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Are alternative magnesium sources the key for a viable downstream transfer of struvite precipitation? Assessment of process feasibility and precipitate characteristics

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ABSTRACT

Phosphorus (P) recovery in source-separated decentralised wastewater treatment processes is an eco-efficient strategy in accordance with a circular economy perspective. Struvite ($MgNH_4PO_4.6H_2O$) capture allows a reduction of P discharged to surface waters and generates a product known for its slow-release fertiliser properties. However, the cost and availability of current commercial Mg^{2+} sources hinder the downstream transfer of struvite precipitation. Although some alternative sources are available, there is a lack of information on how they compare to conventional sources; it is also not known how the $Mg:PO_4$ ratio affects process performance or fertiliser product suitability. Therefore, this research evaluated the performance of two alternative sources, *seasalt* and *seawater bittern,* at different $Mg:PO_4$ ratios. The results indicate that *seasalt* may be a problematic option owing to its high levels of NaCl, regardless of the $Mg:PO_4$ level, which could affect soil fertility. *Bittern,* meanwhile, showed a high yield at pH 8.5 and $Mg:PO_4$ 1.2:1, achieving 99% recovery of PO_4 and increasing also the recovery yield from 60% (using conventional sources) to 82% at $Mg:PO_4$ 1:2. In addition, *bittern* showed larger X-type crystals than commercial sources. The precipitate is composed mainly of struvite and Newberyite ($MgHPO_4.3H_2O$), with traces of K^+, and no presence of NaCl at $Mg:PO_4$ 1.2:1; while at $Mg:PO_4$ 1:2 it forms a mixture of struvite with presence of Ca and K phosphates. In conclusion, *bittern* is an effective raw material to improve the downstream transfer of struvite precipitation into urine-diverting toilets in wastewater treatment systems.

1. Introduction

Urine represents only 1% of municipal wastewaters, yet it is responsible for ~75% and ~45% of total nitrogen (N) and phosphorous (P) discharged into surface waters [1]. Therefore, upstream recovery of phosphates (hereby referred to as PO_4) and nitrogen using source-separating devices, such as urine-diverting toilets (UDT), is a radical innovation towards new sanitation systems targeting nutrient recovery [2]. P conservation and recovery has been the subject of several policy papers in recent decades because of the non-renewable nature and geopolitical risks of mining facilities [3]. Moreover, nitrogen discharge by wastewater treatment plants is an increasing concern, partly because denitrification processes targeting N removal from water simply become a water-to-air trade-off contamination. Both N and P are well-known triggers of water eutrophication, a leading freshwater quality problem highlighted by recent Water Framework Directive assessments [4].

Struvite precipitation is considered an effective way to recover PO_4 and N from different matrixes, including urine [5]. Struvite precipitation in UDT source-separated urine allows the production of a multi-nutrient slow-release fertiliser [6] with decreased cross-contamination from faeces [2]. However, the attractiveness of this process is hindered by the need for an external Mg^{2+} source to achieve a 1:1 ratio of $Mg^{2+}:PO_4^{3-}$

Abbreviations: PO_4, Non specified phosphate form; $Mg:PO_4$, molar ratio of Mg^{2+} to PO_4 ions; *Bittern*, Seawater bittern.

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Table 1
Key mineral cations of *bittern* and *seasalt* used in this study.

Component	*Bittern* (g/L)	*Seasalt* (g/Kg)
Mg^{2+}	80.31 ± 0.26	3.79 ± 0.23
Na^{+}	27.22 ± 0.41	157.30 ± 0.32
K^{+}	24.98 ± 0.16	4.19 ± 0.25
Ca^{2+}	0.06 ± 0.01	0.87 ± 0.11

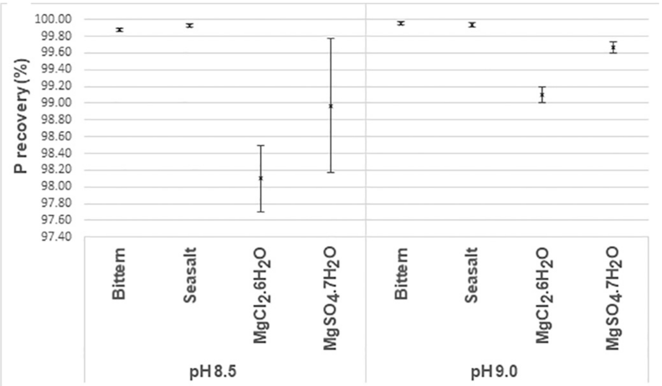


Fig. 1. Mean PO_4 recovery yield with pH and $Mg:PO_4$ ratio 1.2:1 for the different Mg^{2+} sources tested.

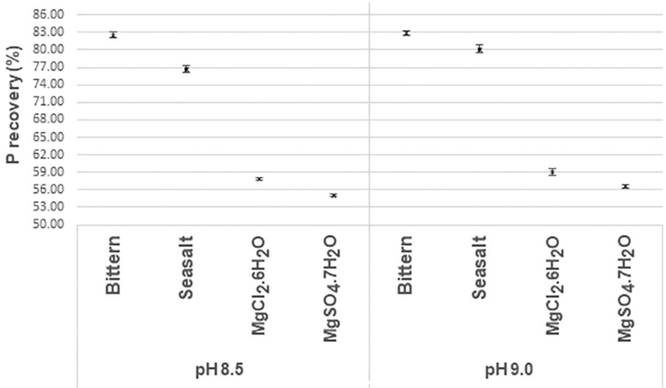


Fig. 2. Mean values of PO_4 recovery yield variation with pH for each Mg source tested at $Mg:PO_4$ 1:2.

(hereby represented by $Mg:PO_4$). Commercial magnesium reactants, mainly magnesium chloride ($MgCl_2.6H_2O$), magnesium sulphate ($MgSO_4.7H_2O$) and magnesium oxide (MgO) are much used, but with distinct problems. $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$ are expensive. MgO is less expensive but presents a much lower solubility either requiring a longer contact time [5] or an additional solubilisation step [7].

Struvite precipitation will be viable for downstream applications if alternative Mg^{2+} sources are affordable and display useful processual properties. Furthermore, downstream viability of struvite precipitation will also benefit if the fertiliser applicability of the crystals formed [6] is not compromised by the alternative Mg^{2+} source used. With the objective to find suitable alternative Mg^{2+} sources, several options were tested and are present in the literature. One such possibility was magnesite ($MgCO_3$) which achieved 92% PO_4 recovery [8] but still has water solubility problems similar to those of MgO [5]. Another known alternative is *seawater*, which yields up to 99% recovery for urine with high PO_4 concentrations (638 mg P L^{-1}) [9] and over 90% for urine with lower PO_4 concentrations (194 mg P L^{-1}) [10]. However, in both cases, dilution with seawater was reported to affect the final product quality and possible applications [10]. Pinatha et al. [11] showed that sea salt (hereby referred to as *seasalt)* can recover 72–91% of the PO_4 from urine. Despite the good results, better ones are envisaged because the pH range was too wide, skipping possible optimal values. In addition, a *seasalt* with a higher Mg content could be used. *Bittern,* a by-product of salt production in saltpans that is much less expensive than commercial salts [12], was also tested with promising results: 90% recovery was obtained with $Mg:PO_4$ 1.1:1 in stored urine [13], over 98% in hydrolysed urine [14] and 99% in industrial wastewaters [12].

A straightforward conceptual design of struvite capture systems is required to reap the benefits of lower contamination granted by source-separated urine in UDT processes. The few studies that went beyond the PO_4 recovery yield were focused on comparing the composition and crystal sizes among alternative Mg^{2+} choices, but none gave information about critical operating factors or impacts on product quality [14], or when the impact on product quality was addressed, it was studied on low-P concentrated solutions (100 mg P L^{-1}) instead of urine [15]. A direct comparison with information on both yield and crystal properties, between alternative and conventional Mg^{2+} sources for struvite precipitation in urine, is needed to understand if any of the possible options is more suitable to be transferred downstream. Alternative sources like *bittern*, *seasalt* or seawater also add Ca^{2+}, K^{+} and other ions alongside Mg^{2+} to the solution [16]. These added ions justify a reevaluation of the viability of struvite process at $Mg:PO_4 < 1:1$, not only in how much recovery yield can be increased with the extra cations but also in how the size and composition of the reaction products are affected. If alternative Mg^{2+} sources can increase P recovery yield at $Mg:PO_4$ 1:2 to much higher values compared to conventional Mg^{2+} sources, while having no known harmful ions or salts in the product composition, this may open an alternative path when 100% struvite purity is not a mandatory condition, such as a possible combination of Ca^{2+} sources used for pH correction [17] with alternative Mg^{2+} sources.

