



Crystallization kinetics and growth of struvite crystals by seawater versus magnesium chloride as magnesium source: towards enhancing sustainability and economics of struvite crystallization

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HIGHLIGHTS

- Higher Mg:P molar ratios improve the struvite crystallization kinetics by seawater.
- PH is the most significant supersaturation regulator for struvite crystal growth.
- Mg:P > 0.2 and N:P > 6 were beneficial for the struvite crystal growth.
- High N:P molar ratio significantly improves the struvite growth by seawater.
- Struvite seeding minimizes the simultaneous precipitation of calcium phosphates.

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ABSTRACT

The recycling of nutrients from wastewater and their recovery in the form of valuable products is an effective strategy to accelerate the circular economy concept. Phosphorus recovery from wastewater by struvite crystallization ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is one of the most applied techniques to compensate for the increasing demand and to slow down the depletion rate of phosphate rocks. Using low-cost magnesium sources, such as seawater, improves the financial sustainability of struvite production. In this study, the potential of seawater for struvite crystallization versus the commonly used magnesium source, MgCl_2 , was tested by crystal growth and kinetic experiments. The impact of ammonium concentration, magnesium concentration and pH on the growth kinetics of struvite in synthetic and real reject water were studied. The results showed that simultaneous precipitation of calcium phosphate was insignificant when using seawater, while presence of struvite seeds diminished it further. Among the supersaturation regulators, pH had the most significant effect on the struvite growth with both MgCl_2 and seawater, while high N:P molar ratios further improved the struvite crystal growth by seawater. The N:P molar ratios higher than 6 and Mg:P molar ratios higher than 0.2 are recommended to improve the crystal growth kinetics. It was concluded that seawater is a promising alternative magnesium source and the control of supersaturation regulators (i.e., Mg:P, N:P and pH) is an effective strategy to control the reaction kinetics and product properties.

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1. Introduction

The new generations of wastewater treatment plants need to target several developments including improving effluent quality, cutting greenhouse gas emissions and recovering energy and valuable resources. The contribution to the global phosphorus load

from domestic sewage to water recipients should be reduced. This is because in many areas of the world either there is not enough water to assimilate the phosphorous or the pollution load is so huge that the water systems can not assimilate everything. In addition, the recovery and recycling of phosphorus from wastewater is gaining momentum in many countries due to vital importance of phosphorus in fertilizer industry and adaption of the circular economy strategies. Further acceleration of phosphorus recovery can be achieved by improving the economic drivers and

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environmental legislations (Shaddel et al., 2019c). Therefore, the improvement of financial sustainability by reducing the operational costs is a strong financial driver for the nutrient recovery technologies. The recovery of phosphorus, among all available resources in wastewater, is a prominent action as it can reduce the conventional mining and moderate the expected future shortage of phosphate rocks used to produce phosphorus fertilizers (Shaddel et al., 2019c).

The preferred method for phosphorus recovery mainly depends on the infrastructure of the existing wastewater treatment plant. However, struvite crystallization is one of the main methods used to recover phosphorus from wastewater due to the physical and chemical properties of struvite mineral ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Li et al., 2019). Struvite forms large diameter crystalline aggregates and show good settling and dewatering properties, as well as low incorporation of heavy metals or pathogenic contaminations, which makes it a good candidate for phosphorus removal and recovery (Shaddel et al., 2019a; Uysal et al., 2010). Struvite is comprised of primary (nitrogen and phosphorus) and secondary (magnesium) macronutrients and has low solubility in water, which results in reduced runoff and improved plant uptake. The crystallization of phosphorus as struvite by addition of an adequate amount of magnesium to the sidestreams that are rich in NH_4^+ and PO_4^{3-} has been recognized as an efficient means of solving operational challenges and recycling the phosphorus to conserve and protect natural resources (Li et al., 2019). However, the use of pure magnesium sources such as magnesium salts (i.e. MgCl_2 and MgSO_4) may stress the total sustainability and economic feasibility of the process (Shaddel et al., 2019a). The cost of struvite production is mainly influenced by chemical costs, especially the cost of magnesium source which can contribute up to 75% of overall costs (Hövelmann and Putnis, 2016). Therefore, using low-cost magnesium sources for struvite production is an effective approach to improve the economics of struvite crystallization while ensuring the quality of final product.

A cost reduction of 18–81% for struvite production was reported by using a low-cost magnesium source (Gunay et al., 2008; Lahav et al., 2013). Various low-cost magnesium sources have been studied for struvite production including bittern (a by-product in salt industry) (Ye et al., 2011), wood ash (Sakthivel et al., 2012), pretreated seawater, and seawater concentrate (nanofiltration, reverse osmosis) (Kim et al., 2016; Lahav et al., 2013). The high heavy metal content in the wood ash and limited access to bittern in many areas have made them less advantageous compared to seawater (Sakthivel et al., 2012). Using seawater in the form of a concentrate can reduce the intake volume, but it does not improve the molar ratio of magnesium with respect to other ions. The removal of interfering ions by pretreatment of seawater is an alternative, however, it increases costs and complexity of the process. On the other hand, raw seawater (untreated seawater) is an environmentally friendly and cost effective alternative, as well as being technically feasible since magnesium is the second most abundant cation in seawater (≈ 1300 mg/L). The availability of an alternative magnesium source in local context is also important, thus, it should be noted that for plants located away from the seashore, using seawater may not be as profitable due to increasing power costs of pumping for long distances, as well as investment and maintenance costs. Additional ions unavoidably will be added to the treatment system, although it is expected that the adverse effect of these ions would not be significant. This is because sidestreams constitute $\approx 1\%$ of the overall flowrate to the plant and likely the influence of salt content from seawater to the main stream is marginal (Lahav et al., 2013; Matsumiya et al., 2000). Further, it is reported that phosphate accumulating organisms

(PAO) can be adopted to seawater and functioning in seawater conditions is as stable as in freshwater conditions (de Graaff et al., 2020).

