which results in reduced diameter or even blocked pipelines and higher operational costs in the sludge handling facilities (Neethiling and Benisch, 2004). Moreover, when this nutrient is not removed from wastewater at WWTPs, it reaches surface aquatic ecosystems promoting eutrophication (an adverse response of the natural ecosystem characterized by an accelerated plant and algal growth) and algae blooms.

Phosphorus is a crucial and non-renewable nutrient essential for modern agriculture which requires extra P to maximize crop yields. The primary source for P-fertilisers is a limited resource, phosphate rocks, which current reserves are predicted to be exhausted within the next century (Cordell *et al.*, 2009, Li *et al.*, 2019). Although phosphorus can be removed from wastewaters by chemical precipitation and/or biological processes, the application of technologies for phosphorus recovery is of major interest due to its marketable value. Indeed, extensive research has been carried out in the last years and is expected to gather worldwide momentum in the near future (Birnhack *et al.*, 2015).

Approximately 17% of the total phosphorus in phosphate rock mined specifically for food production is lost in human excreta via wastewater, mainly in urine (Cordell, 2010). In this context, phosphate recovery from urine is an attractive choice, because phosphorus is present in inorganic form not bonded to the organic matter and urine represents only 1% of the total volume of wastewater while contains up to 50 % of the total phosphate load in municipal wastewaters (Wilsenach *et al.*, 2007; Mo and Zhang, 2013). Although different technologies can be used to recover phosphorus from urine, chemical precipitation in the form of minerals with direct

application to agriculture such as struvite ($MgNH_4PO_4 \cdot 6H_2O$) is being intensively studied by the scientific community (Rahman *et al.*, 2011; Matynia *et al.*, 2013; Capdevielle *et al.*, 2013; Barbosa *et al.*, 2016). Magnesium ammonium phosphate (MAP or struvite) is a slow-release fertiliser that can be produced from urine, being a solid free from micro-pollutants (Ronteltap *et al.*, 2007). Its purity and low heavy metal content (Latifian *et al.*, 2012; Muhmood *et al.*, 2018) contribute to the marketable value of struvite. This ecological fertiliser can complement or partially replace conventional chemical fertilisers to satisfy modern agriculture P requirements.

Many works have already reported struvite recovery from wastewater. Some of them have focused on urine P-recovery as it has been considered one of the most suitable sources for practicing it due to its simplicity and economics (Mihelcic *et al.*, 2011; Dai *et al.*, 2014), but only a few of these studies have used seawater as low-cost magnesium source (Rubio-Rincon *et al.*, 2014). In addition, most of the researches published so far have performed *batch* recovery experiments at lab-scale (Zamora *et al.*, 2017) with P-rich solutions. The conclusions of these studies are difficult to scale-up in real applications (Li *et al.*, 2019) due to the short-term of the experiments and the complexity of the crystallisation process regarding to the crystalliser hydraulics, start-up procedure, solids harvesting, etc., thus, limiting a wide spread implementation in industry. Therefore, in this work the main research effort is to assess P-recovery at pilot-scale and long-term experiments using $MgCl_2$ and seawater as magnesium sources, so as to get valuable results directly applicable from a practical and engineering point of view. Although different sustainable magnesium sources are reported in literature (Kirinovic *el al.*, 2017; Kiani *et al.*, 2019), seawater was chosen as a low-cost and sustainable option to perform the P-recovery process in coastal areas. Real seawater from the Mediterranean Sea was used to assess its efficiency to precipitate P as struvite in a more realistic way, since its composition (with noticeable concentration of ions such as Ca^{2+}, SO_4^{2-}, Na^+,…) could lead to the formation of impurities and other precipitates. Therefore, the major objective of this

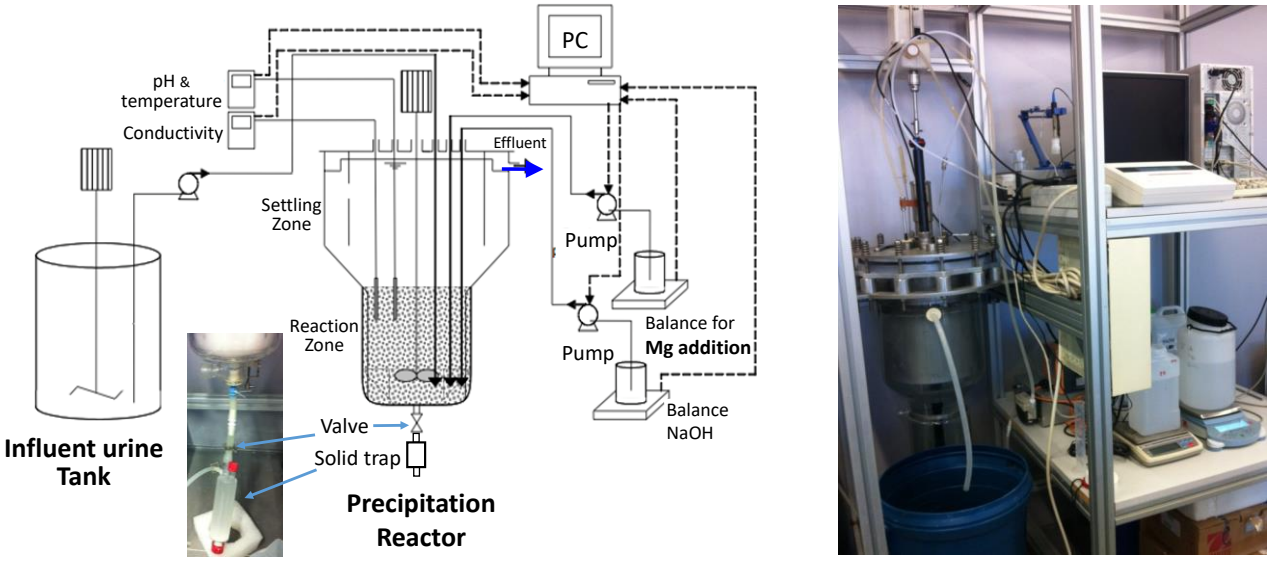
work is to assess the efficiency of the pilot-scale crystallisation reactor to achieve phosphorus recovery producing high quality struvite in long-term experiments.

