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Prevention and control of struvite and calcium phosphate precipitation by chelating agents

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ABSTRACT

The problems stemming from struvite precipitation on pipe walls, valves, faucets, and propellers in the anaerobic sludge digestion processes of wastewater treatment plants have been extensively reported. In addition to the diverse sources of the struvite-forming ions (Mg^{2+}, NH_4^+, and PO_4^{3-}) present in its wastewaters, Israel has hard water with characteristic high concentrations of Ca^{2+} that causes the formation of calcium phosphate on plant equipment. This study focuses on the use of chelating agents to control struvite and calcium phosphate precipitation. The reaction conditions required to prevent the precipitation of either salt by ethylenediaminetetraacetic acid or nitrilotriacetic acid and for the selective precipitation of struvite after calcium chelation are reported. Both chelating agents promoted the chelation in solution of Ca^{2+} over that of Mg^{2+}. In contrast, for precipitated calcium phosphate and struvite, higher chelating agent concentrations were required to dissolve the former than the latter. The amounts of both chelating agents, added in proper concentrations, were sufficient to bind mainly the Ca^{2+} ions, thus preventing the precipitation of $Ca_3(PO_4)_2$ and leaving more phosphate ions available to precipitate Mg^{2+} ions as struvite. Performed properly, this process will remove Ca^{2+} and Mg^{2+} ions from the supernatant. In addition, after separation, the struvite can be collected and used as fertilizer. The potential toxicity of both chelating agents to the biomass was also studied in this work.

Keywords: Struvite; Calcium phosphate; Chelating agents; Anaerobic sludge; Wastewater

1. Introduction

The formation of struvite ($MgNH_4PO_4{\cdot}6H_2O$), a mineral created when equimolar amounts of its three ionic components precipitate during the anaerobic digestion of sludge, is a significant problem in many water treatment plants worldwide. In anaerobic sludge digestion, high levels of NH_4^+ and PO_4^{3-} ions are released from dead bacteria cells. The presence of Mg^{2+} ions in the wastewater causes struvite deposition on pipes, impellers, and other plant equipment, increasing operational costs [1–5]. On the other hand, struvite is a desired fertilizer, and if properly removed from the water being treated at these plants, in addition to its removal solving-related operational and environmental problems, it may also be of commercial benefit. In addition to Mg^{2+}, hard waters also contain

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high concentrations of calcium that causes calcium phosphate formation ($Ca_3(PO_4)_2$) [6].

Previous works studied the potential use of chelating agents such as sodium hexamethaphosphate [7], ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and acetyl acetone (ACAC) [8]. It was also reported that EDTA is more efficient in preventing the precipitation, but those results were obtained in different industrial systems and wastewater compositions [8]. The present work studies the efficiency of chemical treatment in preventing struvite and calcium phosphate precipitation in anaerobically digested supernatants using EDTA and NTA at different molar ratios to the sum of Mg^{2+} and Ca^{2+} concentrations in a pH range from 7.5 to 9.0. Chelating agent efficiency was derived from measuring both the amounts of formed precipitants and also the residual concentrations of Mg^{2+}, Ca^{2+}, NH_4^+, and PO_4^{3-}.

2. Experimental

2.1. Supernatant samples

Samples of anaerobically digested supernatants were obtained from the wastewater treatment plant (WWTP) of Beer-Sheva in southern Israel. Water was characterized using the following methods: total organic carbon analysis with a Dohrmann TOC, DC190 (Tekmar-Dohrmann, Cincinnati, OH, USA). Inorganic anion concentrations (Mg^{2+}, Ca^{2+}, NH_4^+, and PO_4^{3-}) were determined with an Ion Chromatograph (Dionex DX-500) equipped with a conductivity detector. An IonPac CS12 column with a 20-mM methanesulfonic acid mobile phase was used for alkaline earth cation determination and an IonPac AS4A-SC column with a carbonate buffer (1.7 mmol/L $NaHCO_3$ + 1.8 mmol/L Na_2CO_3) mobile phase was used to determine inorganic anions.

After the supernatants were filtered and acidified with 1 M HCl (99.9%, Merck), they were analyzed for heavy metal concentrations by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Spectro, Spectroflame) and for NH_4^+ concentration by measuring the optical density (at 636 nm) of the blue indophenol complex produced after the reaction of NH_4^+ with NaOCl. Table 1 presents a typical analysis of anaerobically digested supernatants from the WWTP in Beer-Sheva.