The potential of seawater for offsetting operating costs for struvite production is demonstrated (Nur et al., 2018; Quist-Jensen et al., 2016; Rubio-Rincón et al., 2014), although much less is unveiled on reaction kinetics and crystal growth with seawater. The crystal growth information is essential for the design and optimization of struvite crystallization to fully realize plant specific benefits. The challenges associated with using seawater for struvite production should be addressed both theoretically and practically. The presence of additional ions, specially calcium, can affect the kinetics of struvite crystallization. Higher calcium concentrations can lead to complexation of calcium and phosphate species (CaHPO_4 (aq), CaPO_4^-) and reduce the activity of precursor ions in the reaction medium, or even result in simultaneous precipitation of calcium phosphate minerals.

The supersaturation regulation has been recognized as an effective strategy to optimize the phosphorus recovery and struvite properties (Shaddel et al., 2019b). However, further investigations are required to optimize the conditions for struvite crystallization by seawater. This is because the supersaturation regulation is possible by both adjustment of precursor concentrations and reaction pH. Several ions (i.e. sodium, chloride, calcium, and sulfate) will inevitably be added into the system with the use of seawater, therefore, simultaneous precipitation of various compounds (i.e. calcium phosphates, calcium carbonate) should be considered and minimized to improve the quality of the produced struvite. Moreover, the struvite crystals experience different degrees of supersaturation during their crystal growth period, while the crystal growth kinetics in the low supersaturation regions were mainly overlooked. Generally, there is surplus of ammonium in sidestreams of anaerobic digestion, and while the phosphorus recovery should be maximized, the magnesium addition should be minimized due to associated costs.

A comprehensive understanding of struvite crystal growth with seawater still requires further systematic evaluation. Therefore, the main objective of this work is to assess the crystal growth kinetics of struvite crystallization by seawater as a sustainable alternative magnesium source. A systematic and comparative approach is employed in the experimental design by comparing the crystal growth rates and particle properties of struvite precipitated with seawater and MgCl_2 under varying operational conditions. The effects of reject type (i.e., synthetic and real reject), ammonium and magnesium concentrations and pH on struvite crystal growth were studied.

The results of this study can be used for the development of struvite crystallizers by using seawater in industrial scale. Further, this study provides a better understanding to modify full-scale installations with an understanding of the true benefits, challenges and operating strategies in struvite production by using seawater.

2. Materials and methods

2.1. Materials

The chemical reagents were purchased from Merck with analytical grade including sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), ammonium chloride (NH_4Cl), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH). Milli-Q water (18.2 M Ω cm) was used for all purposes. The struvite seeds with a purity of ≥ 98 wt% were obtained from Alfa Aesar and sieved to 125–63 μm to be used in seeded experiments. Seeds were

composed of 39% phosphate, 10% magnesium, 7% ammonium and 44% crystal water by mass. The scanning electron microscopy (SEM) (Hitachi S–3400 N) image and the particle size distribution for the seed particles are presented in Figs. S1 and S2. The surface area of the seeds was determined by multiple point BET (Brunauer–Emmett–Teller) from N₂ adsorption and desorption isotherms at 77 K, after degassing at 40 °C for 72 h prior to analyses (Fig. S3). The BET surface area was 374.9 ± 3.4 m²/g with the cumulative pore volume (17–3000 Å) of 0.357 cm³/g and pore size of 30.53 Å based on BJH (Barrett–Joyner–Halenda) method (Figs. S3 and S4) (Herald et al., 2017; Hövelmann et al., 2019; Stone, 1958).

The seawater was obtained from Trondheim fjord (an inlet of the Norwegian Sea) where it was pumped from a depth of 70 m and 800 m away from land. The seawater passed through a sand filter of ~70 µm and then kept in the fridge (1–4 °C) during the experimental period. Table 1 presents the properties of seawater.

2.2. Preparation of solutions

The real reject water was obtained from dewatering of waste biological sludge of a wastewater treatment plant with biological phosphorus removal. The characterization of real reject is presented in Table 2 by determination of solids in wastewater according to Standard Methods 209 (American Public Health, 1960). Synthetic reject water, composed only of ammonium and phosphate at the same concentrations, was prepared from stock solutions with dissolution of the corresponding crystalline solids (NaH₂PO₄·2H₂O and NH₄Cl).

2.3. Methods

All experiments were carried out using a lab-scale crystallization system, composed of a 1 L glass reactor, stirred with a combined mixer controlled by a mechanical stirrer operated at 150 rpm. The combined mixer composed of a common shaft with a Teflon two-blade propeller in the middle and a four-blade propeller (45°) at the end to ensure proper mixing of the crystals (Fig. 1). This mixer configuration reduced the dependency of complete mixing on high rpm values (i.e., high G-values) and allowed for using a low stirring speed, which minimizes the possibility of secondary nucleation due to crystal breakage (Fig. 1). Temperature was regulated by a water bath and maintained at 20 ± 0.5 °C for all experiments. Nitrogen, presaturated with water, was constantly preserved on top of the solutions throughout the crystallization reactions to prevent intrusion of atmospheric carbon dioxide.

The unseeded experiments were carried out by preparation of supersaturated solutions with respect to struvite via addition of MgCl₂ solution or seawater to the reject solution. The reactions were let to proceed for 60 min under constant pH. For this purpose,

Table 2
The characterization of the real reject water.