2. MATERIALS AND METHODS

2.1 Experimental set-up

Figure 1 shows a scheme of the pilot plant used in this struvite precipitation research. As can be seen in Figure 1, the pilot plant consists of a glass stirred crystallisation reactor (20.55 L of volume) equipped with three pumps for influent (synthetic urine), magnesium source (seawater or magnesium chloride) and sodium hydroxide (for pH control) dosing through three independent stainless steel injection tubes, and two balances to monitor the magnesium and sodium hydroxide flows. The precipitation reactor is divided into two parts: the reaction zone (4.95 L in the bottom part), designed according to the typical dimensions of a perfectly mixed reactor and the top part which is the settling zone (15.60 L), that prevents fine particles from being lost with the effluent. Solid harvesting was carried out by settling. A solid trap was installed at the bottom part of the reaction zone (see snapshot detail in Figure 1a), and was connected to the reactor through a manual valve. This purge system allows the harvesting of the larger struvite crystals while the lower size solids remain growing within the reactor. When solid harvesting was desired, the trap was filled with the crystallisation effluent to avoid the hydrodynamic drag of the fluid velocity when the manual valve was opened. This allowed the lower size struvite crystals (with low settling velocity) remain in suspension within the reaction zone of the crystallisation reactor. Once opened the valve that connects the reaction zone with the solid trap, only the larger struvite crystals (able to settle) fell into the trap and were harvested from the reactor. When a prefixed height in the solid trap was achieved (the trap was roughly calibrated for different solid quantities in grams), the valve was closed and the trap emptied. Samples from the harvested mixture were used for further analytical

determinations such as solid size distribution, particles composition or weight of harvested struvite. A detailed description of the pilot plant can be seen in Pastor *et al.* (2008a).



(a) **(b)**

Figure 1. (a) Scheme of the struvite precipitation pilot-plant with snapshot of the purge system for struvite crystal harvesting **(b)** Picture of the whole pilot-plant used in this study.

2.2 Substrates

The crystallisation reactor was fed with synthetic urine that reproduce the ions concentrations observed in urine stored during three days (Table 1) and diluted according to the typical dilution rate 1:4 in no-mix toilets (Udert *et al.*, 2003). Previous studies have shown that after three days of hydrolysis, urine has suitable characteristics to recover P by crystallisation (pH around 8, and N/P molar ratio above the stoichiometric requirements). Since the longer the storage time, the larger the storage tank required, a three-day storage time was selected for urine. The reagents used to prepare the synthetic substrate were: $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl, Na_2SO_4, $Na_3C_6H_5O_7 \cdot 2H_2O$, KH_2PO_4, KCl, NH_4Cl and $(NH_4)_2CO_2$.

Table 1. Synthetic urine used in the experimentation. Compounds concentration is expressed in mg/L

Na^+	Cl^-	K^+	SO_4^{2-}	Ca^{2+}	Mg^{2+}	PO_4-P	NH_4-N	pH
583	1037	320	617	56	13	196	378	8.0

Ammonium concentration in urine exceeds that required for complete phosphorus recovery, but magnesium content is insufficient. The magnesium ions needed for struvite formation were provided by magnesium chloride ($MgCl_2 \cdot 6H_2O$) solution in the first set of experiments, and by Mediterranean seawater in the second set, since it is a low-cost sustainable option in coastal areas. Magnesium chloride was chosen because it allows obtaining the desired Mg/P molar ratio without modifying the pH. The reagent solution used in the experiments was adjusted to 1300 mg Mg^{2+}/L (similar concentration of Mg found in seawater) making it possible a direct comparison with the results obtained with seawater as magnesium source. Along each experiment the pH was adjusted with a sodium hydroxide (NaOH) solution (0.3 M) added on demand through a peristaltic pump.

2.3 Analytical Methods

PO_4-P, NH_4-N, NO_3-N, NO_2-N total phosphorus (TP), total nitrogen (TN) and chemical oxygen demand (COD) analysis were performed in accordance with Standard Methods (APHA, 2012). Total phosphorus of the crystallisation effluent was analysed acidifying the samples to pH around 2-3, ensuring that all phosphorus became soluble, and then analysed as PO_4-P. Soluble calcium, magnesium, potassium, sodium, chloride and sulphate were analysed by ion chromatography (Metrohm IC). Alkalinity was measured by titration using the method proposed by Moosbrugger *et al*. (1992). For the analysis of soluble components, samples were previously filtered through 0.45 µm filters.

149 The precipitated solids obtained in the crystalliser were recovered from the reaction zone and were
150 air dried at room temperature. Scanning Electron Microscopy (SEM) coupled to energy-dispersive
151 X-ray spectroscopy (EDS) was used to determine the morphology and composition of the harvested
152 crystals as well as the main ions spatial distribution. The presence of P, N, Mg, Ca and K were
153 searched by EDS microanalysis by means of a XL-30 ESEM (Philips, Eindhoven, Netherlands).
154 Struvite samples were attached to the SEM stub using silver lacquer. Then, the SEM stub with the
155 sample was introduced into the XL-30 and the pressure was diminished until 10^{-5} bar. After that, the
156 sample surface was visualised and an area was selected for the microanalysis. The spot-size value
157 was modified until a Dead Time (DT) around 30% was achieved.
158
159 Crystal size distribution was determined by Malvern particle-sizer (Mastersizer 3000; measuring
160 range 100 nm – 3 mm). The central value of the distribution was used as representative size and its
161 evolution along the experiments is presented in the results and discussion section.
162
163 Finally, the solids were analysed by X-Ray Powder Diffraction (XRD) in order to check whether
164 struvite crystals were formed. The equipment used for X-ray analyses was a D8 Avance A25
165 powder diffractometer (Bruker, Karlsruhe, Germany). About 0.01 g of sample were placed in a
166 sample holder and then into the X-ray chamber at 1200 ºC. A scanning step of 0.02 º and a pass of
167 0.02 s were fixed as working constants.
168
169 **2.4 Experimental procedure**
170
171 The experimental work was divided into two sets of long-term experiments (see Table 2 for
172 experimental conditions) carried out using the synthetic urine defined in Table 1. The shortest
173 experiment lasted 15 days while the longest experiment 34 days, thus making it possible to
174 reproduce the long-term real operation of the crystalliser, studying relevant engineering issues for

