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Feasibility of phosphate precipitation from digested anaerobic sludge in a continuous aerated reactor

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ABSTRACT

This study investigates the effectiveness of a complete stirred and aerated reactor for deliberate phosphate precipitation as struvite from anaerobic sludge in a domestic wastewater treatment plant and, to achieve the optimum operational conditions in order to reduce the potential formation of struvite downstream of the digester and decrease the phosphate (P) and nitrogen (N) load on the treatment plant. The reactor was fed with anaerobic sludge and operated at different hydraulic retention times (HRT) and aeration rates. Theoretical calculations indicated that a minimum pH of 7.5 would be necessary to attain struvite precipitation to its potential. To reach this pH value, a minimum HRT of 1.0 h with aeration flow rate of 46.7 m^3 air/h/m^3 reactor was necessary. Struvite precipitation kinetics were observed to be much faster than other minerals that can precipitate and a decrease in HRT promotes a precipitate richer in struvite. An increase in the HRT to 2.0 h, for the same aeration rate led to a higher phosphate precipitation with calcium. However, for all HRT and air flows studied, the precipitate obtained can be considered to be poor in struvite (maximum 0.72 mmol/l) and it was responsible for around only 4 and 0.5% decrease in the phosphate and ammonia load on the plant, respectively.

Keywords: Aeration rate; Anaerobic sludge; Hydraulic retention time; pH; Struvite

1. Introduction

Traditional phosphate (P) removal processes from domestic wastewater are based on phosphorus fixation in activated sludge either by a biological biological nutrient removal or chemical (precipitation by metal salts) method. These processes are efficient to reduce the P concentration in wastewater effluents to less than 1 mg L^{-1} [1], but they lead to the accumulation of phosphorus in secondary sludge, an increase in the sludge volume, and contribute by reaction with magnesium and ammonium ions to the precipitation of magnesium ammonium phosphate hexahydrate, more commonly known as struvite ($MgNH_4PO_4 \cdot 6H_2O$). Struvite is known to precipitate and clog pipes and pumps, causing operational difficulties and extra expenses in wastewater treatment plants (WWTP). Therefore, struvite is recognized as a potential hazard at WWTP.

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However, struvite can be recovered from anaerobic digester supernatant through crystallization, if controlled precipitation is applied [2–8]. Recovery of struvite has been reported to reduce sludge volumes under specific conditions by up to 49% when compared to chemical phosphorus removal [9] and to reduce the phosphorus and ammonia/ammonium load of sidestream and sludge liquors recirculation to the head of WWTP (the potential amount of P and N that can be removed amounts approximately to be between 15 and 20% of the total load on the treatment plant).

Struvite formation and precipitation is controlled by degree of supersaturation determined by pH, temperature, and the presence of other ions in solution such as calcium and; can only occur when the product of the active concentrations (activities) of magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO_4^{3-}) ions exceed the solubility product (often denoted as Ksp) for struvite (Eq. (1)).

$$K_{sp} = \left[Mg^{2+}\right]\left[NH_4^+\right]\left[PO_4^{3-}\right] \tag{1}$$

Different solubility product values of struvite were reported in the literature; however, most commonly reported values equal approximately to $pK_{sp} = 13.6$. Moreover, the concentrations of both NH_4^+ and PO_4^{3-} are pH dependent in accordance to Eq. (2) [7] and Eq. (3) [8], respectively.

$$NH_4^+ = \frac{TAN \times [H^+]}{k_N \times [H^+]} \tag{2}$$

$$PO_4^{-3} = \frac{PTk_{P1}k_{P2}k_{P3}}{k_{P1}k_{P2}k_{P3} + k_{P1}k_{P2}[H^+] + k_{P1}[H^+]^2 + [H^+]^3} \tag{3}$$