Parameter	Value	Standard deviation (%)
Tot-P (mM)	4.78	±1.63
PO ₄ -P (mM)	4.42	±1.34
NH ₄ -N (mM)	53.85	±1.34
Na ⁺ (mM)	15.10	±2.11
K ⁺ (mM)	0.88	±1.84
Ca ²⁺ (mM)	1.36	±4.15
Mg ²⁺ (mM)	1.71	±2.40
Initial pH	7.00	±0.01
TSS (%)	2.05	±0.18
VSS (%)	0.62	±0.06
Total COD (mgL ⁻¹)	1838	±6.21
Soluble COD (mgL ⁻¹)	468	±5.73

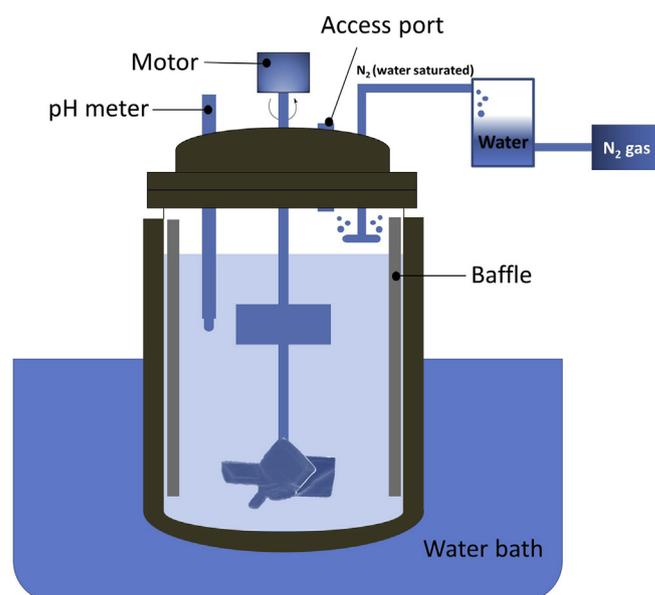


Fig. 1. The schematic representation of the reactor setup.

pH was continuously monitored by a combined glass electrode connected to EasyDirect™ pH Software (Metrohm), and 1 M NaOH was added manually to compensate for pH decrease accompanying the crystal formation.

For the seeded growth experiments, metastable solutions supersaturated with respect to struvite were prepared (Table 3) and growth was initiated by addition of 0.7 g of struvite seeds at a constant stirring speed (150 rpm) and temperature (20 ± 0.5 °C) at pH = 7.5. The seed amount and mixing intensity were optimized in

Table 1
The seawater properties and composition.

Parameter	Values	Standard deviation (%)	Molar conc. (mM)	Mol./Mol. (Mg ²⁺)
pH	7.90	±1.0	–	–
Conductivity (mS/cm)	31.60	±0.3	–	–
Alkalinity (mM)	1.66	±1.0	–	–
Na ⁺ (mgL ⁻¹)	10570	±1.7	459.77	8.76
Mg ²⁺ (mgL ⁻¹)	1276	±2.6	52.49	1.00
Ca ²⁺ (mgL ⁻¹)	447	±6.9	11.15	0.21
K ⁺ (mgL ⁻¹)	393	±4.5	10.00	0.19
Cl ⁻ (mgL ⁻¹)	19325	±6.4	545.00	10.38
SO ₄ ²⁻ (mgL ⁻¹)	2740	±1.5	28.52	0.54
NO ₃ ⁻ (mgL ⁻¹)	160	±4.0	2.60	0.05
Br ⁻ (mgL ⁻¹)	67	±0.3	0.83	0.02
F ⁻ (mgL ⁻¹)	1.30	±0.3	0.06	–

Table 3

The experimental conditions for struvite crystal growth at pH 7.5 and 20 °C.

Target	Exp.	Mg ²⁺ (mM)	NH ₄ ⁺ (mM)	PO ₄ -P (mM)	Mg-source	Initial S _a
NH ₄ -concentration	1	0.93	26.55	4.43	MgCl ₂	1.30
	2	0.93	40.39	4.43	MgCl ₂	1.43
	3	0.93	53.10	4.43	MgCl ₂	1.51
	4	0.93	26.55	4.43	SW	1.25
	5	0.93	40.39	4.43	SW	1.38
	6	0.93	53.10	4.43	SW	1.46
Mg-concentration	7	0.89	26.55	4.43	MgCl ₂	1.28
	8	1.55	26.55	4.43	MgCl ₂	1.52
	9	2.21	26.55	4.43	MgCl ₂	1.69
	10	0.89	26.55	4.43	SW	1.25
	11	1.55	26.55	4.43	SW	1.43
	12	2.21	26.55	4.43	SW	1.55
pH	13	2.21	26.55	4.43	SW, pH = 7.5	1.60
	14	2.21	26.55	4.43	SW, pH = 7.7	1.90
	15	2.21	26.55	4.43	SW, pH = 7.9	2.23

preliminary experiments to avoid additional nucleation and mass transfer to be the limiting factor during the crystal growth, respectively. During the seeded growth experiments, the reaction pH was monitored continuously, and samples were withdrawn for ion analysis at determined time points. All experiments in this study were performed in triplicate.