practical application such as the stability of the process or the evolution of the crystals size. In the first set of experiments, magnesium chloride ($MgCl_2 \cdot 6H_2O$) was used as magnesium source, while in the second set, Mediterranean Seawater provided the magnesium ions required for the struvite precipitation. In all the experiments, the crystalliser was operated in continuous mode for the liquid phase and in batch-wise mode for the solid phase.

Table 2. Experimental conditions of the seven experiments.

Set	Experiment	Mg source	Duration (d)	pH	Molar ratio (Mg/P)	HRT (h)
Set 1	Exp 1	$MgCl_2 \cdot 6H_2O$	27	8.8	1	4.35
	Exp 2		30			3.26/2.45*
	Exp 3		15			1.5
	Exp 4		17			1/0.5*
Set 2	Exp 5	Seawater	34	8.8	1	4.35
	Exp 6		21			
	Exp 7		30			

* Within these experiments different hydraulic retention times (HRT) were tested (i.e., a different HRT was applied without starting a new experiment).

Synthetic urine fed to the crystallisation reactor had a high pH but not enough to counteract the pH decrease caused by the crystallisation process. According to Pastor *et al.*, (2008a) the pH value in the crystallisation reactor is an important parameter to achieve suitable efficiencies, and are maximized at pH=8.8. Therefore, all experiments were performed at this pH value, and this parameter was controlled at the desired set-point adding NaOH on demand using a fuzzy-logic control algorithm (Chanona *et al.*, 2006).

In each experiment, samples from the effluent were taken on a daily basis to measure pH, conductivity, alkalinity, total phosphorus, orthophosphate, ammonium, magnesium, calcium, potassium, chloride and sodium.

Two types of efficiencies were calculated to evaluate the phosphorus precipitation process: precipitation and recovery efficiencies. These efficiencies were calculated along each experiment with the average values obtained from the analyses. Precipitation efficiency (Eq. 1) represents the process efficiency from a thermodynamic point of view since with enough residence time, supersaturation can be almost completely consumed. Recovery efficiency (Eq. 2) takes into account both precipitation and crystal growth efficiencies. It is calculated as the percentage of the total phosphorus entering the crystallisation reactor that is not lost with the effluent (i.e., total phosphorus entering the reactor minus total phosphorus leaving the reactor). The difference between both efficiencies corresponds to the fine crystals that are lost with the effluent of the crystallisation reactor.

$$Precipitation\ efficency = \frac{\left(PO_4 - P_{influent}\right) - \left(PO_4 - P_{effluent}\right)}{PO_4 - P_{influent}} \cdot 100\,\% \qquad \textbf{Eq. 1}$$

$$\text{Recovery efficiency} = \frac{TP_{influent} - TP_{effluent}}{TP_{influent}} \cdot 100\,\% \qquad \textbf{Eq. 2}$$

3. RESULTS AND DISCUSSION

All the experiments in the pilot-plant crystallisation reactor were performed at pH=8.8, Mg/P molar ratio of 1, 400 rpm stirring rate and started-up with 80 grams of struvite crystals as initial seed to avoid fouling on the reactor walls. These initial conditions were determined in a set of preliminary experiments. In these preliminary experiments, different strategies to avoid fouling on the reactor

walls were tested, such as starting-up the experiment with low pH and low Mg/P ratio and gradually increase them until reaching the desired set-points for the experiment, or using different grams of struvite crystals as initial seed of the experiment. Figure 2 shows some pictures from these preliminary experiments. Fouling on the internal reactor walls of the reaction zone as well as on the metallic stirrer occurred during the start-up of the experiment seeded with 9 grams of struvite crystals (see Figures 2a, 2b). The fouling was consequence of high supersaturation of the reactants concentration (i.e., NH_4-N, PO_4-P, Mg^{2+}) in the reaction zone, promoting primary nucleation instead of crystal growth. Conversely, no fouling occurred in the experiments started-up with 80 grams of struvite crystals as initial seed (see Figure 2c). The main conclusion of these preliminary experiments was that with enough struvite seed in the reactor, no fouling occurred making it unnecessary taking any other measure to avoid supersaturation conditions.

(a) **(b)** **(c)**

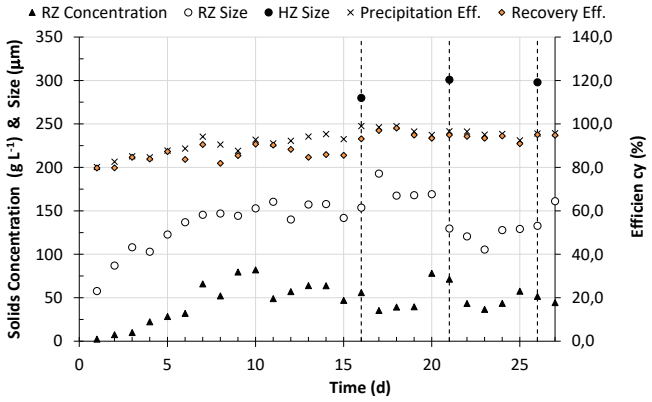
Figure 2. Pictures of some preliminary experiments: **(a)** Fouling on the internal reactor walls of the reaction zone during the start-up of an experiment seeded with 9 grams of struvite crystals after 3 days of operation **(b)** fouling on the metallic stirrer (same experiment as before) **(c)** reaction zone during the start-up of an experiment seeded with 80 grams of struvite crystals after 30 days of operation.