2.2. Synthetic sample preparation for precipitation experiments

To ensure that the laboratory experiments were carried out with a stable composition of water representing supernatants of anaerobic sludge digestion, synthetic samples were prepared. These samples were prepared by adding $CaCl_2$ (99%, Merck), $MgCl_2$ (99%, Merck), and $(NH_4)_2HPO_4$ (99.99%, Sigma) to distilled HPLC-pure water. The final Ca^{2+}, NH_4^+, and PO_4^{3-} concentrations (given in Table 1) were based on the analysis of real supernatant from the Beer-Sheva WWTP. To increase the struvite precipitation potential, the concentration of Mg^{2+} (a limiting element for the formation of struvite) was increased to 180 ppm. The synthesized supernatants were analyzed for their ion concentrations after their preparation.

2.3. Struvite and calcium phosphate preparations for dissolution experiments

Struvite was prepared by mixing $HPO_4(NH_4)_2$ and $MgCl_2$ to yield equimolar concentrations of Mg^{2+}, NH_4^+, and PO_4^{3-}. Calcium phosphate was prepared by mixing $HPO_4(NH_4)_2$ and $CaCl_2$. Both solutions were adjusted to pH 7.4 by adding 0.1 M NaOH (diluted from 99.9%, Merck) and left for 24 h for precipitation. The solids were then filtered through a 0.45-μm pore diameter filter, washed thrice with distilled HPLC-pure water and dried at room temperature for 24 h.

Table 1
Characterization of the anaerobically digested supernatants of the Beer-Sheva WWTP and of the synthetic mixtures used in the study.

Analyte	WWTP supernatant (ppm)	Synthetic mixtures (ppm)	Technique
Ca^{2+}	180	100	IC
Mg^{2+}	42	100	IC
Al	5	–	ICP-OES
Zn	4	–	ICP-OES
Fe	9	–	ICP-OES
C	63	–	TOC
PO_4^{3-}	1,050	1,050	IC
NH_4^+	600	440	Measurement of formed indophenol

2.4. Chelating agents preparation

Chelating agents solutions were prepared by dissolving Na_2EDTA (99%, Sigma), Na_2NTA (99%, Sigma), or ACAC (99.5%, Aldrich) salts into distilled HPLC-pure water and then brought to a 1 M concentration. ACAC was used only in preliminary experiments.

2.5. Chelation experiments

The effect of the chelating agents on struvite and calcium phosphate precipitation was studied by mixing 300-ml samples with each chelating agent in 500-ml jars to reach an initial molar ratio of 2(chelating agent):1(Ca^{2+}+ Mg^{2+}) and then to molar ratios of 1.5:1.0, 1.0:1.0, 0.5:1.0, and 0.0:1.0 in subsequent experiments. These ratios produced EDTA and NTA concentrations of 6, 4.5, 3.0, 1.5, and 0.0 mM/L, respectively. The solutions were then adjusted to a pH value of 7.0–9.0 (according to each experiment) with 1 M HCl or NaOH as needed and mixed for 8, 16, or 24 h at 25°C. Each system was run in duplicate and compared to blank solutions without added chelating agent. The experiments were ended by filtration through a 0.45-μm pore diameter filter and the filtrates were acidified to pH 4.0 to prevent further precipitation. The precipitants obtained were dried at 40°C to prevent crystallographic structure changes (at 60°C water molecules leave the $MgNH_4PO_46H_2O$ struvite molecule) and then weighed. The filtrates were analyzed for Ca^{2+}, Mg^{2+}, PO_4^{3-}, and NH_4^+.

2.6. Dissolution experiments

Struvite and calcium phosphate dissolution by chelating agents was done by mixing 300 mg of struvite or calcium phosphate with 300 ml distilled HPLC-pure water. In the system that tested the two precipitants together, 150 mg of each was mixed with the chelating agents. EDTA or NTA were added to each jar in increasing concentrations and the pH was set to 8.5. After mixing the jars for 8 h at 25°C, the solutions were filtered through a 0.45-μm pore diameter filter and the filtrates were acidified to pH 4.0. The precipitants were dried at 40°C and weighed, and the filtrates were analyzed for Ca^{2+}, Mg^{2+}, PO_4^{3-}, and NH_4^+. Each system was run in duplicate.

2.7. Chelating agents effect on biomass

The toxicities of EDTA and NTA were evaluated using the oxygen uptake rate (OUR) test with activated sludge biomass (Beer-Sheva WWTP) under varied conditions. Experiments were run in a 300-ml BOD bottle using an oxygen electrode and a mixer. Solutions of EDTA and NTA at various concentrations were added to pre-aerated biomass samples, with and without biodegradable organic matter (raw wastewater), taken from the activated sludge system to check-out biomass respiration changes.

3. Results and discussion

3.1. Inhibition of $Ca_3(PO_4)_2$ and struvite formation by EDTA and NTA

A preliminary test evaluated the influence of reaction time on the activity of the chelating agents when the solutions contained all the components necessary for struvite and $Ca_3(PO_4)_2$ formation. In addition to EDTA and NTA, this test evaluated ACAC and was run at three reaction times (8, 16, and 24 h). Compared to the other two chelating agents, the effect of ACAC was found to be very weak in this type of solution under the experimental conditions. Therefore, all further experiments used only EDTA and NTA. In addition, the 8 h period was also demonstrated to be sufficient time for evaluation of chelating agent effects.