The vacuum filtration through a 0.2 µm pore size filter (polypropylene membranes) was used to collect the precipitates at the end of each experiment. The powder X-ray diffraction (XRD) (D8 Advance DaVinci, Bruker AXS GmbH) was used for solid phase characterization in the range of 5–75° with a step size of 0.013° and a step time of 0.67 s. The obtained data were analyzed by DIFRACC.SUITE EVA software (Bruker) and the International Centre for Diffraction Data database (ICDD PDF-4 + 2018). The SEM analyses were performed on samples sputtered with gold on carbon tape. The particle size analyzer with laser diffraction (Beckman Coulter LS230) was used to measure and analyze the particle size distribution. The presented particle sizes were obtained by dynamic light scattering technique and derived based on sphericity of particles, so they should be interpreted as nominal size of crystals for the comparison of the results. The elemental composition of final precipitates was measured by complete dissolution of product in 1 M HNO₃ and the ion concentrations were measured by ion chromatography (940 Professional IC Vario, Metrohm). The experimental and theoretical results of percent phosphorus recovery are calculated by using Eq. (1):

$$P - \text{recovery} \% = \left(\frac{P_{\text{initial}} - P_{\text{final}}}{P_{\text{initial}}} \right) \times 100\% \quad (1)$$

An ion exchange chromatograph (940 Professional IC Vario, Metrohm) with an autosampler (813 compact) was used for characterization of seawater and wastewater. The samples were filtered by 0.45 µm pore size filter (polypropylene membranes) before analysis with ion exchange chromatograph. It should be noted that determination of ion concentrations in seawater with ion chromatography technique is challenging since some of the ions such as sodium and chloride are present in very high concentrations, while certain metals are in such minute quantities (Table 1). The phosphate ion concentrations were determined via spectrophotometry (Hach DR Lange, 1900). Standard Methods 209 (American Public Health, American Water Works, 1960) was used for the determination of solids including total suspended solids (TSS) and volatile suspended solids (VSS).

2.3.1. Crystal growth model

In this study, the crystal growth rates were measured with

seeded batch experiments by monitoring the changes in solution supersaturation (i.e. ion concentrations). This method allows for the determination of overall growth rates without distinguishing between different sizes or individual faces of struvite crystals. The growth rate can be calculated by using Eq. (2) where $\frac{dC}{dt}$ denotes the concentration change of precursor ions due to crystal growth with respect to time and A is the surface area of the seeds (Mullin, 2001). The depletion of magnesium concentration as a function of time was followed to calculate and compare the growth rates of struvite crystals in seeded growth experiments at varying conditions.

$$R = \frac{1}{A} \cdot \frac{dC}{dt} \quad (2)$$

The crystal growth experiments were performed at pH = 7.5 and 20 °C under different operational conditions to investigate the effect of seawater as magnesium source versus MgCl₂ and the effects of Mg²⁺ and NH₄⁺ concentration. The reported studies on struvite crystal growth at varieties of pH values have been performed at ion concentrations (i.e. Mg²⁺, PO₄³⁻, and NH₄⁺) much lower than typical concentration at full-scale (Wei et al., 2017). However, in this study the ion concentrations are similar to typical values of dewatering sidestream of anaerobically digested sludge of a full-scale wastewater treatment plant using enhanced biological phosphorus removal (EBPR). The effects of constituent ion concentrations were studied at pH = 7.5 since additional nucleation to seed growth was observed at pH values higher than pH = 7.5.

3. Results and discussion

3.1. Unseeded experiments

The optimum selection of magnesium concentration and pH are two key parameters in the matrix of regulating parameters to maximize the P-recovery at lowest costs. However, maintaining product quality is more significant when using seawater compared to pure Mg-based chemicals. The full-scale struvite crystallization reactors are working based on the growth of available struvite seeds, while secondary nucleation is necessary to generate new particles after harvesting the struvite from the reactor. In other words, the overall phosphorus recovery and the final product properties are a result of generation of new particles (i.e. secondary nucleation) and the growth of available crystals. Therefore, a series of unseeded experiments (Fig. 2) were performed to investigate the efficiency of seawater for P-recovery and the quality of the obtained precipitate. The detailed results of the unseeded experiments are presented in a dedicated paper, and briefly summarized here

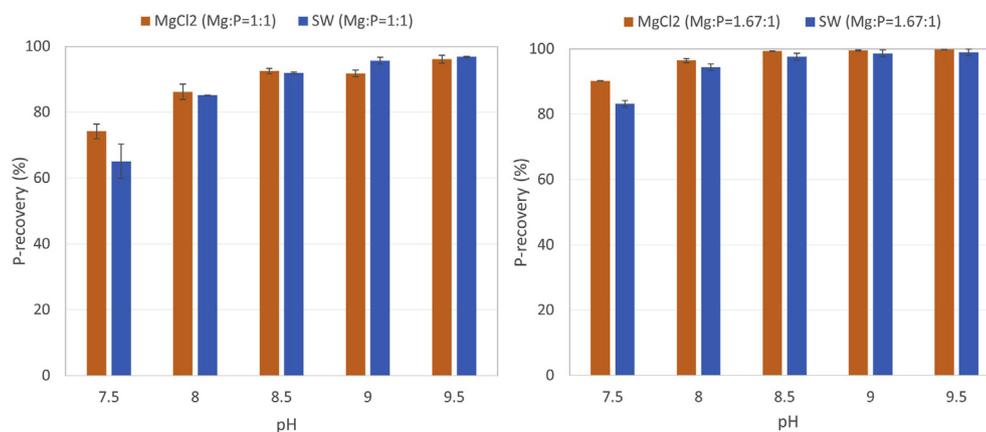


Fig. 2. The measured P-recovery in unseeded crystallization experiments with synthetic reject water by using seawater and MgCl₂ (adapted from Shaddel et al., 2020).