3.1 Experiments with $MgCl_2$ as Mg source

Figure 3 shows the temporal evolution of different monitored parameters in the struvite precipitation experiments that used $MgCl_2$ as precipitant: solid concentration in the reaction zone, size of the solid crystals from the reaction zone (RZ Size) and from the harvest zone (HZ Size), as well as the precipitation and recovery efficiencies along each experiment. As can be seen in Figure 3a, after starting the first experiment (HRT=4.35 h), the concentration of solids in the reaction zone increased, precipitation and recovery efficiencies quickly achieved high values (exceeding 90% at day 7), and both efficiencies began to separate around day 12, reflecting the presence of fine solids that were lost with the effluent. This difference in precipitation and recovery efficiencies was due to operating problems with the magnesium dosage (caused by scale deposits inside the magnesium injection pipeline), and when solved (with acid cleaning and regular maintenance of the injection pipeline) both efficiencies tended to converge again (day 16). Crystal harvesting from the precipitation reactor (at days 16, 21 and 26) allowed the solid concentration in the reaction zone to be relatively steady, enabling suitable continuous operation of the crystallisation process.

Struvite crystal size in the reaction zone followed a similar pattern to the solid concentration evolution, which can be clearly observed in Figure 3a. From day 3 onwards the crystal size was clearly visible at bare eye (> 100 μm), and a noticeable difference in size can be observed between the struvite crystals from the reaction zone (RZ Size) and the harvest zone (HZ Size). This size dissimilarity is consequence of the harvesting system implemented, which included a solid trap in the lower part of the reaction zone (see Figure 1a), acting as a settler, which was connected to the reactor through a manual valve. This purge system allowed the harvesting of the larger struvite crystals while keeping the lower size solids in suspension inside the reactor and letting them grow.

The experimentation results evidenced that the crystallisation process can continuously operate with hydraulic retention times (HRT) as low as 0.5 hours (Figure 3) achieving consistently phosphorus precipitation and recovery efficiencies higher than 90%. The lower the HRT the higher struvite harvesting to maintain a steady solid concentration in the reaction zone (from 190 g of struvite per week at 4.35 hours to 1610 g per week at 0.5 hours; resulting in 0.99 g of struvite per litre of urine). The main effect of lowering the HRT was observed on the average size of the harvested struvite crystals (and mainly on the size of solids from the harvest zone) that decreased from around 300 μm at 4.35 hours to less than 200 μm at 0.5 hours. To enable visual correlation patterns between the different measured parameters and the HRT (i.e., the operational variable modified in each experiment), a scatterplot of all variables is shown in Figure 4. As can be seen in Figure 4a no significant difference existed in the recovery efficiencies achieved at the different HRT tested (independently of the solid concentration in the reaction zone, which is influenced by the crystal solid harvesting), while the harvested struvite crystals reduced in size as the HRT decreased for values lower than 2.45 hours (Figure 4b). At higher HRT values the size of harvested struvite crystals remained similar. An analogous correlation pattern was observed for the struvite crystals from the reaction zone.



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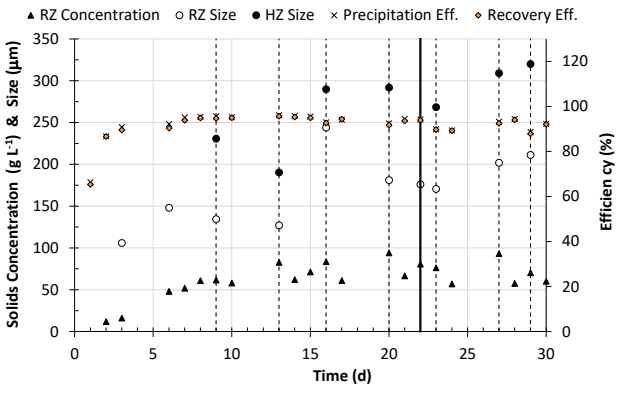