In this study alternative magnesium sources were tested to replace commercial salts and promote downstream struvite precipitation as an option for PO_4 recovery while forming a product suitable for agricultural fertilisation. With this goal in mind, two alternative Mg^{2+} options, *seasalt* and *seawater bittern* (hereby referred to as *bittern),* were compared with conventional Mg^{2+} sources $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$. *Seasalt,* aside from halite (NaCl), has Mg^{2+} as one of its main constituents [18]. The second Mg^{2+} source selected was *bittern* (the remaining solution after NaCl precipitation in saltpans) which contains high amounts of ions such as Ca^{2+} and potassium (K^{+}). The aim was to assess which alternatives were viable at $Mg:PO_4$ 1.2:1, a ratio considered as ideal [19]. Furthermore, the effect of the alternative sources studied at $Mg:PO_4$ ratio 1:2 was also considered.

2. Materials and methods

2.1. Chemicals

Analytical-grade chemicals (KH_2PO_4, NH_4Cl, $MgCl_2.6H_2O$ and NaCl from Panreac; $CaCl_2$ and KCl from Chem-lab; and Na_2SO_4 from Labkem) were used to prepare the synthetic hydrolysed urine solution with concentrations of $PO_4{}^{3-}$ and $NH_4{}^{+}$ closer to the content of a urine solution after hydrolysis of urea to ammonium [19]. The pH corrections were made using 1 M NaOH solution (using analytical-grade NaOH pellets from Panreac).

The additional Mg^{2+} chemical source $MgSO_4.7H_2O$ was from Panreac analytical grade. Commercial *seasalt* was from Nature Foods, and *bittern* was courtesy of Necton - Companhia Portuguesa de Culturas Marinhas, S.A. The chemical composition of both materials was identified by atomic absorption spectrophotometry using a Solaar S series AA, the results of which are presented in Table 1.

2.2. Crystallization process

The optimal experimental conditions were determined in a previous

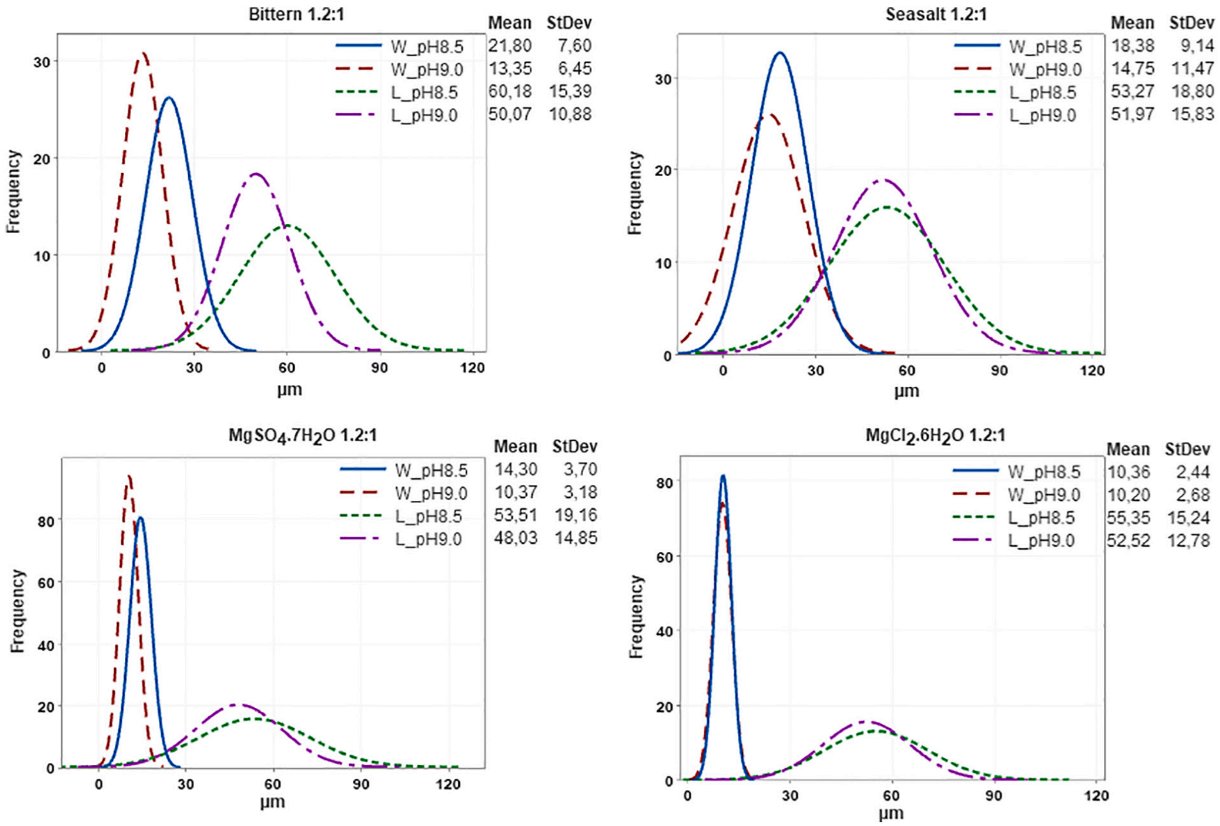


Fig. 3. Distribution of crystal dimensions (W – Width and L – Length), comparison between commercial salts, *bittern* and *seasalt* at Mg:PO_4 1.2:1.

study [19]. The Mg^{2+} sources, conventional and alternative, were added to 0.3 dm^3 of synthetic hydrolysed urine solution to achieve the intended Mg:PO_4 ratios (1.2:1 or 1:2). The procedure included a pH adjustment to 8.5 or 9.0, followed by 30 min of reaction time and 30 min of settling. The crystals were then recovered by filtration, using quantitative paper with pore size 7–9 µm from Filter-Lab, and dried at 50 ± 0.1 °C (temperature value was chosen to accelerate drying while remaining below the initial degradation temperature defined by Sarkar et al. [20]) and stored for further analysis. The filtrate was analysed for phosphate using the vanadomolybdate method according to standard methods [21], using a Hitachi U-2000 Spectrophotometer. All experiments were performed with triplicates, and the analysis of variance (ANOVA) was performed using Minitab 19 to determine if the difference between recovery yield values obtained with each Mg^{2+} source was statistically significant.

2.3. Characterisation by SEM, EDX and XRD

Particle size, morphology and chemical analysis were assessed by scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis. $MgSO_4.7H_2O$ and $MgCl_2.6H_2O$ analysis was performed with an Analytical SEM Hitachi S2400 with a Bruker light element EDS detector, and for *bittern* and *seasalt,* an EG-SEM JEOL 7001F with an Oxford light element EDX detector and electron backscatter diffraction detector was used. All samples were coated in a thin film of gold/palladium to increase conductivity. The images obtained using different apparatus were adjusted to always present the same scale. Measurements on the SEM images were made with ImageJ software, identifying the average length and width of the crystals so different crystal morphologies were taken into account. Material characterisation was complemented by X-ray powder diffraction (XRD). Diffractograms were obtained in a Pan'-Analytical PW3050/60×'Pert PRO (θ/2θ) equipped with an X'Celerator detector and with automatic data acquisition (X'Pert Data Collector [v.2.0] software) using a CuKα radiation as the incident beam, 40 kV-30 mA. Measurements were made by continuous scanning from 7° to 40°, with a step size of 0.017°2θ and a time per step of 19.6 s.