Analyzing the effect of solution pH (ranging from 7.0 to 9.0) on the amounts of precipitants produced (without chelating agents) demonstrated an expected outcome (results not shown), the solubilities of both substances strongly depended on solution pH when Ca^{2+}, Mg^{2+}, NH_4^-, and PO_4^{3-} ions were present [1,2].

Evaluation of the effect of different EDTA concentrations on precipitant formation in a solution containing all the necessary struvite and $Ca_3(PO_4)_2$ components at different pH values showed that EDTA chelation of both Ca^{2+} and Mg^{2+} (i.e. decrease in precipitant amounts) increased with increased chelator concentration (Fig. 1). The higher chelation effect was observed at an EDTA: salts molar ratio range from 1.0 to 1.5. The combined effect of EDTA concentration and pH (similar to the trend observed in the preliminary experiments) was less precipitation at lower pH values, but running a real system at such low pH will result in higher residual concentrations of all the ions in the solutions being recycled back to the WWTP.

The residual concentrations of Mg^{2+} and Ca^{2+} in the treated solutions were tested with and without EDTA (Fig. 2(a) and (b)). In the absence of EDTA (molar ratio 0.0), the concentration of Ca^{2+} in solution was lower compared to that of Mg^{2+}. When EDTA was added, the concentration of Ca^{2+} left in solution, at pH 8.5 and 9.0, and at an EDTA: salts molar ratio of 1.0, was higher than that of Mg^{2+}. This indicates that Ca^{2+} precipitation was decreased to a lesser extent than was that of Mg^{2+}. Under these experimental con-

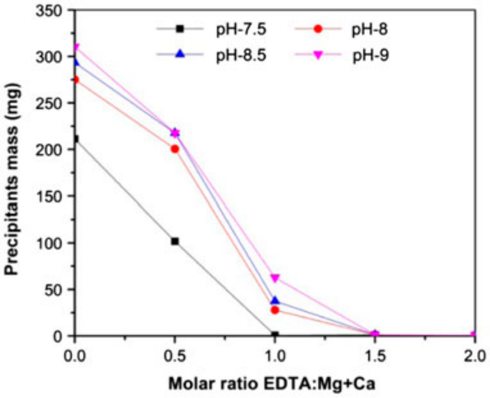

Fig. 1. Effect of EDTA on struvite and calcium phosphate precipitation.

ditions, Ca^{2+} chelation by EDTA occurred prior to Mg^{2+} chelation, regardless of the K_{sp} values of these two salts. This finding is supported by the more stable complex that Ca^{2+} vs. Mg^{2+} forms with EDTA, as expressed by the higher stability constant of the EDTA–Ca complex (10.7) compared to EDTA–Mg (8.7) [9]. These results demonstrate that the residual Ca^{2+} concentration in the treated solution was higher than the Mg^{2+} concentration. In other words, chelation by EDTA favored Mg^{2+} precipitation as struvite while Ca^{2+} remained in the solution. Higher concentrations of chelating agents will prevent the precipitation of both salts, but at some point, such conditions will begin to dissolve precipitated struvite, as shown in subsequent experiments.

The concentrations of the other components of both salts also increased in the solution when the molar ratio of EDTA added to the mother liquor was increased (Fig. 2(c) for NH_4^+ and Fig. 2(d) for PO_4^{3-}). It should be noted that the initial concentrations of these two ions were higher than those of Ca^{2+} and Mg^{2+} (see Table 1). Moreover, they were not limiting factors for the precipitation of either struvite or $Ca_3(PO_4)_2$. The optimal pH range for EDTA chelation of Ca^{2+} and Mg^{2+} is 8.0–10.0, in which range Ca^{2+} is expected to be chelated before Mg^{2+} [10]. The findings of the current work indicate that almost no acidification of the waste flux should be needed for a process based on EDTA treatment and that selective struvite precipitation could be achieved to separate it from $Ca_3(PO_4)_2$.

The effect of NTA on the amount of precipitants formed in solutions (identical to those tested with EDTA) at different pH values is shown in Fig. 3. In the absence of chelator (molar ratio 0.0), struvite and $Ca_3(PO_4)_2$ precipitation decreased at lower pH values.