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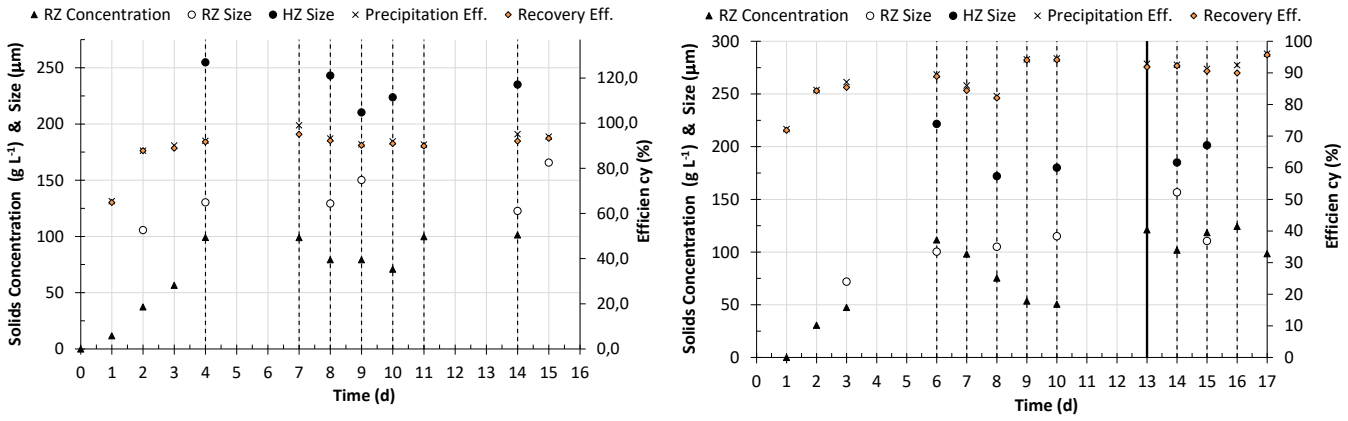
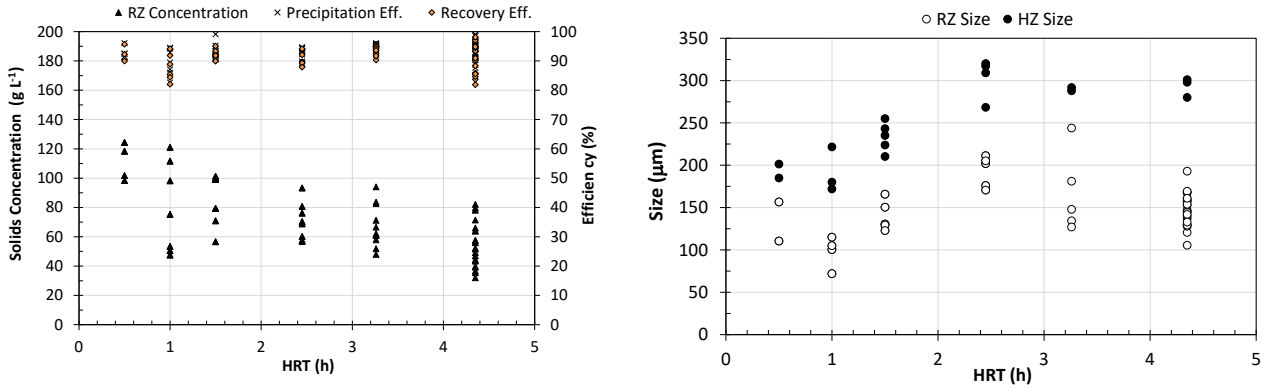


(c) **(d)**

Figure 3. Time course evolution of recorded parameters in the struvite precipitation experiments that used $MgCl_2$ as precipitant: (a) Experiment 1 – HRT=4.35 h (b) Experiment 2 – HRT =3.26 h and 2.45 h (c) Experiment 3 – HRT =1.5 h (d) Experiment 4 – HRT=1 h and 0.5 h. Parameters shown: Solid concentration in the reaction zone (RZ Concentration), size of the solid crystals from the reaction zone (RZ Size), size of the crystals from the harvest zone (HZ Size), precipitation efficiency and recovery efficiency. Days when struvite crystals were harvested from the crystallisation reactor are labelled with a vertical dashed line. Each vertical solid line signals a change in the HRT within the experiment (i.e., a different HRT was applied without starting a new experiment).



(a) **(b)**

Figure 4. Hydraulic retention time versus recorded parameters in the struvite precipitation experiments that used $MgCl_2$ as precipitant. Parameters shown in: **(a)** Solid concentration in the reaction zone, precipitation efficiency and recovery efficiency; **(b)** Size of the solid crystals from the reaction zone (RZ Size) and size of the crystals from the harvest zone (HZ Size).

3.2 Experiments with seawater as Mg source

Another set of crystallisation experiments was performed using seawater instead of magnesium chloride as precipitant. As previously indicated, seawater was chosen as a low-cost and sustainable option to perform the P-recovery process in coastal areas. Real seawater from the Mediterranean Sea was used to assess its efficiency to precipitate P as struvite in a more realistic way. Average composition of the seawater used for the crystallisation experiments is shown in Table 3. As can be seen in this table, seawater presents noticeable concentration of ions such as Ca^{2+}, SO_4^{2-}, Na^{+},… which could lead to the formation of impurities and other precipitates.

Table 3. Average seawater composition of the samples from the Mediterranean Sea used in the experimentation. Average values and Standard Deviation of 70 samples. Compounds concentration is expressed in mg/L, Alkalinity as $mgCaCO_3/L$ and Conductivity in mS/cm.

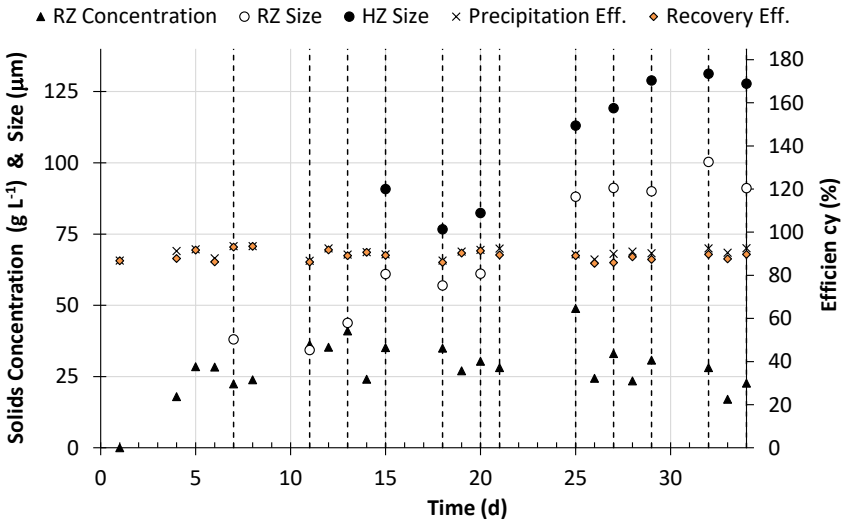
Na^+	Cl^-	K^+	SO_4^{2-}	Ca^{2+}	Mg^{2+}	PO_4-P	NH_4-N	NO_2-N	NO_3-N	Alkalinity	Conductivity	pH
10947	20639	468.7	3022.3	441.6	1322	0.025	0.34	0	0.04	102.7	53	7.90
±1185	±2168	±34.6	±345.7	±52.9	±124.4	±0.005	±0.12		±0.02	±5.1	±6	±0.04

Figure 5 shows the temporal evolution of different monitored parameters in the struvite precipitation experiments that used Mediterranean Seawater as magnesium source: solid concentration in the reaction zone (RZ Concentration), size of the solid crystals from the reaction zone (RZ Size) and from the harvest zone (HZ Size), as well as the precipitation and recovery efficiencies. All experiments were carried out at the highest HRT tested in the $MgCl_2$ set of experiments (4.35 h).