3. Results and discussion

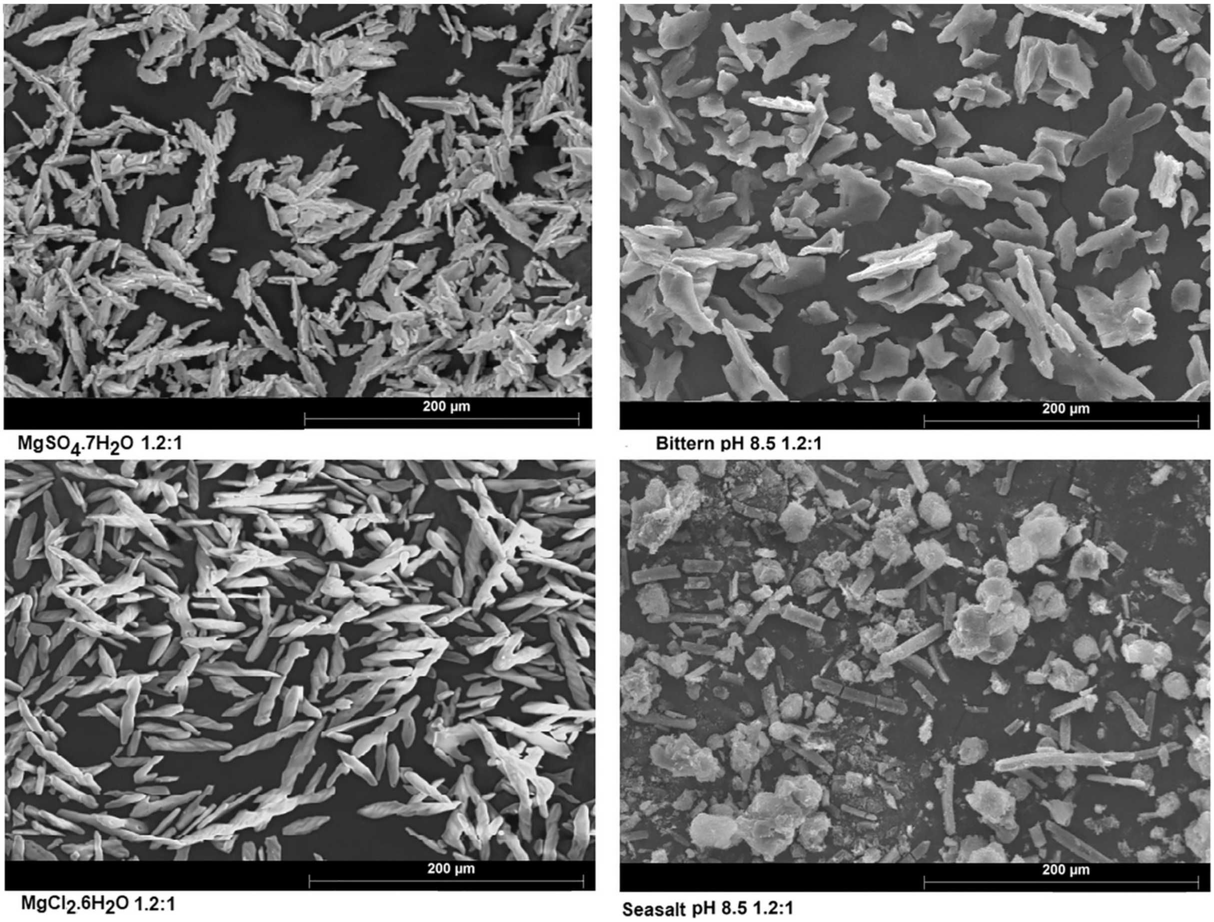
3.1. Effects of alternative Mg^{2+} sources on PO_4 recovery yield

3.1.1. Mg:PO ratio 1.2:1

Fig. 1 shows the effect on the mean PO_4 recovery yield values using $MgCl_2.6H_2O$, $MgSO_4.7H_2O$, *bittern* and *seasalt* at pH 8.5 and 9.0 with Mg:PO_4 ratio of 1.2:1.

At pH 8.5, all P recoveries were high (>99.6%) regardless of the Mg^{2+} source used, but the only statistically significant differences in P recovery yield were the ones between *bittern* and $MgCl_2.6H_2O$ (*P*-value = 0.013) and between *seasalt* and $MgCl_2.6H_2O$ (P-value = 0.011). The higher standard deviation of $MgSO_47H_2O$ results at this pH level made all remaining differences between P recovery yields non-statistically significant ($P > 0.050$). At pH 9.0, the difference between alternative and commercial Mg^{2+} sources was clearer. The difference between P recovery yields obtained with *bittern* and $MgCl_2.6H_2O$ (*P*-value = 0.000) was statistically significant as was the difference between bittern and $MgSO_47H_2O$ (*P*-value = 0.008). The differences in P recovery yield between *seasalt* and $MgCl_2.6H_2O$ (P-value = 0.000), as well as between *seasalt* and $MgSO_47H_2O$ (P-value = 0.011) are also statistically significant. The main conclusions to take from Fig. 1 is the general tendency for alternative Mg^{2+} sources achieving a higher P recovery yield than commercial salts, but there is no statistically significant difference between *bittern* and *seasalt* regardless of the pH level(*P*-value >0.050).

Regarding the results for *bittern*, PO_4 recovery was above the 90% value achieved by Etter et al. [13] using an Mg:PO_4 value of 1.1:1. It was also slightly larger than the 96% P recovery obtained by Bradford-Hartke et al. [15] using an Mg:PO_4 ratio of 1.3:1 in low P



$MgSO_4.7H_2O$ 1.2:1

Bittern pH 8.5 1.2:1

$MgCl_2.6H_2O$ 1.2:1

Seasalt pH 8.5 1.2:1

Fig. 4. SEM images of crystals obtained with different Mg^{2+} sources at 1.2:1 $Mg:PO_4$ and pH 8.5.

concentrations (100 mg P L^{-1}). Concerning *seasalt*, the results obtained in this study, 99% recovery at 1.2:1, are higher than those recorded by Pinatha et al. [11], who achieved a recovery yield of 91% at an $Mg:PO_4$ ratio of 1.25:1 using a *seasalt* with significant compositional differences (absence of both K^+ and Na^+ from the composition) from the one used in this paper.

If there is no visible significant difference between the P recovery yields when using *seasalt* and *bittern*, Table 1 show an important detail in this discussion. There was a difference in Mg^{2+} content in each alternative source. Whereas 1 kg of the *seasalt* contained 3.76 g of Mg^{2+}, 1 L of *bittern* contained 80 g of Mg^{2+}. The major impact of this different ionic concentration was how much of each source must be added to achieve a 1.2:1 $Mg:PO_4$ ratio. For 1 L of untreated hydrolysed urine, approximately 150 g of *seasalt* was needed to achieve a 1.2:1 ratio, but *bittern* needed less than 10 mL to achieve the same 99.9% PO_4 recovery yield. This means 1 kg of *seasalt* can be used to treat 6 L of urine at an $Mg:PO_4$ ratio of 1.2:1, whereas 1 L of *bittern* can treat 100 L of urine under the same conditions. Obviously, this is a highly significant difference for UDT design and feasibility.

3.1.2. Mg:PO ratio 1:2

Fig. 2 presents the mean values of recovery yields achieved with each Mg^{2+} source tested under suboptimal conditions, $Mg:PO_4 = 1:2$. There was a significant difference (*P*-value <0.050) between the performance of commercial magnesium reactants and both *bittern* and *seasalt*, with commercial salts always granting less than 60% PO_4 recovery regardless of pH. Therefore, changing to an alternative Mg source granted between 15% and 22% greater PO_4 recovery in comparison with either of the two commercial reactants.

When an $Mg:PO_4$ ratio of 1:2 was adopted, the recovery yield at pH 9.0 was always slightly above that at pH 8.5. This fact is in agreement with studies supporting the idea that struvite crystallization follows the pathway given by reaction (1) and not reaction (2), as previously assumed [22]. The pH increase from 8.5 to 9.0 promoted the amount of PO_4 existing in $HPO_4{}^{2-}$ form instead of as $H_2PO_4{}^{-}$.

$$Mg^{2+} + NH_4{}^{+} + HPO_4{}^{2-} + 6H_2O \leftrightarrow MgNH_4PO_4.6H_2O + H^{+} \tag{1}$$

$$Mg^{2+} + NH_4{}^{+} + PO_4{}^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4.6H_2O \tag{2}$$

When commercial Mg^{2+} salts are used, and $Mg:PO_4$ is below 1:1, once the amount of Mg^{2+} available to interact with $PO_4{}^{3-}$ or $HPO_4{}^{2-}$ is depleted the reactions to form new magnesium-based PO_4 components stop [22]. At this point any further recovery of PO_4 is obtained with its reaction with Ca^{2+} already present in the urine. This explains why the P recovery yield for commercial salts reached a maximum value of 59.1%. These data confirm Mg^{2+} as the limiting reagent for struvite precipitation under these conditions [22]. However, when *bittern* or *seasalt* is used, this effect can be partially mitigated because external additional cations such as Ca^{2+} and K^+ can continue to react with PO_4 ions, which then explains the increase in yield over 80%; the compositional analysis presented ahead in this paper was performed to answer these doubts over this possible effect. These results confirm $Mg:PO_4 < 1:1$ as unviable