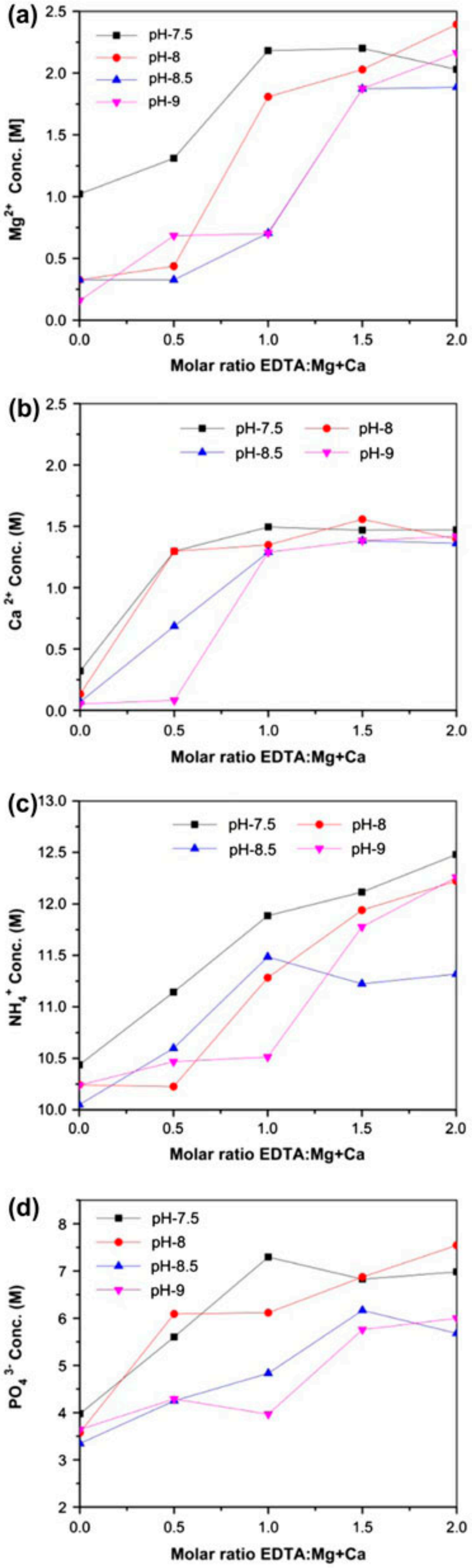

Fig. 2. Effect of EDTA and pH on concentrations of Mg^{2+} (a), Ca^{2+} (b), NH_4^+ (c), and PO_4^{3-} (d) in the treated solutions.

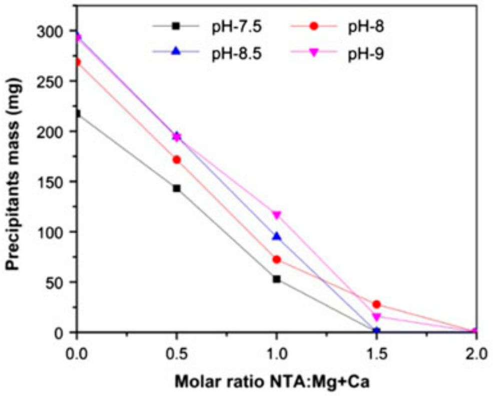

Fig. 3. Effect of NTA on struvite and calcium phosphate precipitation.

As with EDTA, the ability of NTA to prevent struvite and $Ca_3(PO_4)_2$ precipitation similarly depended on its concentration and on solution pH. The strongest chelation effect was obtained at an NTA: salts molar ratio range from 1.5 to 2.0 (instead of 1.0–1.5 as with EDTA), indicating the need for a higher NTA concentration because of the relatively weaker chelation effect of NTA. That weaker chelation effect may be attributed to the relatively less stable complexation of NTA, whose molecular structure leads to a tetradentate binding in contrast to the hexadentate binding caused by EDTA. Moreover, because it contains two water molecules, the NTA-cation complex is inherently weaker than the EDTA-cation complex, which forms a closed structure that prevents the entrance of water.

Analyses of ion component concentrations in the treated solutions revealed results for NTA similar to those of EDTA. Mg^{2+} concentration decreased relative to Ca^{2+} at an NTA: salt molar ratio of 1.0 and pH values of 8.5 and 9.0 (Fig. 4(a) and (b), respectively). Nevertheless (and emphasizing precipitant amount data in Figs. 1 and 3), the effect of NTA on the precipitation is also shown to be lower compared to that of EDTA. The concentrations of NH_4^+ and PO_4^{3-} in the treated solutions also increased with higher molar ratios of NTA (Fig. 4(c) and (d)), supporting the precipitation mass results shown in Fig. 3. The outcomes presented in this work show that under appropriate conditions, NTA is also able to achieve selective struvite precipitation, during which $Ca_3(PO_4)_2$ remains in solution. Although the concentration of NTA required to cause this effect is higher than that of EDTA, its use at higher concentrations may also be acceptable, considering its relatively low price and its good biodegradability.

