



Struvite crystallization under a marine/brackish aquaculture condition



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HIGHLIGHTS

- K_{sp}^0 ($10^{-13.06}$) and ΔH_f^0 (25.7 kJ mol^{-1}) of struvite under the saline condition were obtained.
- Natural presence of Mg^{2+} and release of NH_4^+ led to low PO_4^{3-} in the digester.
- Minimal solubility of struvite under marine/brackish conditions was at pH around 10.
- Average crystal size of struvite under the conditions decreased with pH.
- High NH_4^+ enhanced formation of ammonia precipitates, e.g. struvite and dittmarite.

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ABSTRACT

The results in this study show that struvite was formed in the digester at pH 7.7 due to the magnesium naturally present and the released ammonia and phosphate, resulting in low phosphate concentration in the digester. Apparently the digester already provided proper conditions for struvite formation. Under the brackish condition, the estimated thermodynamic solubility product and enthalpy change of struvite formation were $10^{-13.06}$ and 25.7 kJ mol^{-1} , respectively. The average crystal size under marine/brackish condition decreased with pH, but increased with temperature. X-ray diffraction measurements indicate struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) and dittmarite ($\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$) were predominant phosphorus species produced in filtrates of the digester. However, struvite and newberyite ($\text{HMgPO}_4 \cdot 3\text{H}_2\text{O}$) were the predominant species precipitated from synthetic brackish waters after dosing MgCl_2 . It is pronounced that (waste)water characteristics played also an important role on the nature of phosphate precipitates. Under high NH_4^+ condition, phosphorus precipitates containing ammonia were dominant, compared to other amorphous phosphates.

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1. Introduction

Nowadays phosphorus ending up in waste streams such as effluents from recirculation aquaculture systems (RAS) is a concern because the emission of phosphorus causes eutrophication of local water bodies. Meanwhile, steady supply of P fertilizer is essential for sustainable agricultural production to feed the soaring population (Cordell et al., 2009). In recent years there is an increasing concern about the exhaustion of exploitable phosphorus reserves (Vaccari, 2009; Xu et al., 2015), leading to a decline in phosphate rock production in some countries and finally resulting in the soaring price of phosphate rock. Due to the aforementioned issues, there is an increasing attention to investigation of struvite ($\text{NH}_4\text{-MgPO}_4 \cdot 6\text{H}_2\text{O}$) precipitation and thereby recovery of phosphorus from various types of P rich waste streams, such as urine and

rejected water from digesters (He et al., 2016; Lahav et al., 2013; Liu et al., 2013; O'Neal and Boyer, 2013; Ronteltap et al., 2007, 2010). However, to date no report on struvite crystallization/precipitation under an aquaculture brackish condition is available yet, although there is a potential to recover P from P-rich sludge from aquaculture recirculation systems.

Most studies on struvite crystallization/precipitation are carried out under low ionic strength conditions. Several studies on struvite precipitation under high ionic strength are available (Bhuiyan et al., 2007; Crutchik and Garrido, 2011; Crutchik et al., 2013; Liu et al., 2013; O'Neal and Boyer, 2013; Ronteltap et al., 2007, 2010). The ionic strength influences activity coefficients of ions, particularly the multivalent ions, such as Mg^{2+} and PO_4^{3-} , which may further affect the thermodynamic parameters of struvite formation, such as the thermodynamic solubility product and the enthalpy of struvite formation. Theoretically, under high ionic strength conditions, struvite solubility increases due to the decreased activity coefficients of Mg^{2+} , NH_4^+ and PO_4^{3-} . However,

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limited literature on struvite behavior under high ionic strength conditions, i.e. marine/brackish conditions, is available, and thus further investigation on struvite formation under the high salinity condition is needed.

In marine/brackish RAS, spontaneous struvite formation could occur, due to the naturally present Mg in the marine/brackish culturing water, and ammonia and phosphate released from degradation of fish faeces and/or fish feed (Zhang et al., 2013, 2016). Therefore, uncontrolled struvite scaling might become a problem for the piping system of marine/brackish RAS. Moreover, when anaerobic digestion for sludge stabilization is applied, the production of a P- and N- rich stream in and from the digestate will further enhance struvite precipitation. Furthermore, the digestate from a digester with controlled struvite precipitation in treating the salty sludge could further serve as fertilizer for salty plants. Therefore, a better understanding of struvite precipitation under marine/brackish aquaculture conditions is conducive to avoiding struvite scaling and to better unveiling struvite precipitation in the anaerobic digestion process treating saline (waste)waters.