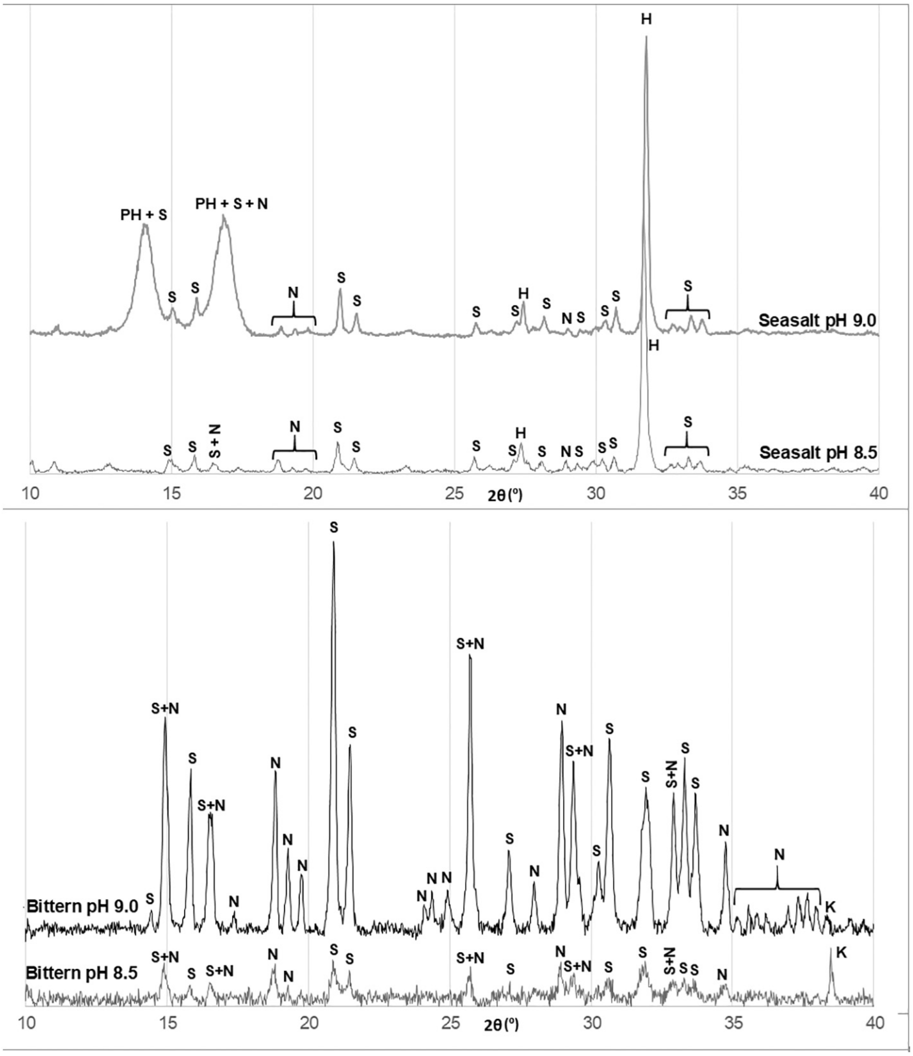


Fig. 5. XRD diffractograms of precipitates obtained using *seasalt* and *bittern* at 1.2:1 Mg:PO_4. Legend: S – *Struvite*($MgNH_4PO_4.6H_2O$) [30], N – Newberyite ($MgHPO_4.3H_2O$) [30], H – Halite(NaCl) [32], PH – Phosphorroesslerite ($MgHPO_4.7H_2O$) [33], K – ($Mg_2KH(PO_4)_2.15H_2O$) [33].

for commercial reactants [23]. However, for alternative Mg^{2+} sources, this result was not so clear, the final answer being dependent on the quality of the particles obtained at this Mg:PO_4 ratio for this source.

3.2. Crystal composition and morphology

3.2.1. Mg:PO_4 ratio 1.2:1

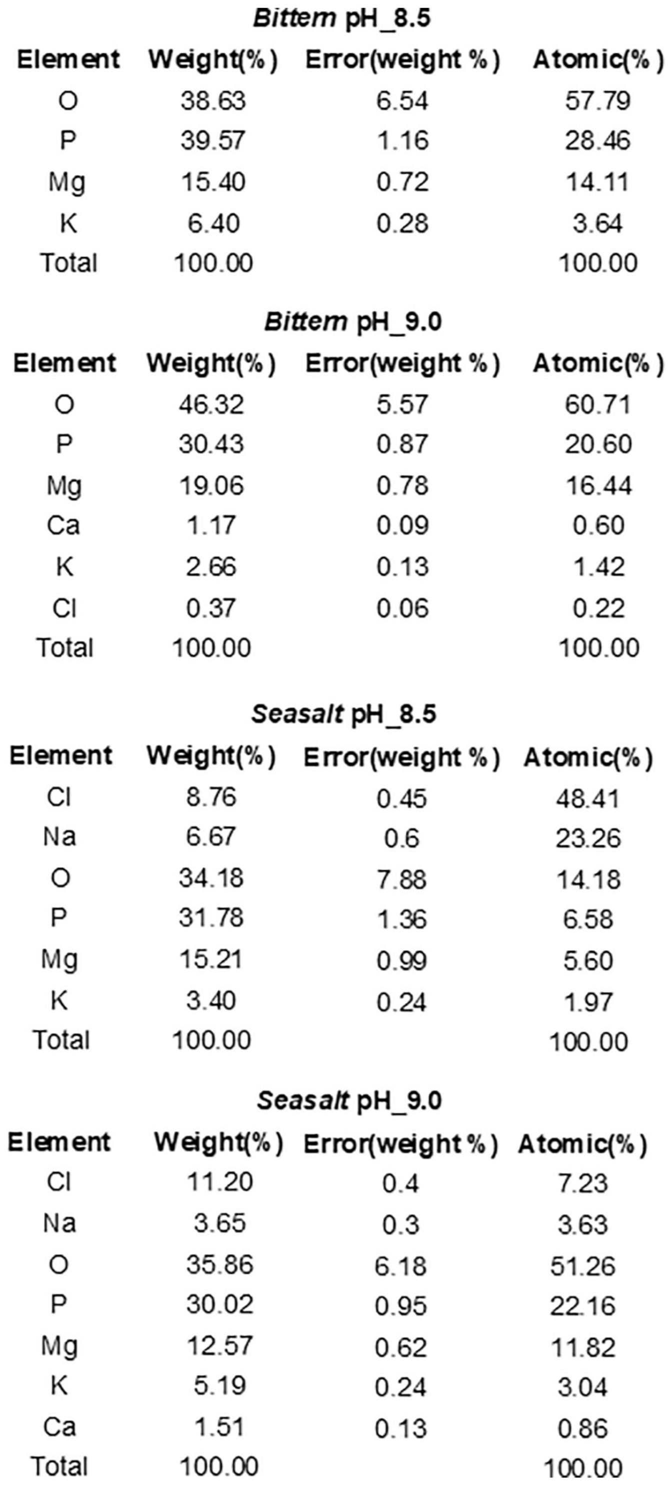
Fig. 3 shows the crystal area distribution obtained using commercial salts, *bittern* and *seasalt* at Mg:PO_4 1.2:1.

The first tendency observable in Fig. 3 is how pH 8.5 forms crystals with higher length and width than at pH 9.0, agreeing with the known tendency for crystals to become thinner as pH increases [24]. Focusing on crystal dimensions at pH 8.5, where larger crystals were formed, there was a distinction between the length and width of the crystals obtained using commercial and alternative Mg^{2+} sources. The two commercial sources $MgCl_2.6H_2O$ (Width 10.4 ± 2.4 μm; length 55.4 ± 15.2 μm) and $MgSO_4.7H_2O$ (width 14.3 ± 3.7 μm; length 53.5 ± 19.1 μm) produced, in general, smaller and thinner crystals compared to *bittern* (width 21.8 ± 7.6 μm; length 60.2 ± 15.4 μm) and *seasalt* (width 18.4 ± 9.1 μm; length 53.3 ± 18.8 μm). Between the two alternative Mg^{2+} sources, *bittern* not only produces crystals with higher average width and length than those obtained with *seasalt*, it also tends to have a lower number of crystals with smaller dimensions than those obtained with *seasalt*.