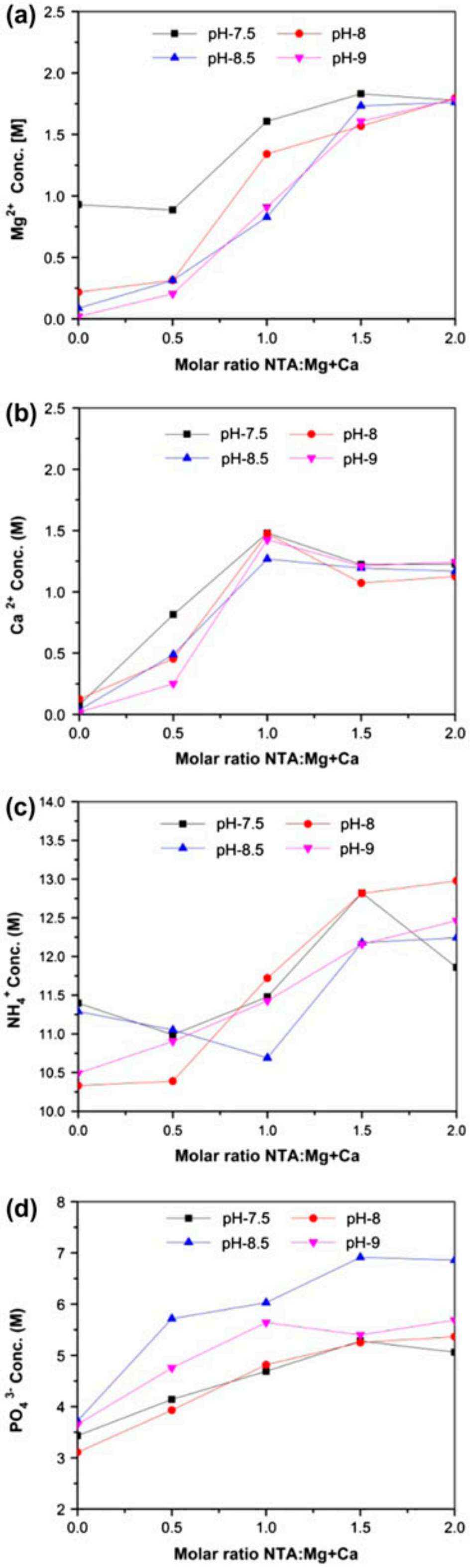

Fig. 4. Effect of NTA and pH on concentrations of Mg^{2+} (a), Ca^{2+} (b), NH_4^+ (c), and PO_4^{3-} (d) in the treated solutions.

3.2. Controlled precipitation of struvite

Both EDTA and NTA were previously shown to bind Ca^{2+} and Mg^{2+} under specific conditions of pH and chelator: cation molar ratios. Moreover, both agents chelated Ca^{2+} prior to Mg^{2+} (Fig. 2(a) and (b) for EDTA and Fig. 4(a) and (b) for NTA), as expressed by the lower chelator concentrations needed to bind Ca^{2+}. This finding may have application in the selective precipitation of struvite while preventing $Ca_3(PO_4)_2$ precipitation. Moreover, these results indicate that in addition to minimizing water treatment plant operational problems, implementation of the discussed chelation method will also produce pure precipitated struvite with potential commercial value.

Further experiments were done to identify the most suitable chelating agent concentrations and pH ranges for the selective and early binding of Ca^{2+} to find the concentration that achieves a more specific chelation. Hence, a narrower molar ratio range was chosen and chelator concentration increments were smaller. A pH of 8.5 was found to be optimal for the chelation activities of both EDTA and NTA and for the selective binding of Ca^{2+}.

Table 2 shows for the treated solution (pH 8.5) the amounts of precipitants produced when EDTA was present in a molar ratio range from 0.0 to 1.2 and the fractions (%) of all ion components. Precipitant weights decreased and the concentrations of all the ions in the solution increased with increasing EDTA concentrations. Moreover, at a molar ratio of 0.4, the differences between the concentrations of Ca^{2+} and Mg^{2+} in the solution were maximal. The relative amounts of Ca^{2+} (74.32%) and Mg^{2+} (8.83%) were at the largest ratio (8.41) achieved in this series of experiments. Concentrations in the solution of ammonium and phosphate ions remained relatively low. Higher concentrations of the chelating agent increase the binding of both cations, reducing the Ca^{2+}:Mg^{2+} ratio. Therefore, at pH 5, the optimal molar ratio of EDTA:($Ca^{2+} + Mg^{2+}$) for obtaining the purest struvite precipitation with the lowest $Ca_3(PO_4)_2$ concentration is 0.4.