(Shaddel et al., 2020). The results showed that final P-recovery mainly depends on the Mg:P molar ratio and the reaction pH (Fig. 1). Further, it was shown that satisfactory P-recovery efficiency (65–99%) can be achieved by using seawater for struvite crystallization. This confirms the potential of seawater for struvite production, although slight reduction in phosphorus recovery was observed (≈ 1 –6%) when seawater was used compared to MgCl₂ salt as the magnesium source. The bigger difference in P-recovery at lower pH values (i.e. pH = 7.5) was mainly due to the strong effect of decreasing supersaturation with seawater on the kinetics of the precipitation reaction. The higher ionic strength due to introduction of additional ions in seawater in the reactor lowers the ionic activity product and supersaturation with respect to struvite, so maintaining higher pH is necessary to compensate for this effect. However, under the current experimental conditions increasing pH above 8.5 is not advantageous as it has minimal improving effect. The quality of the final product was also investigated by XRD analysis and complete dissolution of the final precipitates. The presence of struvite as the main phase in the final precipitate was confirmed, although insignificant amounts of calcium carbonate (<1%) and trace amounts of sodium and potassium (<0.1%) were also detected in the re-dissolved samples precipitated from real reject water. Maintaining a high N:P molar ratio in the reaction solution was shown to be critical to precipitate struvite in competition with other potential phases (Shaddel et al., 2020). Overall, it was concluded that appropriate product properties by using seawater for struvite crystallization is achievable in addition to comparable P-recovery efficiency with respect to MgCl₂.

Further, crystallization kinetics and crystal growth data are important in the design and operation of struvite crystallizers as the reaction kinetics is decisive in the determination of retention time and the reactor volume. Therefore, the kinetics of struvite crystallization by seawater and MgCl₂ were studied under the similar operational conditions, which enables us to compare the impact of seawater in struvite crystallization versus MgCl₂.

3.2. Seeded growth experiments

The struvite reactor design and overall optimization of economy and process efficiency require crystal growth and reaction kinetic data. The reaction kinetic data can be used to optimize the hydraulic reaction time (HRT) and phosphorus recovery efficiency. Therefore, the seeded growth experiments were performed to evaluate the crystal growth and reaction kinetics by seawater and MgCl₂.

3.2.1. Effect of Ca²⁺ ions

An important aspect to be considered while using seawater as the magnesium source for struvite crystallization is its calcium content. During struvite crystallization, calcium ions, when present in the solution, can potentially compete with magnesium ions to react with phosphate species both for complexation and simultaneous precipitation. However, the interfering effect of calcium ions on struvite precipitation strongly depends on operational conditions, where both strong interference (Jaffer et al., 2002) and insignificant effects (Krähenbühl et al., 2016; Le Corre, 2006) on struvite crystallization were reported in the literature. Moreover, formation of calcium phosphates in the early stages of crystallization (1–30 min) followed by their dissolution in later stages has been reported at high ammonium (>300 mg/L) and phosphate (>100 mg/L) concentrations. In the crystal growth experiments of this study, the calcium concentration was stable during the crystal growth, indicating that simultaneous precipitation of calcium phosphate phases did not occur. The prevention of the possible formation of calcium-bearing precipitates can be explained by the presence of struvite seeds, high ammonium concentration and the applied Mg:P molar ratio in these experiments. The ammonium concentration is one of the determining factors that can enhance struvite precipitation in the presence of calcium. This is explained by inhibition of the initial step of precursor-controlled reaction or as a result of Mg²⁺ ions blocking the surface growth sites of Ca-phosphates and slowing down the growth rate of calcium precipitates (Golubev et al., 1999; Gunnars et al., 2004). An increase of N:P molar ratio increases the buffer capacity of solutions and precipitation kinetics of struvite, which makes it kinetically more favorable with respect to potential calcium phosphates at similar conditions (Crutchik and Garrido, 2011). Enhanced buffer capacity of the solutions results in lowering the required pH for nucleation of struvite, which in turn favors the precipitation of P as struvite and improves the product purity by reducing the share of other compounds (i.e. calcium phosphates) (Capdevielle et al., 2013). The calcium interference was insignificant in crystal growth experiments, although the ammonium and magnesium concentrations as well as pH are among key parameters affecting the growth kinetics of struvite crystal. Therefore, the effect of ammonium and magnesium concentration on struvite crystal growth by MgCl₂ and seawater was further studied, and the results are presented in the following sections.

3.2.2. Effect of NH₄⁺ concentration

The particular processes in wastewater treatment plants, feed and seasonal variations often create changes in the composition of

the input material to the crystallizer. Further, the sidestreams after dewatering of EBPR sludge are rich in phosphorus, while the anaerobic digestion of sludge produces surplus of ammonium with respect to phosphate and magnesium. Therefore, the ammonium concentration (N:P molar ratio) can be regulated by adjusting the share of pre-digestion and post-digestion sidestreams to the crystallizer (Shaddel et al., 2019a). The N:P > 6 is beneficial to maximize the recovery efficiency and purity of struvite (Vaneckhaute et al., 2017). Therefore, the N:P molar ratio was varied as N:P = 12:1, 9:1 and 6:1.

All the reaction conditions were kept constant except the ammonium concentration to investigate the role of ammonium on the struvite growth kinetics (Table 3). The consumption rate of magnesium ion in Fig. 3 reflects the kinetics of crystal growth. The results showed that the crystal growth and kinetics of struvite crystallization increases at higher ammonium concentration. The kinetics of crystal growth with seawater was $\approx 5\text{--}20\%$ slower with respect to MgCl_2 . The presence of additional ions in the seawater reduces the activity of precursors which consequently reduced the crystal growth kinetics. The thermodynamic modeling by Visual MINTEQ software showed that under the operational conditions in this study magnesium activity was reduced due to the formation of MgSO_4 (aq) and MgCl^+ complexes (7.8% of total concentration), and ammonium activity was slightly lowered by the formation of NH_4SO_4^- (0.16% of total concentration) in the crystal growth experiments by seawater.