where k_N is the dissociation constant for ammonia/ammonium (5.57×10^{-10}); k_{P1} for orthophosphoric acid (H_3PO_4)/dihydrogen phosphate ($H_2PO_4{}^-$) (7.25×10^{-3}); k_{P2} for dihydrogen phosphate/hydrogen phosphate ($HPO_4{}^{-2}$) (6.31×10^{-8}); k_{P3} for hydrogen phosphate/phosphate (4.80×10^{-13}); TAN is the total ammonia/ammonium nitrogen concentration and P_T is the total phosphate concentration. NH_4^+ is the dominant species out of TAN at pH values lower than ~pH 9.25 and PO_4^{3-} is the dominant species out of P_T only at pH values higher than ~pH 12.5. In conclusion, an optimum pH value must exist in order to keep both NH_4^+ and PO_4^{3-} at high concentrations to attain struvite precipitation. Too low pH values will reduce PO_4^{3-} fraction and on the other hand, too high pH values will reduce NH_4^+ concentrations. The optimal pH range for struvite precipitation is reported to be between pH 8.0 and 10.7 [10]. Typically, this range of pH is assessed at wastewater treatment plants downstream of the sludge anaerobic digester, where pH is increased from ~pH 7.0 due to CO_2 stripping to the atmosphere.

Many studies on phosphate recover in laboratory and full-scale wastewater treatment plants are available to date [3–8,10–16]. However, almost all studies concentrate on struvite removal from the belt press filtrate of anaerobic digester, the effect of phosphorus concentration, molar ratio of Mg: P, impurities in the solution, crystal retention time in the reactor, pH, temperature, and kinetics factors. Limited studies reported on the effect of hydraulic retention times (HRT) on struvite formation in the anaerobic sludge. Marti et al. [17] predicted phosphorus precipitation in an anaerobic digestion pilot plant using experimental data and mass balance analysis. The results showed a significant phosphorus precipitation as struvite and a low precipitation of calcium phosphates.

The objective of this work was to define the best reactor operation conditions to attain deliberate phosphate precipitation, in order to reduce the precipitation potential (PP) of struvite downstream of the digester, relieve the ammonia and P flux on the WWTP. The following study will be carried out at a laboratory-scale continuous completely mixed reactor fed with the mixed liquor from an anaerobic digester operated at the Karmiel (Israel) WWTP at different HRT and aeration rates.

The scope of the present study was limited to the precipitation of struvite (and other phosphate containing minerals) from the sludge of the anaerobic digester before final disposal. The primary aim was to reduce the struvite PP close to zero, or even negative, before releasing the anaerobic sludge to the dewatering step (either belt press or centrifuge) in order to prevent struvite precipitation and potential clogging of pump/pipes.

2. Material and methods

A pilot scale completely stirred tank reactor (CSTR) with a working volume of 32.1 L, followed by a 5.7-L settling compartment was built to study the feasibility of struvite precipitation at the domestic wastewater treatment plant located at Karmiel, Israel (Fig. 1). The reactor was fed continuously with anaerobic sludge from a 500-L container.

Results of previous study conducted with belt press supernatant at different HRTs and air flows [2] and to avoid the short circuit due to shorter HRTs in

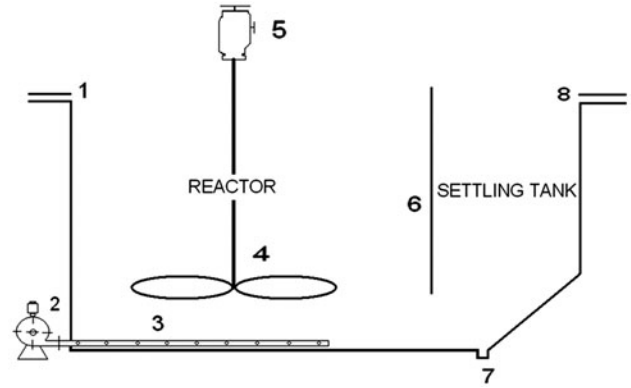

Fig. 1. The 32.1 l CSTR followed by a 5.7-L settling tank.
Notes: (1) inflow; (2) air blower; (3) air diffuser; (4) stirrer; (5) stirrer engine; (6) separation wall; (7) struvite collector; (8) outflow.

full-scale reactor, initially the CSTR was operated at 0.5-h HRT. The CSTR was operated at three different HRTs, viz. 0.5-h HRT at air flow rates of 24.3, 37.4, and 46.7 m^3 air/h/m^3 reactor and; at 1.0 and 2.0-h HRT at constant air flow rate of 46.7 m^3 air/h/m^3 reactor. The fine air bubbling was responsible for supersaturated CO_2 stripping, resulting in increase in the pH.