As can be seen in Figure 5, precipitation efficiency with seawater was consistently over 90%, while the recovery efficiency was close to 90% (88.9% on average). Although general patterns and

316 behaviour with seawater were similar to the results of $MgCl_2$ as precipitant (compare Figure 3a with
317 5a), remarkable differences can be observed. The main difference between both precipitants is the
318 struvite crystal solid size, which is in this case (Mediterranean Seawater as magnesium source)
319 clearly smaller. Both crystal sizes were smaller, the solids from the reaction zone (90 μm vs 150
320 μm) and the harvested solids (125 μm vs 300 μm). This reduction in the crystal solid size can be
321 due to the higher concentration of calcium in the seawater. Several authors (Le Corre *et al.*, 2005;
322 Wang *et al.*, 2005; Pastor *et al.*, 2008b) have reported the influence of calcium concentration on
323 struvite formation, evidencing a reduction in crystal size and a higher presence of amorphous form
324 at the expense of the typical cuboid crystals of struvite as the concentration of calcium increased. Le
325 Corre *et al.* (2005) indicated that Ca/Mg molar ratio of 0.5 inhibited struvite growth, generating
326 amorphous calcium phosphate precipitated on struvite surface; and Ca/Mg molar ratio above 1 gave
327 rise to the formation of an amorphous precipitate rather than crystalline struvite. Pastor *et al.*
328 (2008b) observed a lower struvite formation at Ca/Mg molar ratio of 1.6. Gao et al. (2018) observed
329 that the increase of Ca^{2+} concentration influenced potassium struvite crystallization from urine due
330 to the formation of calcium phosphate. Li *et al.* (2016) also observed that a calcium concentration
331 with a calcium to magnesium ratio of less than one helps increase the particle size of the crystals
332 without negatively impacting on the product purity. Thus, the particle size can potentially be used to
333 infer the product purity. However, these effects are less potent at a high ammonia nitrogen
334 concentration, which diminishes the negative impact of calcium. In this work, the Ca/Mg ratio was
335 0.2 and 0.4 for the experiments using magnesium chloride and seawater, respectively. The Ca/Mg
336 ratio slightly increased when seawater was used, which could favour the reduction of the crystal
337 solid size observed in these experiments.
338
339 Another difference in the experiments with seawater as magnesium source is the presence of
340 impurities and amorphous precipitates. Although the Ca/Mg molar ratio increase observed in
341 seawater experiments was not high enough to inhibit struvite formation, this increase could help to

give rise to the formation of this amorphous precipitate. Figure 6 shows their presence in the solid trap. However, a clear difference was observed in the settling velocity of the struvite crystal solids and the amorphous precipitates, which as can be seen in Figure 6, rested as a layer on top of the struvite. This clear difference in the two layers formed naturally within the solid trap suggest that the separation of the amorphous matter from the struvite crystals at industrial scale could be possible and relatively straightforward. Anyway, specific experiments would be required to evaluate the feasibility of this separation and its associated economic cost. In the remaining experiments (Figures 5b and 5c), with durations up to 30 days, similar results were observed (high precipitation and recovery efficiencies and the crystal size of the crystals from the harvest zone noticeable higher than the solids from the reaction zone).



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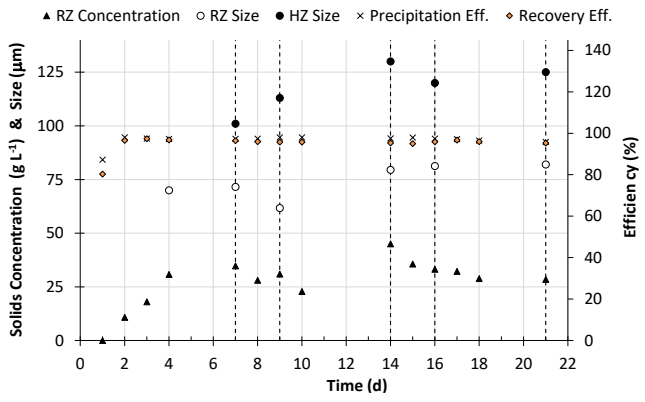

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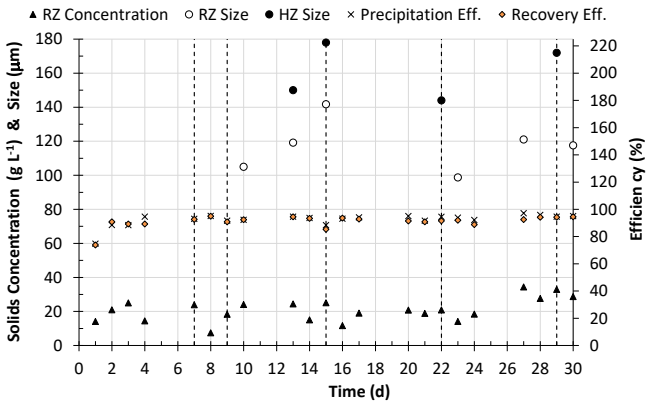


(c)

Figure 5. Time course evolution of recorded parameters in the struvite precipitation experiments that used Mediterranean Seawater as magnesium source: (a) Experiment 5 (b) Experiment 6 (c) Experiment 7. All experiments were performed at 4.35 hours of HRT. Parameters shown: Solid concentration in the reaction zone (RZ Concentration), crystals solid size in the reaction zone (RZ Size), crystals solid size of the harvest zone (HZ Size), precipitation efficiency and recovery efficiency. Days when struvite crystals were harvested from the crystallisation reactor are labelled with a vertical dashed line.