In general, the rate of supersaturation consumption in the experiments with MgCl_2 as the magnesium source is higher than seawater (Fig. S5). Higher ammonium concentrations enhanced the rate of magnesium consumption for both MgCl_2 and seawater. Considering the supersaturation consumption during the growth period, the N:P molar ratio higher than 6 is beneficial for struvite crystal growth. However, the sole increase of N:P molar ratio higher than 6 will not significantly improve the kinetics of struvite crystallization if the other constituent ions are limited (i.e. Mg and

P). In other words, if the N:P molar ratio is higher than 6, the increase of Mg:P molar ratio or pH is a more efficient strategy to enhance the struvite crystal growth. The improving effect of higher ammonium concentrations on the magnesium consumption was more significant in the experiments by using seawater as magnesium source. Therefore, higher ammonium concentration (i.e., N:P) is beneficial for struvite crystal growth and in practice during the periods with higher ammonium in the influent, the magnesium addition and pH should be accordingly adjusted to reduce the overall operational cost.

3.2.3. Effect of Mg^{2+} concentration

Although seawater is a readily available source of magnesium, the magnesium dosing should be optimized to maximize the phosphorus recovery efficiency and the crystal growth kinetics and to avoid overdosing of seawater. The overdosing of magnesium beyond the process needs increases the risk of uncontrolled struvite precipitation in other process stages and in the case of seawater, it results in unwanted residual ions in the system. Therefore, the impact of magnesium concentration on the kinetics of struvite crystallization for both MgCl_2 and seawater was investigated.

Fig. 4 presents the consumption rate of magnesium and Fig. S6 the consumption rate of supersaturation for the crystal growth experiments by MgCl_2 and seawater. The results showed that the major part of the supersaturation ($\approx 60\%$) was consumed in the first 10 min of the growth experiments and in average the kinetics of crystal growth with seawater was $\approx 10\text{--}24\%$ slower with respect to MgCl_2 . As mentioned previously, when seawater is used, additional ions are also introduced in the reaction medium, which results in a higher ionic strength. The effect of high ionic strength on crystal growth kinetics is twofold. Increasing ionic strength can lead to a reduction in the double-layer thickness around the crystals and hence enhance the mass transfer of monomers to the crystal surface (Stubičar et al., 1993; Tai et al., 2006). Yet, the activity of the

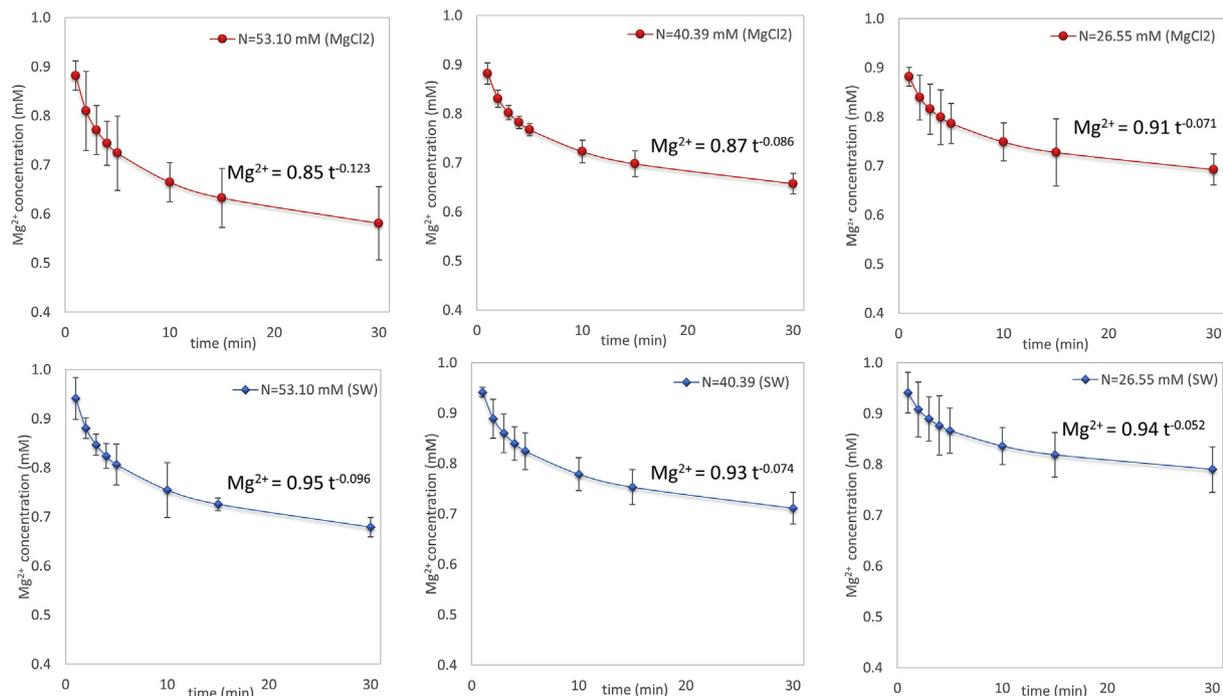


Fig. 3. The magnesium consumption as a function of time at an initial magnesium concentration of 0.925 mM and varying ammonium concentrations (a) 53.10, (b) 40.39, and (c) 26.55 mM with using MgCl_2 or seawater (SW) as the magnesium source.