Chemical analysis was carried out according to standard methods for the examination of water and wastewater. The reactor influent and effluent were monitored regularly for alkalinity, pH, EC, temperature, magnesium, calcium, TAN, and P_T. Magnesium and calcium concentrations were measured in the liquid phase using ECP. TAN and P_T were measured in the liquid phase using a colorimetric analysis.

3. Results and discussion

The concentrations of the relevant components of the anaerobic sludge of WWTP Karmiel were analyzed and appear in Table 1. The concentration of magnesium, calcium, TAN, and P_T were high and in accordance were high, typical for Israeli WWTP and does not follow the disposal standards of Israel.

While the question whether struvite will precipitate or not can be predicted by comparing magnesium, ammonium, and phosphate concentrations to the solubility product (Eq. (1)), the amount of precipitated struvite cannot be calculated based on the solubility product alone. The amount of precipitated struvite can be approximated based on the value of its PP. The PP model used in this research is the one developed by Loewenthal et al. [18], which is based on the solubility product for struvite (Eq. (1)), ammonium concentration as function of TAN and pH (Eq. (2)) and phosphate concentration as function of P_T and pH equations (Eq. (3)), and changes in pH based on alkalinity changes (Eq. (3)).

$$\begin{aligned}\text{Alkalinity}_{\left(H_2CO_3^*, NH_4^+, H_2PO_4^-\right)} &= 2\left[CO_3^{\,2-}\right] + [HCO_{3-}] \\ &\quad + 2\left[PO_4^{\,3-}\right] + \left[HPO_4^{2-}\right] \\ &\quad + [NH_3] + [OH^-] - [H^+] \\ &\quad - [H_3PO_4]\end{aligned} \tag{4}$$

The model inputs are the TAN, $P_{T,}$ and Mg concentration and pH and initial alkalinity. The first step is the determination of struvite precipitation or solubility (Eq. (1)). If precipitation is confirmed, a step process is used to determine the amount of struvite that should precipitate: a small amount of struvite is assumed to precipitate, reducing the concentrations of TAN, $P_{T,}$ and Mg in the liquid phase. pH is recalculated based on the new TAN and P_T concentrations (and the initial alkalinity and C_T—total carbonate species), Eq. (4). New NH_4^+ and PO_4^{3-} are recalculated based on TAN and P_T concentrations and pH, Eqs. (2) and (3). Struvite solubility is determined again (Eq. (1)) and process restarts until struvite solubility equals zero (no precipitation and no solubility).

Table 1
Average composition of the anaerobic sludge from the anaerobic digester in the Karmiel WWTP

Parameter	Units	Value (*n* = 5)
Total ammonia nitrogen	mg/l as N	510 ± 10
Phosphate	mg/l as P	514 ± 8
Magnesium (Mg^{2+})	mg/l	21 ± 2
Calcium (Ca^{2+})	mg/l	32 ± 4
pH	–	7.1–7.2
Alkalinity (ref species: H_2CO_3*)	mg/l as $CaCO_3$	1949 ± 25
TSS	mg/l	24300 ± 250
VSS	mg/l	17630 ± 185
Nitrate (NO_3^-)	mg/l as N	8 ± 2

Based on the anaerobic sludge composition, PP was calculated to be −196 mg/l (solubility). The negative value was caused by the low pH 7.1; however, as sludge is exposed to the air, pH is expected to increase and, for the same sludge composition at pH 7.8, a PP of +157 mg/l (precipitation) was calculated. Results inferred that the maximum PP for this sludge is relatively low, +190 mg/l (1.4 mmol/l), caused by the low magnesium concentration. The TAN and P_T concentrations observed in this study were higher than the one observed by Lew et al. [2] for sludge supernatant, affecting the minimum theoretical reactor pH value necessary to reach a minimum magnesium effluent concentration of 4 mg/l, pH 7.50 against the pH 8.00.