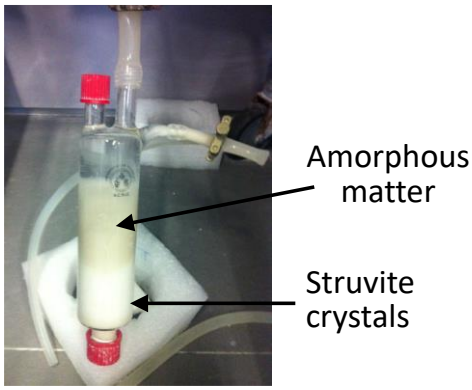
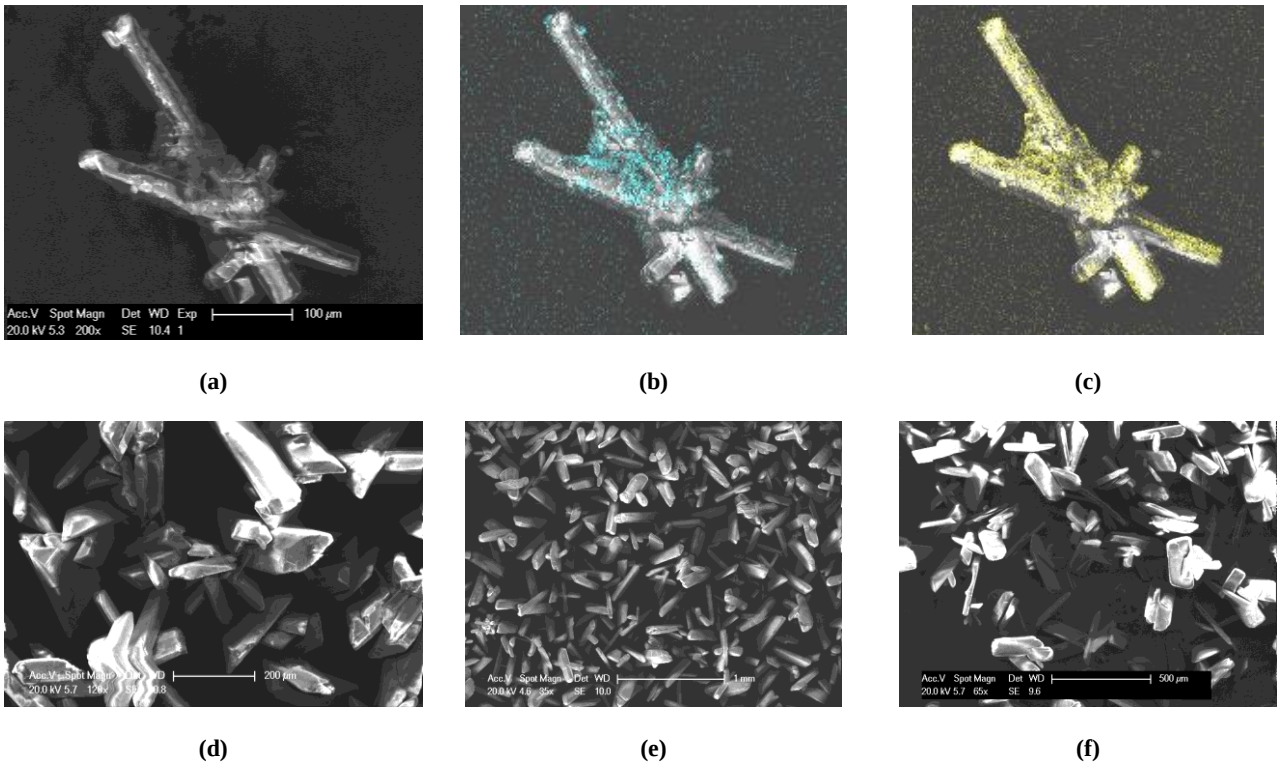


Figure 6. Picture of the solid trap with harvested solids from the crystallisation reactor at the end of the Experiment 5.

Several SEM images of the struvite precipitates from Experiment 5 carried out using seawater (upper part of the figure) and from Experiment 1 carried out using magnesium chloride (bottom part) as precipitants are shown in Figure 7. As can be seen in Figure 7a, the amorphous matter not only grew independently of struvite but also grew, covered and merged several orthorhombic struvite crystals. The calcium mapping (Figure 7b) clearly revealed the presence of calcium in this unstructured matter, which could probably be a mixture of calcite and amorphous calcium phosphate. In contrast, perfect cuboid crystals (Figures 7 d, 7e, 7f) were observed in the experiments were magnesium chloride was used as precipitant. Moreover, the qualitative composition (expressed as percentage of N, P, Mg and C) of the harvested crystals obtained by EDS, shown in Figure 8, revealed the presence of calcium in the precipitates formed in Experiment 5 carried out using seawater.