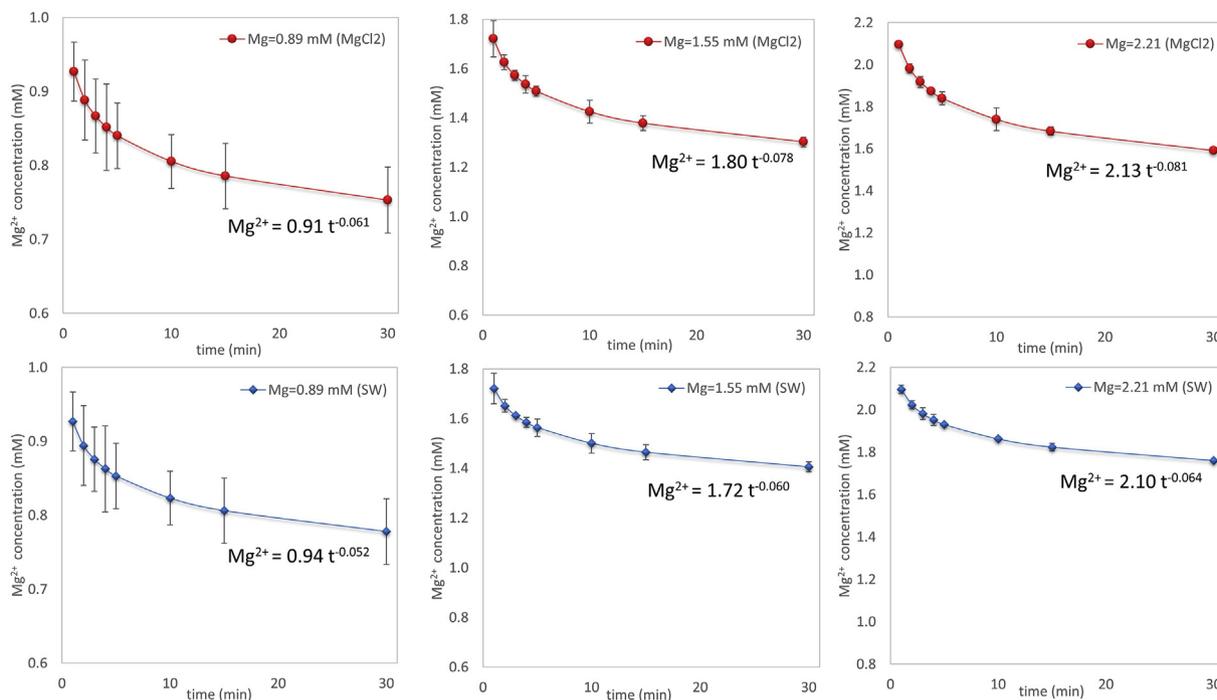


Fig. 4. The magnesium consumption as a function of time at an initial ammonium concentration of 26.55 mM and varying magnesium concentrations (a) 0.89, (b) 1.55, and (c) 2.21 mM with using MgCl_2 or seawater (SW) as the magnesium source.

precursor ions of struvite reduces with high ionic strength due to ion complexation by foreign ions in seawater. The overall decrease in the struvite growth rates with seawater indicated the second effect to be more pronounced on the reaction kinetics.

The $\text{Mg}^{2+} = 0.89$ mM resulted in slower growth kinetics than other experimental conditions and it can be considered as the lower cutoff for the consumption of magnesium, where extending the reaction time at lower magnesium concentrations than this value is not effective. The reaction kinetics is determining in the operation of struvite crystallizer since slow reaction kinetics will increase the operational costs associated with mixing and pumping which will further affect the economic sustainability of the process.

3.2.4. Effect of pH

The regulation of Mg:Ca molar ratio is an effective strategy to improve the reaction kinetics while maintaining the purity of struvite in crystallization by using seawater as the magnesium source. The original Mg:Ca molar ratio in seawater is higher than 4 (Table 1) and it is important to use this privilege during the period of crystal growth by regulation of growth kinetics. It was reported that under relevant ion concentration in the municipal wastewater the kinetics of struvite precipitation is faster than calcium phosphate precipitation (Lahav et al., 2013), which is advantageous in the case of struvite crystallization by seawater. Therefore, the reaction pH should be adjusted to an optimum value that results in: i) maximum phosphorus recovery efficiency, ii) proper reaction kinetics and iii) at the same time does not trigger the precipitation of calcium phosphates after consumption of magnesium by struvite crystallization (Shih et al., 2017). The effect of pH was studied by using real reject water rather than synthetic reject water that was used in previous sections. The increase of pH beyond $\text{pH} = 7.5$ in synthetic reject water triggered particle nucleation, which was identified by a pH reduction before addition of the seeds. However, the real reject water was stable at pH values higher than 7.5.

The results of magnesium consumption kinetics in Fig. 5 shows

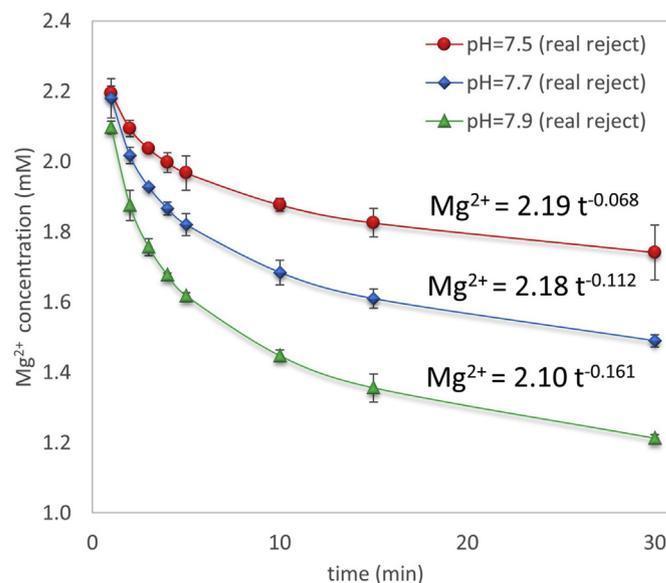


Fig. 5. The magnesium consumption at $\text{NH}_4\text{-N} = 26.55$ mM and different pH values in crystal growth experiments with seawater and real reject water.

