



KTH Land and Water
Resources Engineering

STRUVITE PRECIPITATION AND BIOLOGICAL DISSOLUTION

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SUMMARY

The struvite precipitation is used in wastewater treatment to reduce the phosphates concentration from the effluent in order to fulfill the local regulation. Struvite or magnesium ammonium phosphate (MAP) has a pH dependent low solubility ($pK_s=10.26$). Thus, if the conditions are favorable almost all the phosphates can be eliminated.

There are several parameters that influence the precipitation besides the pH: temperature, ionic strength of the solution, and magnesium ammonium and phosphate's molar ratios. If an efficient removal is required these parameters should be optimized. If our goal is to reduce the phosphates the pH optimum value is close to 9.2 for MAP precipitation. On the other hand, if our aim is to remove the ammonium a higher pH will reduce even more its concentration. Among the biograpy different authors mention different pH values. Therefore, an in situ optimization of the reactor may be needed. The optimum loading of the reactor is supposed to be close to $Mg:NH_4:PO_4=1.7:1:1.1$ M but again there are differences among the studies. The loading stoichiometry also depends on the main goal of the reaction.

The struvite precipitation is proved to be an efficient process but it is sometimes not applied due to the relative high costs of the raw chemicals that are needed compared to the conventional methods for phosphate removal, usually NaOH is used to control the pH and some magnesium salt to supply the needed magnesium concentration. A biological dissolution of struvite would help reducing this cost and making the process more feasible. In addition, the struvite can be sold directly as a proved slow release fertilizer. Moreover, the metals and heavy metals content of the produced struvite are lower than the content of the ground itself so there is no hazard due to chemical contamination.

SWEDISH SUMMARY

Utfällning av struvit används vid avloppsvattenrening för att minska fosfatkoncentrationen i utgående avloppsvatten för att uppfylla lokala utsläppsvillkor. Struvit eller magnesiumammoniumfosfat (MAP) har en pH-beroende löslighetsprodukt ($pK_s = 10,26$). Om betingelserna är gynnsamma kan därför nästan all fosfat avlägsnas.

Flera parametrar inverkar på utfällningen förutom pH-värde: Temperatur, jonstyrka hos lösningen och molförhållandet ammonium och fosfat. Om ett effektivt avlägsnande skall uppnås behöver dessa parametrar optimeras. Om målet är att minska fosfathalten är ett optimalt pH-värde ca 9,2 för utfällningen av MAP. Om däremot målet är att minska ammoniumhalten är ett högre pH värde gynnsamt. Olika studier redovisade i litteraturen ger varierande värden för optimalt pH-värde. Därför erfordras en optimering av fällningsreaktorn in situ. Den optimala tillförseln till reaktorn är kring $Mg:NH_4:PO_4 = 1,7:1:1,1$ baserat på mol men återigen finns det skillnader mellan olika studier. Lämplig stökiometri beror även på huvudsakligt mål med reaktionen.

Struvitfällning har visat sig vara en effektiv process men har ibland inte tillämpats på grund av relativt höga kemikaliekostnader jämfört med de för traditionell teknik för utfällning av fosfor. För MAP utfällning används ofta NaOH för kontroll av pH-värdet och tillskott av magnesiumsalt. En biologisk upplösning av struvit kan därför underlätta att minska denna kostnad och göra processen mer konkurrenskraftig.

Struvit kan dessutom säljas direkt som ett långsamt upplösbart gödselmedel. Därtill är vanligtvis innehållet av tungmetaller för den producerade struviten lägre än innehållet i marken så därför är risken liten för kontaminering av marken.