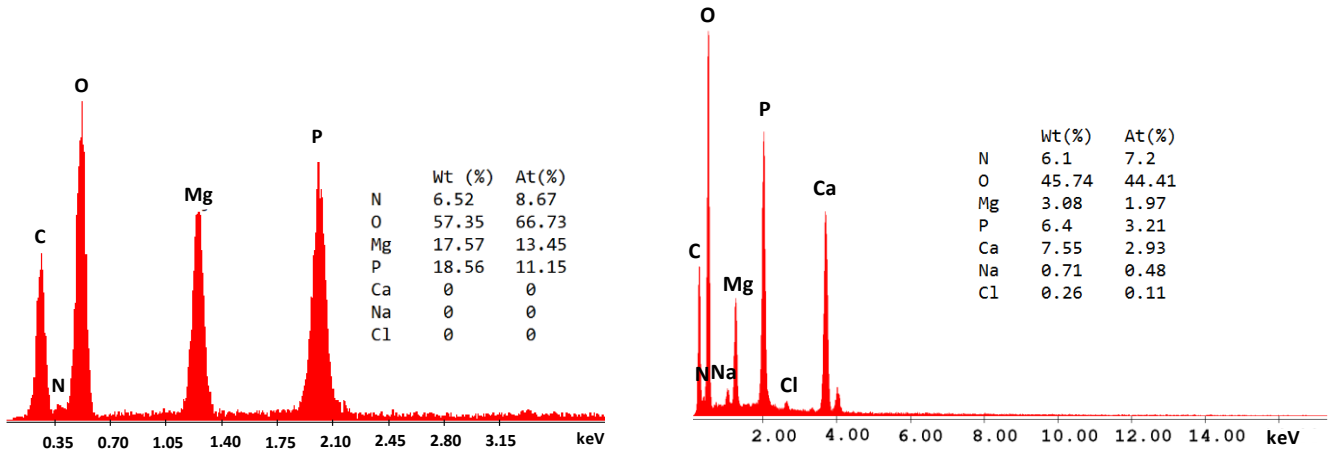
Finally, to further understand the nature of the precipitates formed according to the magnesium source, XRD was used to determine the identity of the precipitates. The XRD pattern of the precipitates from experiments 1 and 5 are shown in Figure 9. The XRD patterns from samples obtained in the magnesium chloride experiments matched well with the peaks for pure struvite. In samples from seawater experiments, the diffractogram revealed some background noise, which indicated the presence of amorphous precipitate.



(a) **(b)** **(c)**

(d) **(e)** **(f)**

Figure 7. (a) SEM image of precipitates from the largest experiment carried out using seawater as magnesium source (Experiment 5) where an amorphous matter growing on several cuboid struvite crystals can be seen **(b)** Calcium mapping **(c)** Magnesium mapping. Bottom figures correspond to SEM images from experiments using $MgCl_2$ as precipitant **(d,e)** Experiment 1 – HRT=4,35 h **(f)** Experiment 2 – HRT=3,26 h.



(a) **(b)**

Figure 8. X-ray microanalysis results for the struvite obtained from **(a)** Experiment 1 (using $MgCl_2$ as Mg source) and **(b)** Experiment 5 (seawater as Mg source).

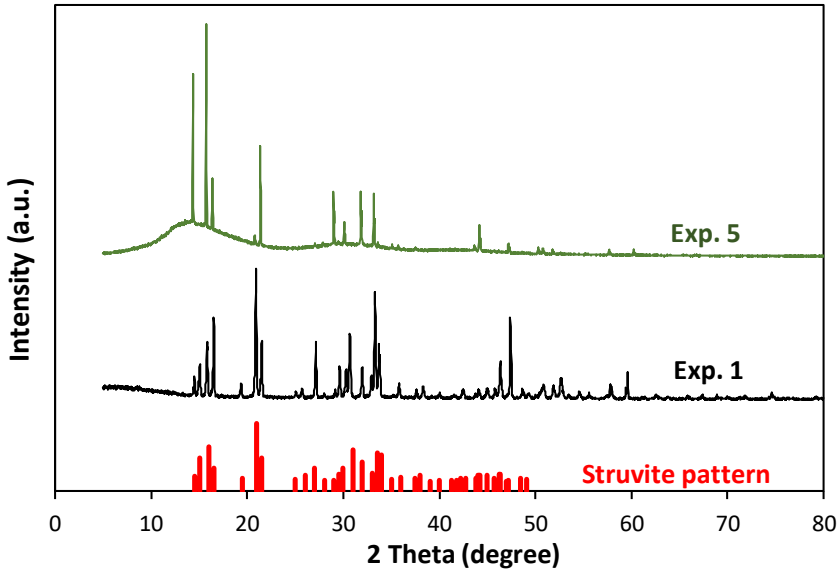


Figure 9. X-ray diffraction spectra of the precipitates from Experiment 1 ($MgCl_2$ was used as Mg source) and Experiment 5 (seawater was used as Mg source), together with the standard struvite pattern.

4. CONCLUSIONS

In this work, interesting experimental results at pilot-plant scale of struvite crystallization from urine using magnesium chloride and Mediterranean Seawater as magnesium sources are presented, thoroughly analysed and discussed. The main conclusions that can be drawn from this study are:

- Struvite crystallization in the pilot-scale reactor can be stable, with high P precipitation and recovery efficiencies (exceeding 90% and 87%, respectively), achieving 0.99 grams of struvite per litre of urine irrespective of the variations in the operational conditions.
- To avoid fouling on the reactor walls due to primary nucleation instead of crystal growth, it is of paramount importance starting-up the process with enough struvite seed in the reactor.
- Crystal solids harvesting from the precipitation reactor allow the solid concentration in the reaction zone to be relatively steady which is important to enable suitable continuous operation of the crystallisation process.
- Settling allows the harvesting of the larger struvite crystals while the lower size solids remain in the reactor making it possible its growth.
- The hydraulic retention time (HRT) does not affect the phosphorus precipitation and recovery efficiencies, but as the HRT decreases the harvested struvite crystals tend to be smaller.
- Larger struvite crystals were obtained (around 2-fold) using magnesium chloride instead of seawater as magnesium source.
- Using seawater as low-cost magnesium source to perform P-recovery from urine in coastal areas is feasible. High phosphorus precipitation and recovery efficiencies are possible (close to 90%) with struvite crystals visible at bare eye (> 100 μm).
- Impurities appeared in the P-precipitates using seawater as struvite magnesium source. The lower settling velocity of the amorphous precipitates in comparison with the struvite precipitates suggest that their separation at industrial scale could be relatively straightforward.

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