3.1. Struvite precipitation at different HRTs and air flows

The CSTR was operated for 12 h at constant 0.5-h HRT at different air flow rates (24.3, 37.4, and 46.7 m^3 air/h/m^3 reactor) and at constant air flow rate of 46.7 m^3 air/h/m^3 reactor at different HRTs (0.5, 1.0, and 2.0 h). The effluent species concentration and pH were determined at steady-state operational conditions for each air flow applied, which was achieved after four hours of operation. Changes in air flow and HRT may influence the hydraulic parameters in the reactor; however, this effect was not studied.

Results revealed an increase in the pH value from 7.1 (original anaerobic sludge pH) to 7.22, 7.33, and 7.43 at the 24.3, 37.4, and 46.7 m^3 air/h/m^3 reactor flow rates, respectively, at the constant HRT of 0.5 h (Table 2). The maximum pH reached at constant 0.5-h HRT (pH 7.43) was still lower than the theoretical pH value required to reach the magnesium concentration of 4 mg/l, pH 7.5. Hence, for this HRT, an air flow rate of 46.7 m^3 air/h/m^3 reactor was not significant to attain total struvite precipitation—a further increase in the air flow/HRT would be necessary; however, this air flow was the maximum possible in the present study. A further increase in the air flow could cause spilling of the reactor contents.

Similar trend was found in pH when HRT was increased to 1.0 and 2.0 h, pH 7.57 and pH 7.72, respectively (Table 2); indicating that struvite can precipitate to its potential at around 1.0-h HRT

The increase in the pH was caused by a more efficient CO_2 stripping since the air-to-water contact area increased. According to Lew et al. [2], higher pH values were achieved under the same reactor operation conditions. Two reasons were envisaged for these lower effluent pH values: (1) anaerobic sludge has a lower initial pH than the supernatant of dewatering system; and (2) the kinetics of CO_2 stripping from sludge are different than the supernatant of dewatering system.

The air flow rate and HRT affect both pH and Mg^{2+}, TAN, $P_{T,}$ and Ca^{2+} concentrations. The pH increases with an increase in the air flow rate and HRT, while a decrease in Mg^{2+}, TAN, $P_{T,}$ and Ca^{2+} concentrations was observed from the influent to the effluent. Results inferred that the decrease in the species concentrations was attributed to either precipitation as struvite and/or of calcium phosphate solids. However, it was found that a fraction of TAN concentration stripped off to atmosphere from the reactor. Batch experiments were carried out to investigate the relation among TAN, HRT, and air flow rate to ammonia stripping in the CSTR at a known pH. Results revealed that the TAN stripping was approximated by Eq. (5). The equation was based on a 4-hour experiment with sampling every 15 min, which resulted a high correlation (R^2), higher than 0.90.

$$\frac{\Delta NH_{3(g)}}{\Delta t} = 1.32 \times 10^{-3} \times \text{Air Flow} + 0.017 \tag{5}$$

Based on influent and effluent species concentration, species molar removals from the aqueous phase were calculated for each air flow rate, taking in

Table 2
TAN, Mg^{2+}, P_T and calcium molar removal at different air flows and HRTs and their respective effluent pH values

HRT (h)	Air flow (m^3 air/h/m^3 reactor)	Effluent pH	TAN (mmol/l)	Mg^{2+} (mmol/l)	P_T (mmol/l)(%)	Ca^{2+} (mmol/l)
0.5	24.3	7.22	0.35	0.36	0.44/23[a]	0.67
0.5	37.4	7.33	0.46	0.47	0.59/27[a]	0.90
0.5	46.7	7.43	0.61	0.63	0.82/32[a]	1.23
1.0	46.7	7.57	0.73	0.71	1.02/42[a]	1.55
2.0	46.7	7.72	0.82	0.84	1.20/45[a]	1.81

[a] phosphate percentage that precipitated as other minerals than struvite.

consideration NH_3 stripping and are shown in Table 2. An increase in the Mg^{2+}, TAN, P_T, and Ca^{2+} molar removal was observed with an increase in the air flow for the constant 0.5-h HRT. Moreover, a further increase in the species removal was observed with a further increase in the HRT to 1.0 and 2.0 h.