that magnesium consumption rate at $\text{pH} = 7.5$ was increased by ≈ 32 and 45% at $\text{pH} = 7.7$ and 7.9 , respectively. The higher magnesium consumption rate is the result of higher initial supersaturation at higher pH values, which provides higher driving force for crystal growth. The practical implication of these findings can be used for the adjustment of the hydraulic retention time (HRT) with respect to magnesium consumption in full-scale. It is important to regulate the HRT based on the kinetics of magnesium consumption rate both for reduction of operational costs and for keeping the Mg:Ca molar ratio at a level that minimizes the simultaneous

precipitation of calcium phosphates. In general, the pH regulation is an effective strategy to adjust the solution supersaturation since pH is a more effective variable than precursor concentrations and struvite solubility on supersaturation.

3.3. Product properties

The XRD analyses of the products (Fig. S7) after growth reactions with seawater showed that struvite was the main precipitated phase. Previous studies showed that Mg:Ca>1 can avoid the formation of crystalline calcium phosphates and the co-precipitated CaP phase with struvite has primarily amorphous structure, which cannot be clearly detected by XRD analysis (Lee et al., 2013). Moreover, small crystalline size and low crystallinity can prevent those phases to be detected by XRD measurements. Therefore, samples taken after crystal growth reactions were completely dissolved and analyzed also with ion chromatography. As it was expected due to the stable calcium concentration during the crystal growth, the final precipitate was further confirmed to be pure struvite. This showed that insignificant simultaneous precipitation of calcium compounds in unseeded experiments was not detected and the seeding under current experimental conditions further improved the product quality.

The particle size distribution of struvite seeds before and in the end of the crystal growth experiments (media size of the seeds = 106.2 μm) were measured to determine the increase of the particle size under different reaction conditions. Fig. S2 presents the particle size distribution of the original seeds before the growth experiments and Fig. 6 in the end of crystal growth experiments. The median size for the experiments with MgCl_2 is generally bigger than experiments with seawater ($\approx 3.5\%$), in accordance with the observed growth rates. It was shown that this difference is more pronounced at lower initial supersaturations and higher ammonium concentrations was beneficial to improve the growth at low supersaturation. However, in the case of $\text{Mg}^{2+} = 0.89$ (Mg:P = 0.2) the growth was limited by low magnesium concentration. The lower ion activities and complexation of struvite constituent ion reduces the crystal growth rate and the final size of the crystals.

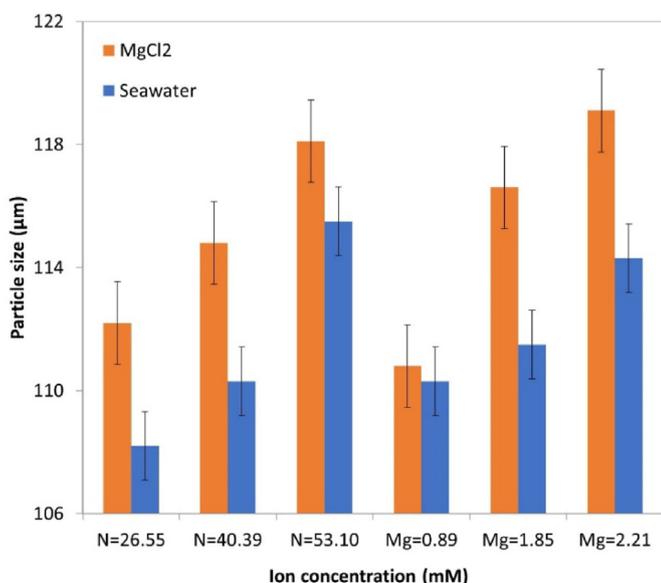


Fig. 6. The median size of particles after 60 min growth experiments (Seed median size = 106.2 μm).

4. Conclusion

The crystal growth and kinetic experiments for struvite crystallization under different experimental conditions showed the potential of seawater as an alternative magnesium source. The simultaneous precipitation of calcium phosphate, under the experimental conditions in this study, was not a major obstacle for struvite crystallization using seawater. The insignificant precipitation of calcium phosphate in unseeded experiments was further diminished in the presence of struvite seeds. The slower crystal growth kinetics with seawater was mainly due to extra ions added to the reactor which resulted in reduction of ion activities and available supersaturation for crystal growth. However, it was shown that at higher Mg:P and N:P molar ratios the struvite growth kinetics is comparable for both seawater and MgCl_2 . Among the supersaturation regulators, pH has the most dominant effect on crystal growth kinetics, where the magnesium consumption rate at pH = 7.5 was increased by 32 and 45% at pH = 7.7 and 7.9, respectively. Further, high N:P molar ratio enhanced the struvite crystal growth by seawater as the magnesium consumption rate at N:P = 12 was 20% and 40% higher than N:P = 9 and N:P = 6, respectively. The results showed that for the reject water composition used in this study, the molar ratio of N:P > 6 improves the crystal growth kinetics while the growth kinetics would be limited at a molar ratio of Mg:P < 0.2. The result of this study can be used for the design of a struvite crystallizer by using seawater. Further, the presented results for the low supersaturation window of struvite crystal growth are useful for the optimization of reactor volume and hydraulic retention time which further affects the operation costs.

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Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Sina Shaddel: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Tonje Grini:** Data curation, Investigation, Writing - review & editing. **Jens-Petter Andreassen:** Supervision, Methodology, Writing - review & editing. **Stein W. Østerhus:** Funding acquisition, Supervision, Writing - review & editing. **Seniz Ucar:** Conceptualization, Methodology, Validation, Writing - review & editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126968>.

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