Despite the lack of data in the literature, the results were in line with literature reports regarding the interrelation among pH, Saturation Index (SI) and crystal size. Liu et al. [14] showed that *bittern* produced larger crystals when used in matrixes with lower SI than when higher SI matrixes were used; here, the effect was replicated but at two different pH values, with larger crystals forming at pH 8.5 than at pH 9.0. The increase in pH led to a higher SI, promoting crystal formation over crystal growth [25]. This increase in nucleation generated more crystals at the cost of their size in terms of width and length. The specific difference as to why alternative sources generate larger crystals may be explained using Fig. 4.

For the commercial salts, the crystals were more elongated but thinner with the occasional formation of Y-shaped crystals. Between commercial salts, the crystals obtained with $MgSO_4.7H_2O$ showed a more laminar aspect than those obtained with $MgCl_2.6H_2O$, which had a smoother appearance.

Seasalt led to a mixture of elongated crystal structures and the formation of agglomerates, explaining why it appears to generate larger and thicker crystals than the commercial salts. The crystals formed in this study show a morphology that is different from the trapezoidal form obtained by Pinatha et al. [11]. The composition of these agglomerates, through XRD and EDX analysis, is needed because there is no report of such agglomerates in other studies using *seasalt* as the Mg^{2+} source. Furthermore, these agglomerates seem to be the reason for the higher



***Bittern* pH_8.5**

Element	Weight(%)	Error(weight %)	Atomic(%)
O	38.63	6.54	57.79
P	39.57	1.16	28.46
Mg	15.40	0.72	14.11
K	6.40	0.28	3.64
Total	100.00		100.00

***Bittern* pH_9.0**

Element	Weight(%)	Error(weight %)	Atomic(%)
O	46.32	5.57	60.71
P	30.43	0.87	20.60
Mg	19.06	0.78	16.44
Ca	1.17	0.09	0.60
K	2.66	0.13	1.42
Cl	0.37	0.06	0.22
Total	100.00		100.00

***Seasalt* pH_8.5**

Element	Weight(%)	Error(weight %)	Atomic(%)
Cl	8.76	0.45	48.41
Na	6.67	0.6	23.26
O	34.18	7.88	14.18
P	31.78	1.36	6.58
Mg	15.21	0.99	5.60
K	3.40	0.24	1.97
Total	100.00		100.00

***Seasalt* pH_9.0**

Element	Weight(%)	Error(weight %)	Atomic(%)
Cl	11.20	0.4	7.23
Na	3.65	0.3	3.63
O	35.86	6.18	51.26
P	30.02	0.95	22.16
Mg	12.57	0.62	11.82
K	5.19	0.24	3.04
Ca	1.51	0.13	0.86
Total	100.00		100.00

Fig. 6. EDX Results for *seasalt* and *bittern* at 1.2:1 Mg:PO_4.

range of crystal dimensions shown in Fig. 3 when using *seasalt*.

The use of *bittern* leads to X-shaped crystals that are generally thicker and larger than when using commercial sources, contrasting with the trapezoidal crystals obtained by Bradford-Hartke et al. [15] using a solution with lower concentration of P and without the other main ions present in urine that change the solution's ionic strength and thus the SI of the solution. The presence of high concentrations of ammonium [26] and/or high SI (as was expected from the addition of a complex source such as *bittern*) are commonly reported as promoting the occurrence of X-shaped crystals, transiting to rod/needle-like ones as the SI decreases [27] and becoming even thinner and smaller as pH increases [28]. Those X-shaped crystals are also known to have poorer pack tightening than the particles obtained with $MgCl_2.6H_2O$ [26], explaining the size differences. The origin of X-shaped crystals is well accepted, but there is still no agreement about what causes the 2D or 3D growth of crystals that generates this X shape. Hypotheses such as the collision of independent crystals or oriented aggregation of smaller particles in specific parts of the forming struvite crystal have been suggested, but the reason why this happens is yet to be clarified [29].

At Mg:PO_4 ratio of 1.2:1, the XRD and EDX results for both commercial magnesium salts replicated what was found elsewhere for $MgCl_2.6H_2O$ as a mixture of struvite and its storage degradation form, newberyite [19]. Newberyite is a common mineral found with struvite. It is usually considered a degradation product of struvite under humid conditions [30]. Despite the use of a temperature lower than the instability range pointed out by Sarkar et al. [20] in this study, the value chosen might have favoured the production of newberyite as well. The newberyite concentration also increases with decreasing ammonium levels, [30] which can occur when NH_4^+ is removed with struvite formation, and some NH_3 is evolved owing to the basic pH [31]. Figs. 5 and 6 present, respectively, the XRD diffractograms and EDX results obtained for *seasalt* and *bittern* at a 1.2:1 Mg:PO_4 ratio.

Struvite was detected for both *bittern* and *seasalt* not only with the presence of Mg, O and P peaks in EDX data but also as confirmed by the specific struvite peaks in the diffractograms. The major fraction of PO_4 recovered was as struvite formed at both pH levels. Newberyite peaks were more evident when *bittern* was used.

With *seasalt* though, at pH 9.0, some peaks appear around 14 and 16° which are usually found in phosphorroesslerite, explaining the presence of K in EDX. This phase is usually highly unstable and easily transforms into newberyite during storage by dehydration [34]. Because of this, it is not easily captured by EDX. The presence of phosphorroesslerite may mean either that newberyite would be forming if more storage time was given or that its formation preceded the formation of K-struvite (MgKPO4.6H2O), which tends to form at a higher pH [33], justifying why the diffractogram at pH 9.0 had this mineral and the one at pH 8.5 did not. There was Ca^{2+} detected in EDX, but in the absence of an identifiable phase in XRD, the only assumption is the incorporation of Ca^{2+} in the struvite/newberyite crystals lattice. When Ca^{2+} is present in the reaction media, it is known to be present alongside struvite crystals. According to Hao et al. [35], it seems to be easier to detect it at pH higher than 8.5, thus explaining its presence at pH 9.0 and not at pH 8.5.

A concerning feature of the diffractograms and EDX results for *seasalt* is the high abundance of Na and Cl, identified as halite by XRD. This fact proves that the increased size of *seasalt* crystals in this study were undoubtedly affected by co-precipitation of halite over the struvite crystals. The presence of NaCl in the precipitation product with *seasalt* may be problematic. Some plants can tolerate high levels of NaCl, but salinity is usually a problem for soil fertility [36]. NaCl also affects the uptake of other macronutrients such as K^+ and Ca^{2+} [37]. For this reason, unless a crystal washing step is added to remove part of the halite formed, *seasalt* is not an appropriate Mg^{2+} source to recover PO_4 if struvite is intended for use as a soil fertiliser.

When *bittern* was used, both halite and phosphorroesslerite seemed absent at either pH level. The diffractogram also showed a peak at ~38° that is typical of the mineral $Mg_2KH(PO_4)_2.15H_2O$, supported by the presence of K in EDX results. This mineral was mentioned by Lahalle et al. [33] as being the immediate precursor of K-struvite at intermediate pH levels. Its appearance at pH 8.5 and not at pH 9.0 is in agreement with this idea: K-struvite is easier to precipitate at higher pH levels [38], decreasing the concentration of $Mg_2KH(PO_4)_2.15H_2O$, and the presence of K-struvite is hard to confirm because its peaks are masked by regular struvite ones. The presence of Ca^{2+} at pH 9.0 follows the same tendency found for *seasalt*.