It is commonly regarded that pH and supersaturation have major impacts on struvite precipitation (Hanhoun et al., 2011). In addition, temperature as well affects struvite solubility and the enthalpy change of struvite formation (Bhuiyan et al., 2007; Hanhoun et al., 2011). Thus, the effects of pH, supersaturation, and temperature on struvite precipitation under marine/brackish aquaculture conditions are of great interest to be investigated.

This study aims to understand struvite precipitation in digestates from an anaerobic digester treating the salty sludge from a marine/brackish RAS. Thus, in order to simplify the analyses in the batch tests, artificial mimicked supernatants of digestate were employed, and precipitation of the precipitates, such as calcium phosphate, calcium carbonate, and magnesium carbonate, was not considered. In this study, first the thermodynamic parameters, i.e. solubility product and the reaction enthalpy change of struvite precipitation under marine/brackish aquaculture conditions, were estimated based on experimental results from artificial marine/brackish water and filtrate of digestate from an anaerobic digester treating sludge from a brackish RAS. Experimental results were compared with values reported in literature. In addition, pH adjustments of the digestate from the digester were carried out to investigate phosphate solubilization and precipitation. More-

over, the effects of pH and temperature on particle size distribution (PSD) of the formed precipitates in artificial brackish water were investigated. The PSD of struvite formed in the synthetic brackish water was compared with the PSD of struvite formed in the actual filtrate. The latter elucidates the impact of the water matrix on struvite formation under the marine/brackish conditions.

2. Material and method

2.1. Reagent, stock solution and digestate

The artificial brackish water for tests of struvite precipitation (No. 1–13 and 18–21) was prepared as listed in Table 1. All the used chemicals purchased from Sigma (The Netherlands) were analytical grade. The digestate was collected from a lab-scale anaerobic digester (4 L) fed with sludge from a brackish aquaculture recirculation system.

2.2. Experimental set-up for struvite precipitation tests and pH adjustment of digestate

Tests of struvite precipitation were carried out in 1 L beakers with a jar test apparatus (VELP-JLT6). 500 mL of the synthetic marine/brackish solution (Table 1) or filtrate of the digestate from an anaerobic digester treating sludge from a brackish RAS, supplemented with varying amounts of MgCl₂ stock solution, were mixed in the beaker. During the test, the beaker was covered with a piece of parafilm to minimize NH₃ volatilization. Preliminary struvite precipitation tests were carried out to assess the dynamics of ammonia and reactive phosphorus concentrations. The results (Fig. 1) show that the equilibria of ammonia and reactive phosphorus were reached within 75 min. Thus, in the study, 75 min were allowed for each test to ensure that equilibrium was reached. Solutions were stirred with paddles at 300 rpm over 75 min. At the end of the experiments, samples were taken to analyze the particle size distribution. Then, a 10 mL sample was filtered with membrane filters (0.45 μm, Whatman) and afterward stored in a fridge at 4 °C for later ion analyses.

Digestate with a pH of 7.7 from the lab-scale anaerobic digester treating sludge from a brackish RAS was collected. pH adjustments of the digestate using 10 M HCl and 12.5 M NaOH solutions were

Table 1
Initial values of the tests of artificial brackish waters and the filtrates.

Test No.	Temperature (°C)	Ionic strength (M)	[NH ₄] (mM)	[P _{ortho}] (mM)	Mg/P initial	K (mM)	Na (mM)
1	25	0.50	243	16	0.12	5.12	198
2	25	0.59	286	20	0.41	5.12	210
3	25	0.67	357	19	0.58	5.12	214
4	25	0.53	257	14	0.78	5.12	192
5	25	0.44	179	12	0.91	5.12	196
6	25	0.43	179	10	1.09	5.12	180
7	25	0.41	179	8	1.37	5.12	174
8	25	0.38	150	6	1.82	5.12	175
9	25	0.37	143	5	2.19	5.12	172
10	4	0.43	179	10	1.09	5.12	180
11	32	0.43	179	10	1.09	5.12	180
12	46	0.43	179	10	1.09	5.12	180
13	56	0.43	179	10	1.09	5.12	180
14	25	–	226	12	1.00	19.2	280
15	25	–	230	23	0.50	18.9	262
16	25	–	220	5	1.44	19.2	250
17	25	–	227	6	2.19	18.9	245
18	25	0.43	179	10	1.09	5.12	180
19	25	0.43	179	10	1.09	5.12	180
20	25	0.43	179	10	1.09	5.12	180
21	25	0.43	179	10	1.09	5.12	180

Note: –, not available; No. 1 to 13 were synthetic brackish waters; No. 14 to 17 were filtrate that was harvested from the digestate of the digester using a membrane filter with a pore size of 0.45 μm (Whatman, Germany). Assays No. 18 to No. 21 were the tests for different pH values using the same recipe with No. 6.

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