Similar to EDTA, NTA addition in increments of increasing molar ratio caused a gradual decrease in precipitant amounts, raising Ca^{2+}, Mg^{2+}, NH_4^+, and PO_4^{3-} concentrations in the solutions (see Table 2). As noted before, the initial concentrations of NH_4^+ and PO_4^{3-} were higher than those of Ca^{2+} and Mg^{2+}, and therefore, they were not limiting factors for either struvite or $Ca_3(PO_4)_2$ precipitation. However, the molar ratio of NTA needed to cause the largest concentration difference between Ca^{2+} and Mg^{2+} in the supernatant was 0.6, and Ca^{2+} (72.46%) and Mg^{2+} (24.00%) ions were present at a ratio of 3.02. As before, ammonium and phosphate ions kept their concentrations in the solution relatively low, and higher concentrations of the chelator would reduce the Ca^{2+}:Mg^{2+} ratio. Therefore, the molar ratio of NTA:($Ca^{2+} + Mg^{2+}$) at pH 8.5 for obtaining the purest struvite precipitation with the lowest $Ca_3(PO_4)_2$ concentration is 0.6.

Examination of the data shows two main differences between EDTA and NTA (Table 2). First, larger NTA than EDTA concentrations were needed to achieve similar chelation action. Second, the action of EDTA produced a greater ratio between the chelation of both cations, which is due to differences between the stability constants of EDTA with Mg^{2+} and Ca^{2+} (8.7 and 10.7, respectively) and of NTA with Mg^{2+} and Ca^{2+} (5.73 and 6.42, respectively) [9].

Despite the lower Ca^{2+}:Mg^{2+} ratio achieved by NTA, it may still have application, depending on the target of the process (only to prevent plant operational problems, for example) and the purity requirements

Table 2
Chelation effect of EDTA and NTA on Mg^{2+} and Ca^{2+}expressed by the solid phase mass and by the ion fractions in the liquid-phase.

	EDTA				NTA			
Molar ratio	Precipitant mass [mg]	% Mg^{2+}	% Ca^{2+}	Ca^{2+}/Mg^{2+}	Precipitant mass [mg]	% Mg^{2+}	% Ca^{2+}	Ca^{2+}/Mg^{2+}
0.4	361	8.83	74.32	8.41	270	22.89	47.78	2.09
0.5	266	17.20	79.48	4.62	222	23.50	70.25	2.09
0.6	194	35.18	82.33	2.34	166	24.00	72.46	3.02
0.7	186	44.16	88.67	2.01	164	35.66	77.34	2.17
0.8	111	61.38	91.09	1.48	152	43.01	78.48	1.82
0.9	65	91.62	98.97	1.0	122	59.79	80.90	1.35
1.0	22	95.66	101.21	1.0	110	70.63	90.09	1.28
1.2	0.0	98.95	99.40	1.0	108	68.18	94.00	1.38

for the struvite (i.e. whether it will also be used in agriculture).

3.3. Dissolution of struvite and calcium phosphate with EDTA and NTA

The control of struvite and $Ca_3(PO_4)_2$ precipitation in water treatment plants can be based on the routine addition of chelating agents in specific plant sections to prevent the formation of precipitants on especially sensitive parts of the process equipment. On the other hand, the dissolution of already precipitated struvite and $Ca_3(PO_4)_2$ that typically causes plant operational problems may be another feasible treatment for the required equipment remediation, especially in sections with limited access. Therefore, the remediation option of using both chelating agents to dissolve the two precipitated salts was also investigated.

3.3.1. Dissolution of $Ca_3(PO_4)_2$

Experiments of $Ca_3(PO_4)_2$ dissolution with EDTA and NTA at different concentrations showed that both chelating agents decreased the amount of $Ca_3(PO_4)_2$ precipitant in a dose-dependent manner, consequently causing increased concentrations of Ca^{2+} and PO_4^{3-} ions in the liquid phase (Fig. 5(a) and (b), respectively). Although more than 80% of the precipitant was already dissolved at an EDTA:Ca^{2+} molar ratio of 1.0, a molar ratio of 2.0 was required to achieve complete dissolution.

Complete dissolution of $Ca_3(PO_4)_2$ was not achieved by NTA at the same concentrations and experimental conditions as for EDTA, but at a molar ratio from 1.5 to 2.0, about 60% of the precipitant mass was dissolved. Chemical dissolution of the precipitants depends on the surface of the solids, their crystal structures and solvent concentration [11,12]. Moreover, this process also depends on time and may require several hours [8]. In the presence of NTA, ions in the supernatant were only moderately increased relative to the more pronounced effect of EDTA (Fig. 5(a) and (b), respectively).

3.3.2. Dissolution of struvite

Both chelating agents at a molar ratio of 1.0 caused the complete dissolution of struvite, showing almost identical behavior under the same experimental conditions. The decrease in precipitant masses was proportional to the increase of the ion concentrations in the liquid phase. These results indicate that struvite dissolution occurs with faster kinetics compared to that of $Ca_3(PO_4)_2$ (Fig. 6).