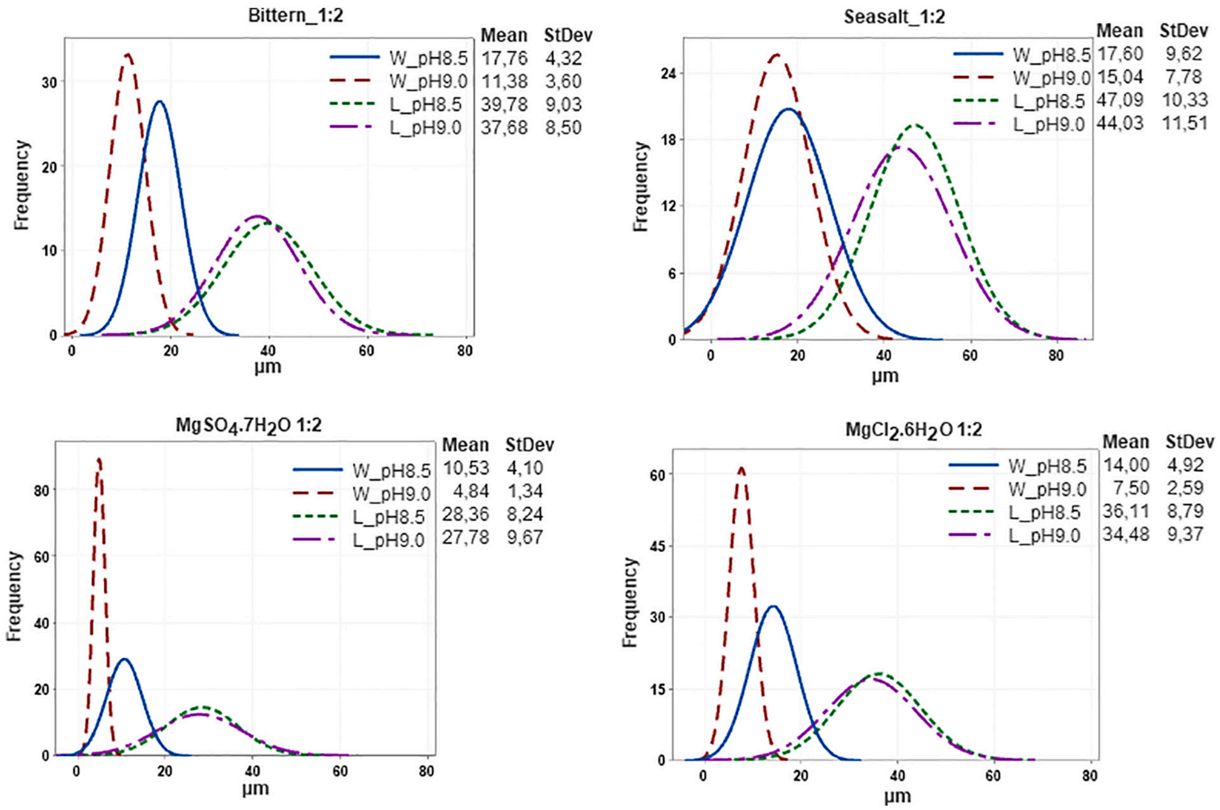


Fig. 7. Distribution of crystal areas for each of the sources at Mg:PO_4 1:2, where W – width and L – length.

3.2.2. *Mg:PO_4 ratio 1:2*

The distribution of crystals' dimensions (width and length) at Mg:PO_4 1:2 conditions is presented in Fig. 7. It shows that as pH increases from 8.5 to 9.0, the crystals have a tendency to reduce in width and length, following what was already visible at Mg:PO_4 ratio 1.2:1. The best source when using a Mg:PO_4 ratio of 1:2 was clearly *bittern* at pH 8.5 (width of 17.8 ± 4.3 and length of 39.8 ± 9.0) when compared to *seasalt* (width of 17.6 ± 9.6 and length of 47.1 ± 10.3) but mostly with $MgCl_2.6H_2O$ (width of 14.0 ± 4.9 and length of 36.1 ± 8.8) and $MgSO_4.7H_2O$ (width of 10.5 ± 4.1 and length of 28.4 ± 8.2).

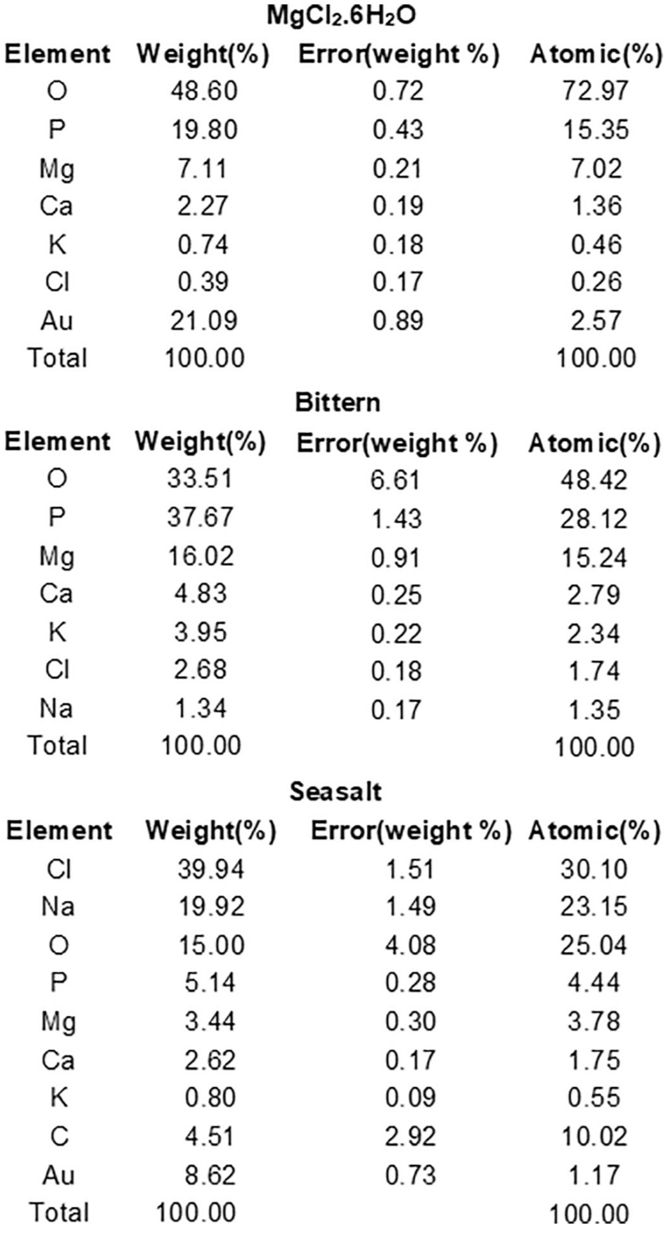
Knowing how higher SI affects crystal sizes, smaller crystals might have been expected for this source based on the complexity of *bittern* composition. However, along with SI, another factor gains relevance. For both commercial reactants, once the Mg^{2+} ions are depleted, the evolution of the reaction is severely affected, and with it the growth of the crystals is strongly compromised. The larger crystals obtained with *bittern* must be related to the higher quantity of cations available to react with PO_4 after the Mg^{2+} ions are depleted; as such, crystal growth could continue for longer, and it may compensate the nucleation promoted by higher SI [39].

When Mg:PO_4 was set at 1:2, $MgSO_4.7H_2O$ showed the poorest P recovery yield and formed the smallest crystals from the four Mg^{2+} sources tested, proving this Mg^{2+} source to be the least viable at 1:2 Mg:PO_4. Therefore, it was not considered for further analysis.

Fig. 8 presents the EDX results for $MgCl_2.6H_2O$, *seasalt* and *bittern* at pH 8.5 (the level with larger crystals). At Mg:PO_4 1:2, the EDX results show the existence of a main phase composed of Mg, O and P regardless of crystal morphology with the co-existence of K and Ca ions in the matrix for $MgCl_2.6H_2O$, *seasalt* and *bittern*.

The diffractograms for all three Mg^{2+} sources at pH 8.5 are presented in Fig. 9. The precipitates were a mixture of struvite and newberyite ($MgHPO_4.3H_2O$), regardless of the Mg^{2+} source used. Apart from newberyite and struvite, the diffractograms showed some irregularities at the baseline and some peaks of lesser phases. This pattern fit ammonium phosphate hydrates with structure varying among $NH_4CaPO_4.H_2O$ (Powder Diffraction File no. 20–202), $NH_4CaP_3O_9.3H_2O$ (Powder Diffraction File no. 29–109) and an ammonium potassium phosphate with no known specific formula (Powder Diffraction File no. 1–925), matching the presence of Ca and K in the sample, referred to as 'NH_4K| Ca'in the diffractogram. Powder diffraction files were taken from Gates-Rector and Blanton [40]. *Seasalt* once again presented high amounts of Na and Cl elements present in EDX, confirmed as NaCl through XRD analysis.