One mole of struvite ($MgNH_4PO_4$) contains one mole of each Mg^{2+}, ammonia, and phosphate, respectively; however, TAN can only precipitate as struvite, indicating that the TAN molar removal can be assumed to be the struvite precipitated. A similar trend of TAN and Mg^{2+} molar removal was observed at all the air flow rates and HRTs studied indicating that also Mg^{2+} was precipitating as struvite only. Moreover, since Mg^{2+} showed the lowest influent concentration, it can be assumed to be the limiting species for struvite formation in the system.

Phosphate removal concentration was always higher than ammonia and magnesium, indicating that phosphate was precipitating as other mineral besides struvite, probably with calcium. The excess phosphate precipitate (phosphate that did not precipitate as struvite) increased in a lower degree with an increase in the air flow rate and in a higher degree with an increase in the HRT. The increase can be explained by the fact that struvite precipitation kinetics are much faster than other minerals that can precipitate in a reactor fed with anaerobic sludge. Moreover, the increase in the HRT from 1.0 to 2.0 h was followed by a low increase in the excess phosphate precipitation, indicating that probably around 2.0-h HRT phosphate and calcium precipitate together to its maximum potential. Similar results were observed by Marti et al. [17].

Musvoto et al. [19] observed, based on K_{sp} values for different minerals reported in the literature, that five different minerals can be identified as the minerals most likely to precipitate in a reactor fed with anaerobic sludge and aerated: struvite ($MgNH_4PO_4$), newberyite ($MgHPO_4$), amorphous calcium phosphate ($Ca_3(PO_4)_2.xH_2O$), calcite ($CaCO_3$), and magnesite ($MgCO_3$). Based on the results (molar ratio of the different ions) obtained from the present study, Mg^{2+} precipitated only as struvite leading to no formation of magnesite and newberyite.

Excess precipitated phosphate formed amorphous calcium phosphate (at a 3:2 ratio). No calcite was formed since the ratio of excess phosphate and calcium was around 3:2 for all HRTs studied. Marti et al. [17] observed that hydroxylapatite (HAP) is thermodynamically the most stable calcium phosphate product to precipitate. However, HAP can only be formed from amorphous calcium phosphate and after a long period of time, which was not the case in this study. Huchzermeier and Tao [20] observed that calcium and alkalinity are the most probable interference on struvite precipitation. Calcium did not significantly change P removal efficiency, but decreased struvite purity because of calcium phosphate formation, especially when Ca:P ratio is greater than 0.5:1.

4. Conclusions

The CSTR could be a good alternative to attain phosphate precipitation in wastewater treatment plants to prevent potential clogging of pump/pipes downstream of anaerobic digesters. Results inferred that a minimum pH of 7.5 must be required to attain struvite precipitation to its potential based on the sludge influent composition. The required pH value could be attained at an HRT of 1.0 h with aeration flow rate of 46.7 m^3 air/h/m^3 reactor. A further increase in the HRT would lead to phosphate precipitating more as calcium phosphate than as struvite.

Magnesium was observed to be the limiting specie on struvite formation due to its low concentration, leading to a maximum sutruvite precipitation of around 0.72 mmol/l. This struvite formation can be responsible for around only 4 and 0.5% decrease in the phosphate and ammonia load on the wastewater treatment plant, respectively.

Struvite precipitation kinetics were observed to be faster than other minerals that can precipitate and a decrease in the HRT promotes a precipitate richer in struvite. However, for all HRT and air flows studied, the precipitate obtained can be considered to be poor in struvite and can hardly be reused in agriculture (a high Ca content makes it insoluble for normal agricultural use). X-ray diffraction and/or X-ray fluorescence methods would indicate the purity of precipitated.

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