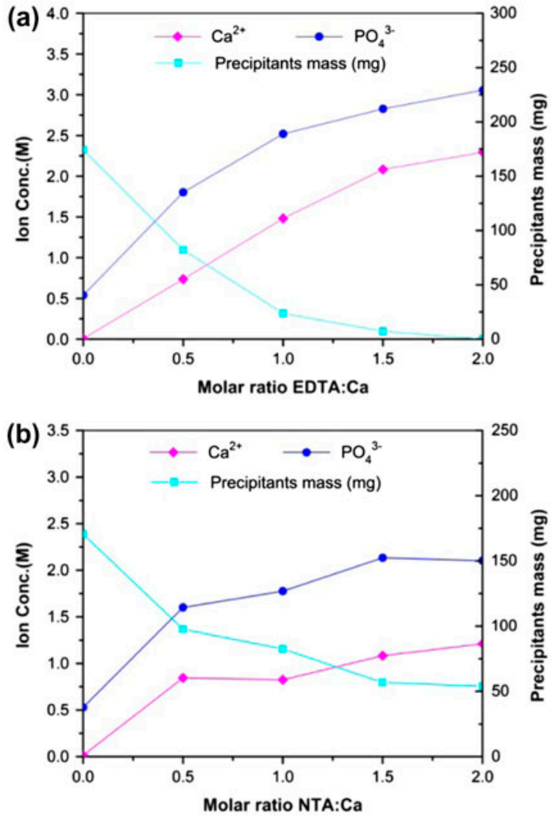

Fig. 5. Dissolution of calcium phosphate. Effect of different EDTA (a) and NTA (b) doses, at pH 8.5, on precipitant masses and on ion concentrations in the treated solutions.

3.3.3. Dissolution of a $Ca_3(PO_4)_2$ and struvite mixture

The dissolution by EDTA of both precipitated salts together was almost identical to its effects for both of them separately. About 75% of the precipitants were dissolved at a molar ratio from 0.5 to 1.0 while the total mass was dissolved at a molar ratio of 2.0. This effect also correlated with the increase in ion concentrations in the liquid phase (Fig. 7(a)).

The moderate decrease in precipitant masses and the lower concentrations of Ca^{2+} in the liquid phase when using NTA (Fig. 7(b)) demonstrate that it is less able to dissolve the precipitated salts once they formed.

3.4. Chelator effect on activated sludge biomass

The use of chelating agents in controlling and preventing the formation of struvite may influence the biological activity of the wastewater treatment process. It is therefore necessary to evaluate whether the supernatant streams recycled back into the process negatively affect its efficiency. To that end, screening tests to study the potential toxicity of EDTA and NTA were

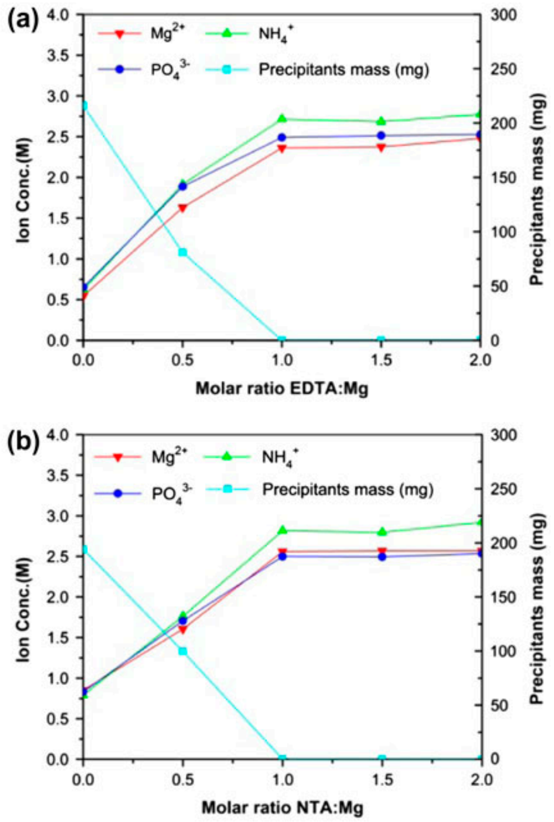

Fig. 6. Dissolution of struvite. Effect of different EDTA (a) and NTA (b) doses, at pH 8.5, on precipitant masses and on ion concentrations in the treated solutions.