In *bittern*, EDX and XRD indicate that Ca and K phosphates are likely present not as single-formed minerals but as phases developing together with the main struvite phase. This is probably the reason why these crystals grow more than the ones obtained with commercial magnesium reactants. Also, despite a small amount of Na being in the EDX, unless hidden by the most abundant phases, there is no obvious structure of halite (NaCl). The fact that Na is present in such a low concentration and other macronutrients (K, Ca, Mg, PO_4 and NH_4) are present in higher concentrations makes crystals produced with *bittern* at Mg:PO_4 1:2



MgCl₂.6H₂O

Element	Weight(%)	Error(weight %)	Atomic(%)
O	48.60	0.72	72.97
P	19.80	0.43	15.35
Mg	7.11	0.21	7.02
Ca	2.27	0.19	1.36
K	0.74	0.18	0.46
Cl	0.39	0.17	0.26
Au	21.09	0.89	2.57
Total	100.00		100.00

Bittern

Element	Weight(%)	Error(weight %)	Atomic(%)
O	33.51	6.61	48.42
P	37.67	1.43	28.12
Mg	16.02	0.91	15.24
Ca	4.83	0.25	2.79
K	3.95	0.22	2.34
Cl	2.68	0.18	1.74
Na	1.34	0.17	1.35
Total	100.00		100.00

Seasalt

Element	Weight(%)	Error(weight %)	Atomic(%)
Cl	39.94	1.51	30.10
Na	19.92	1.49	23.15
O	15.00	4.08	25.04
P	5.14	0.28	4.44
Mg	3.44	0.30	3.78
Ca	2.62	0.17	1.75
K	0.80	0.09	0.55
C	4.51	2.92	10.02
Au	8.62	0.73	1.17
Total	100.00		100.00

Fig. 8. EDX results for $MgCl_2.6H_2O$, *bittern* and *seasalt* at 1:2 $Mg:PO_4$.

suitable for application in fertiliser. The higher quantities of both Ca^{2+} and K^+ in EDX data of *bittern* compared to $MgCl_2.6H_2O$ and *seasalt* gives one possible explanation to why *bittern* at 1:2 $Mg:PO_4$ ratio can increase P recovery yield to higher values than when using commercial Mg^{2+} sources.

4. Conclusions

Two alternative magnesium sources, *bittern* and *seasalt*, were tested against two conventional sources, $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$, in the framework of a UDT approach in wastewater treatment systems.

The study showed that bittern can be a low-cost alternative Mg source, leading to a high P recovery efficiency at both $Mg:PO_4$ ratio of 1.2:1 and $Mg:PO_4$ ratio of 1:2. Furthermore, *bittern* leads to larger crystals than commercial Mg sources, with a positive effect on product recovery efficiency. The obtained crystals include both struvite and newberyite and no sodium, a major advantage when compared with *seasalt* use because of soil salinisation.

Crystallization at pH 8.5 leads to a product with less newberyite and with a fair amount of K ($Mg_2KH(PO_4)_2.15H_2O$), which can contribute to a higher-value fertiliser value owing to the presence of another macronutrient. At $Mg:PO_4$ ratio of 1:2, a similar composition is obtained, but as K^+ and Ca^{2+} phosphates instead of $Mg_2KH(PO_4)_2.15H_2O$, maintaining the multi-nutrient characteristics of the crystals.

In conclusion, *bittern* is a strong option as an Mg source for precipitation of UDT-source separated urine, increasing the downstream transferability of the process while generating struvite crystals with fertiliser applicability. In addition, struvite recovery using low-cost

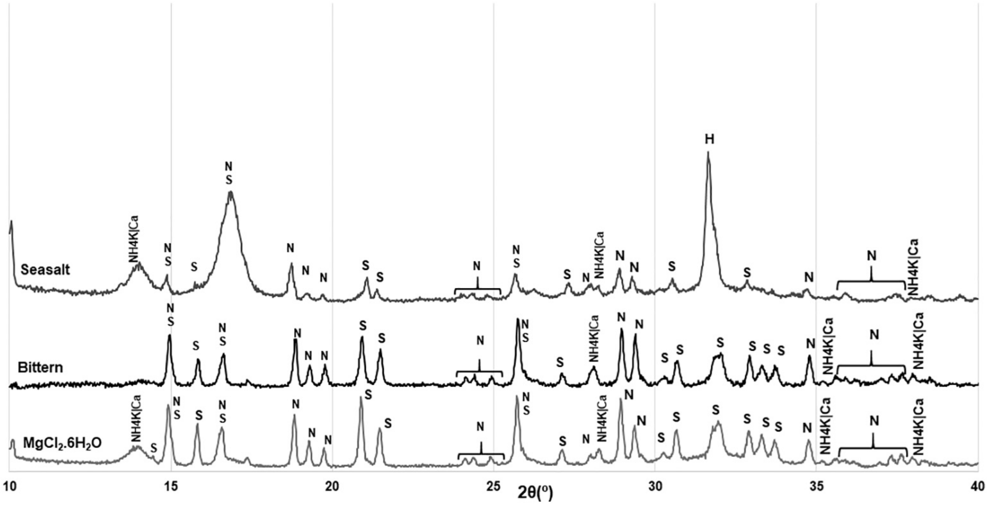


Fig. 9. Diffractograms at $Mg:PO_4 < 1:1$, showing the comparison between two different pH and time levels. S – Struvite [30], N – Newberyite [30] and H – Halite [32]).

magnesium sources will mitigate future runoff thanks to the slow-release properties of this natural fertiliser product, thus mitigating water contamination pressures. Besides, its performance at $Mg:PO_4$ 1:2 opens an explorable path to a simultaneous use of alternative Mg^{2+} sources as a main reactant and Ca^{2+} sources as a pH correction reactant, in systems where pure struvite is not an *à priori* requirement.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2021.102508.

References

[1] S. Antonini, S. Paris, T. Eichert, J. Clemens, Nitrogen and phosphorus recovery from human urine by struvite precipitation and air stripping in Vietnam, Clean - Soil, Air, Water. 39 (2011) 1099–1104, https://doi.org/10.1002/clen.201100036.

[2] P. Simha, A. Zabaniotou, M. Ganesapillai, Continuous urea–nitrogen recycling from human urine: a step towards creating a human excreta based bio–economy, J. Clean. Prod. 172 (2018) 4152–4161, https://doi.org/10.1016/j.jclepro.2017.01.062.

[3] D. Cordell, S. White, Tracking phosphorus security: indicators of phosphorus vulnerability in the global food system, Food Secur. 7 (2015) 337–350, https://doi.org/10.1007/s12571-015-0442-0.

[4] M. Preisner, E. Neverova-Dziopak, Z. Kowalewski, Mitigation of eutrophication caused by wastewater discharge: a simulation-based approach, Ambio 50 (2021) 413–424, https://doi.org/10.1007/s13280-020-01346-4.

[5] I. Kabdaşlı, O. Tünay, Nutrient recovery by struvite precipitation, ion exchange and adsorption from source-separated human urine–a review, Environ. Technol. Rev. 7 (2018) 106–138, https://doi.org/10.1080/21622515.2018.1473504.

[6] K. Sathiasivan, J. Ramaswamy, M. Rajesh, Struvite recovery from human urine in inverse fluidized bed reactor and evaluation of its fertilizing potential on the growth of Arachis hypogaea, J. Environ. Chem. Eng. 9 (2021), 104965, https://doi.org/10.1016/j.jece.2020.104965.

[7] P. Stolzenburg, A. Capdevielle, S. Teychené, B. Biscans, Struvite precipitation with MgO as a precursor: application to wastewater treatment, Chem. Eng. Sci. 133 (2015) 9–15, https://doi.org/10.1016/j.ces.2015.03.008.

[8] S. Xu, L. Luo, H. He, H. Liu, L. Cui, Nitrogen and phosphate recovery from source-separated urine by dosing with magnesite and zeolite, Pol. J. Environ. Stud. 24 (2015) 2269–2275, https://doi.org/10.15244/pjoes/43611.

[9] F.J. Rubio-Rincón, C.M. Lopez-Vazquez, M. Ronteltap, D. Brdjanovic, Seawater for phosphorus recovery from urine, Desalination 348 (2014) 49–56, https://doi.org/10.1016/j.desal.2014.06.005.