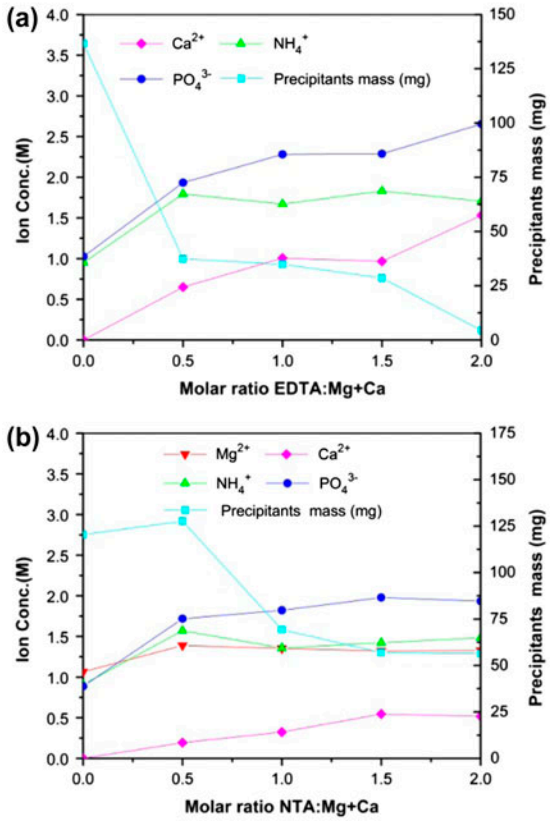

Fig. 7. Dissolution of struvite and calcium phosphate. Effect of different EDTA (a) and NTA (b) doses, at pH 8.5, on precipitant masses and on ion concentrations in the treated solutions.

carried out on activated sludge biomass from the Beer-Sheva WWTP using the OUR test.

3.5. Toxicity test

The effects of EDTA and NTA on the OUR in different combinations of raw wastewater (highly biodegradable organic matter) and chelators were measured using higher fractions of EDTA and NTA in the experiments than are expected in a real system (Table 3). Comparing the values of endogenous respiration (experiment 1) and organics respiration (experiment 2) to the values obtained in the presence of the two chemicals (experiments 3–6) reveals that the potential toxicities of the chemicals are expected to be negligible.

Table 3
Effect of EDTA and NTA on OUR of activated sludge biomass.

Experiment	Biomass added	Raw wastewater volume (ml)	Chelating agent	Volume of 1 M chelator added (ml)	OUR (mg O_2/L/h)
1	+	–	–	–	23
2	+	30	–	–	121
3	+	30	NTA	3	107
4	+	30	EDTA	3	105
5	+	30	NTA	1	106
6	+	30	EDTA	1	101

4. Conclusions

This work investigated a method to control and prevent precipitation of struvite and calcium phosphate by the controlled use of the chelating agents EDTA and NTA. The efficiency of these materials was studied at various pH values and concentrations. EDTA was found to be more effective in the prevention of precipitation than NTA. The optimal molar ratio of EDTA to Mg^{2+} and Ca^{2+} ions was 1.0–1.5, whereas the ratio for NTA was in the range of 1.5–2.0. Although the NTA dose requires higher amount than that of EDTA to prevent precipitation, its potential use may still be considered because of its lower cost and better biodegradability. The addition of either of the chelating agents in the proper amount will preferably affect the calcium phosphate. In industrial water systems, where precipitation of insoluble salts is a detrimental phenomenon, such a treatment may be a feasible solution.

It was demonstrated that a selective and more stable chelation of Ca^{2+} by both chelating agents to prevent mainly $Ca_3(PO_4)_2$ precipitation has several advantages. First, it may enable the controlled precipitation of a highly pure struvite that can later be recycled as a beneficial product. Second, it will favor the higher consumptions of phosphate and nitrogen for struvite formation and reduce their subsequent concentrations in the supernatant that is recycled back to the main process. The release of phosphorus from calcium phosphate by calcium chelation, leading to the increase of struvite formation, was also recently reported [13]. Unlike most other compounds, calcium phosphate is increasingly insoluble at higher temperatures [14], a fact that may be used to separate calcium phosphate from the supernatant after struvite precipitation. The preference for Ca^{2+} chelation allowed us to determine the optimal pH and chelator concentrations required for this selective process. Previous works reported different chelation efficiencies, but those experiments were run in systems with chemical compositions and under experimental conditions that differed from the current work. The high calcium and magnesium concentrations of the hard waters in Israel present an additional challenge, due to the precipitation of calcium phosphate in addition to struvite.

Struvite and calcium phosphate were shown to be successfully dissolved by both chelating agents. However, higher chelator concentrations were required to dissolve calcium phosphate. The different behavior of the two precipitants (struvite precipitates on pipe system walls whereas calcium phosphate remains in the stream) is an advantage for precipitant dissolution by chelating agents because they will dissolve struvite first and then calcium phosphate, but the latter will occur only after a prolonged period of time. Hence the required amounts of chelating agents become smaller.

The potential benefit of nutrient recovery by engineering struvite precipitation was recently studied in two water resource recovery facilities in Florida and reported as effective [15]. OUR tests performed with a typical activated sludge biomass to screen potential toxicity showed that the expected effect of the added doses of chelating agents may be negligible.

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