[10] D. Aguado, R. Barat, A. Bouzas, A. Seco, J. Ferrer, P-recovery in a pilot-scale struvite crystallisation reactor for source separated urine systems using seawater and magnesium chloride as magnesium sources, Sci. Total Environ. 672 (2019) 88–96, https://doi.org/10.1016/j.scitotenv.2019.03.485.

[11] Y. Pinatha, C. Polprasert, A.J. Englande, Product and cost perspectives of phosphorus recovery from human urine using solid waste ash and sea salt addition – a case of Thailand, Sci. Total Environ. 713 (2020), 136514, https://doi.org/10.1016/j.scitotenv.2020.136514.

[12] S. Zangarini, T. Pepè Sciarria, F. Tambone, F. Adani, Phosphorus removal from livestock effluents: recent technologies and new perspectives on low-cost strategies, Environ. Sci. Pollut. Res. 27 (2020) 5730–5743, https://doi.org/10.1007/s11356-019-07542-4.

[13] B. Etter, E. Tilley, R. Khadka, K.M. Udert, Low-cost struvite production using source-separated urine in Nepal, Water Res. 45 (2011) 852–862, https://doi.org/10.1016/j.watres.2010.10.007.

[14] X. Liu, Z. Hu, J. Mu, H. Zang, L. Liu, Phosphorus recovery from urine with different magnesium resources in an air-agitated reactor, Environ. Technol. (United Kingdom) 35 (2014) 2781–2787, https://doi.org/10.1080/09593330.2014.921732.

[15] Z. Bradford-Hartke, A. Razmjou, L. Gregory, Factors affecting phosphorus recovery as struvite: effects of alternative magnesium sources, Desalination 504 (2021), 114949, https://doi.org/10.1016/j.desal.2021.114949.

[16] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Impact of calcium on struvite crystal size, shape and purity, J. Cryst. Growth 283 (2005) 514–522, https://doi.org/10.1016/j.jcrysgro.2005.06.012.

[17] O.F. Schoumans, W.J. Chardon, M.E. Bechmann, C. Gascuel-Odoux, G. Hofman, B. Kronvang, G.H. Rubæk, B. Ulén, J.-M. Dorioz, Mitigation options to reduce phosphorus losses from the agricultural sector and improve surface water quality: a review, Sci. Total Environ. 468–469 (2014) 1255–1266, https://doi.org/10.1016/j.scitotenv.2013.08.061.

[18] M.J. Atkinson, C. Bingman, Elemental composition of commercial seasalts, J. Aquaric. Aquat. Sci. VIII (1997) 39–43, https://doi.org/10.1080/19393210.2010.520340.

[19] D.M. Rodrigues, R. do Amaral Fragoso, A.P. Carvalho, T. Hein, A.Guerreiro de Brito, Recovery of phosphates as struvite from urine-diverting toilets: optimization of pH, Mg:PO4 ratio and contact time to improve precipitation yield and crystal morphology, Water Sci. Technol. 80 (2019) 1276–1286, https://doi.org/10.2166/wst.2019.371.

[20] A.K. Sarkar, Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems, J. Mater. Sci. 26 (1991) 2514–2518, https://doi.org/10.1007/BF01130204.

[21] E.W. Rice, L. Bridgewater, A.P.H. Association, A.W.W. Association, W.E. Federation, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 2012.

[22] Y. Liu, S. Kumar, J.H. Kwag, C. Ra, Magnesium ammonium phosphate formation, recovery and its application as valuable resources: a review, J. Chem. Technol. Biotechnol. 88 (2013) 181–189, https://doi.org/10.1002/jctb.3936.

[23] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Phosphorus recovery from wastewater by struvite crystallization: a review, Crit. Rev. Environ. Sci. Technol. 39 (2009) 433–477, https://doi.org/10.1080/10643380701640573.

[24] C.C. Su, R.R.M. Abarca, M.D.G. de Luna, M.C. Lu, Phosphate recovery from fluidized-bed wastewater by struvite crystallization technology, J. Taiwan Inst. Chem. Eng. 45 (2014) 2395–2402, https://doi.org/10.1016/j.jtice.2014.04.002.

[25] A. Kozik, N. Hutnik, K. Piotrowski, A. Matynia, Continuous reaction crystallization of struvite from diluted aqueous solution of phosphate(V) ions in the presence of magnesium ions excess, Chem. Eng. Res. Des. 92 (2014) 481–490, https://doi.org/10.1016/j.cherd.2013.08.032.

[26] Y. Liu, H. Qu, Interplay of digester supernatant composition and operating pH on impacting the struvite particulate properties, J. Environ. Chem. Eng. 5 (2017) 3949–3955, https://doi.org/10.1016/j.jece.2017.07.065.

[27] F. Abbona, R. Boistelle, Growth morphology and crystal habit of struvite crystals (MgNH4PO4.6H2O), J. Cryst. Growth 46 (1979) 339–354.

[28] X. Zhang, J. Hu, H. Spanjers, J.B. van Lier, Struvite crystallization under a marine/brackish aquaculture condition, Bioresour. Technol. 218 (2016) 1151–1156, https://doi.org/10.1016/j.biortech.2016.07.088.

[29] S. Shaddel, S. Ucar, J.P. Andreassen, S.W. Sterhus, Engineering of struvite crystals by regulating supersaturation - correlation with phosphorus recovery, crystal morphology and process efficiency, J. Environ. Chem. Eng. 7 (2019), 102918, https://doi.org/10.1016/j.jece.2019.102918.

[30] X. Lu, K. Shih, X.Y. Li, G. Liu, E.Y. Zeng, F. Wang, Accuracy and application of quantitative X-ray diffraction on the precipitation of struvite product, Water Res. 90 (2016) 9–14, https://doi.org/10.1016/j.watres.2015.12.014.

[31] A. Ezquerro, Struvite precipitation and biological dissolution, in: TRITA LWR Degree Project Department of Land and Water Resources Engineering, Royal Institute of Technology, Stockholm, Sweden, 2010.

[32] D. Walker, P.K. Verma, L.M.D. Cranswick, R.L. Jones, S.M. Clark, S. Buhre, Halite-sylvite thermoelasticity, Am. Mineral. 89 (2004) 204–210, https://doi.org/10.2138/am-2004-0124.

[33] H. Lahalle, C.Cau Dit Coumes, D. Lambertin, C. Cannes, Influence of boric acid on the hydration of magnesium phosphate cement at an early age, in: 14th Int. Congr. Chem. Cem 2, 2015, pp. 1–17. http://www.iccc2015beijing.org/dct/page/1.

[34] H. Lahalle, C.Cau Dit Coumes, C. Mercier, D. Lambertin, C. Cannes, S. Delpech, S. Gauffinet, Influence of the w/c ratio on the hydration process of a magnesium phosphate cement and on its retardation by boric acid, Cem. Concr. Res. 109 (2018) 159–174, https://doi.org/10.1016/j.cemconres.2018.04.010.

[35] X.D. Hao, C.C. Wang, L. Lan, M.C.M. Van Loosdrecht, Struvite formation, analytical methods and effects of pH and ca 2+, Water Sci. Technol. 58 (2008) 1687–1692, https://doi.org/10.2166/wst.2008.557.

[36] E. Tavakkoli, P. Rengasamy, G.K. McDonald, High concentrations of Na+ and cl-ions in soil solution have simultaneous detrimental effects on growth of faba bean under salinity stress, J. Exp. Bot. 61 (2010) 4449–4459, https://doi.org/10.1093/jxb/erq251.

[37] P. García-Caparrós, A. Llanderal, M.T. Lao, Sodium chloride effects on water and nutrient uptake efficiency in Sarcocornia fruticosa containerized production, Commun. Soil Sci. Plant Anal. 47 (2016) 2306–2314, https://doi.org/10.1080/00103624.2016.1243712.

[38] H. Huang, J. Li, B. Li, D. Zhang, N. Zhao, S. Tang, Comparison of different K-struvite crystallization processes for simultaneous potassium and phosphate recovery from source-separated urine, Sci. Total Environ. 651 (2019) 787–795, https://doi.org/10.1016/j.scitotenv.2018.09.232.

[39] C.M. Mehta, D.J. Batstone, Nucleation and growth kinetics of struvite crystallization, Water Res. 47 (2013) 2890–2900, https://doi.org/10.1016/j.watres.2013.03.007.

[40] S. Gates-Rector, T. Blanton, The powder diffraction file: a quality materials characterization database, Powder Diffract. 34 (2019) 352–360, https://doi.org/10.1017/S0885715619000812.