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TABLE OF CONTENT

| | |
|---|------------|
| <i>Summary</i> | <i>iii</i> |
| <i>Swedish summary</i> | <i>iii</i> |
| <i>Aknoledgement</i> | <i>v</i> |
| <i>Table of Content</i> | <i>vii</i> |
| <i>Abstract</i> | <i>1</i> |
| 1. Introduction | 1 |
| 1.1. Current different technologies for map precipitation | 3 |
| 1.2. Different line disposals incorporating the struvite process | 5 |
| 1.2.1. Possible designs for plant-lines with struvite dissolution process | 6 |
| 1.2.2. Economy of the process..... | 7 |
| 1.3. Struvite solution by bacteria activity | 8 |
| 1.3.1. Anammox | 8 |
| 1.3.2. Nitrification bacteria | 8 |
| 1.3.3. Possible sub products of the dissolved solution | 9 |
| 1.3.4. Struvite's characteristics and benefits as a fertilizer | 9 |
| 1.4. Parameters for MAP precipitation | 10 |
| 1.4.1. Solubility | 11 |
| 1.4.2. Kinetics of precipitation | 12 |
| 1.4.3. Precipitation mechanism | 13 |
| 1.4.4. Reactive molar ratios | 14 |
| 1.4.5. pH influence | 17 |
| 1.5. Phosphates | 20 |
| 1.5.1. Eutrophication | 21 |
| 1.5.2. Current treatments for phosphate removal | 21 |
| 1.5.3. Chemical release of phosphorus from sewage sludge | 23 |
| 1.5.4. Chemical treatments..... | 24 |
| 1.5.5. Parameters | 24 |
| 1.6. Ammonium | 24 |
| 1.7. preventing undesired MAP | 25 |
| 2. Methods | 25 |
| 2.1. Nitrification bacteria | 25 |
| 2.1.1. Struvite dissolution by nitrification bacteria. | 25 |
| 2.1.2. Ammonium removal with the final leachate from the struvite dissolution reactor. | 25 |
| 2.1.3. Influence of dissolved oxygen in struvite biological dissolution by nitrification bacteria. | 26 |
| 2.1.4. Maximum struvite that can be admitted by the reactor of nitrification bacteria | 26 |
| 2.2. Anammox bacteria | 26 |
| 3. Results | 27 |
| 3.1. Nitrification bacteria | 27 |
| 3.1.1. Struvite dissolution by nitrification bacteria: | 27 |
| 3.1.2. Ammonium removal with the final leachate from the struvite dissolution reactor. | 29 |
| 3.1.3. Influence of dissolved oxygen in struvite biological dissolution by nitrification bacteria. | 29 |
| 3.1.4. Maximum struvite that can be admitted by the reactor of nitrification bacteria | 30 |
| 3.2. Anammox bacteria | 31 |
| 3.2.1. Strvite dissolution by anammox bacteria..... | 31 |
| 4. Discussion and conclusion | 32 |
| 4.1. Nitrification bacteria | 32 |
| 4.1.1. Struvite dissolution by nitrification bacteria. | 32 |
| 4.1.2. Ammonium removal with the final leachate from the struvite dissolution reactor. | 32 |

| | | |
|-------------|---|-----------|
| 4.1.3. | Influence of dissolved oxygen in struvite biological dissolution by nitrification bacteria. | 33 |
| 4.1.4. | Maximum struvite that can be admitted by the reactor of nitrification bacteria | 33 |
| 4.2. | Anammox bacteria..... | 33 |
| 4.2.1. | Struvite dissolution by anammox bacteria | 33 |
| 5. | <i>Conclusion.....</i> | 34 |
| 6. | <i>references.....</i> | 35 |

ABSTRACT

Struvite is a salt that is formed out of Mg^{2+} , NH_4^+ and PO_4^{3-} and it crystallizes in form of $MgNH_4PO_4 \cdot 6H_2O$. Struvite's (magnesium ammonium phosphate or MAP) precipitation has recently been regarded as an interesting technique to remove phosphate and ammonium from waste water. The high elimination rates and the possibility of recycling the struvite as a direct slow release fertilizer make this process feasible and appealing. However, the costs due to the raw chemicals needed are drawbacks that leave aside the application of the process in some facilities. The MAP biological dissolution makes possible a recycling of magnesium and phosphate, a fact that reduces the process's costs and will help making it even more feasible and environmentally friend. This thesis goes also through the parameters, reactions and different techniques that optimize the struvite precipitation process.

Key words: phosphate removal; struvite precipitation; struvite biological dissolution; ammonium removal.

1. INTRODUCTION

Struvite is a well know salt that is formed within pipes of different processes where magnesium ammonium and phosphate appear under weak alkaline conditions (Uludag-Demirer, 2005). Sometimes, the amount is so big that it even drives at the collapse of the flow and the shutdown of the line process.

Struvite or MAP (magnesium ammonium phosphate) is a white crystalline substance consisting of magnesium, ammonium and phosphate in equimolecular ratios; with the formula: $MgNH_4PO_4 \cdot 6H_2O$.

The low solution rate of this salt is used in waste water treatment technology to reduce the phosphate and also ammonium concentrations in order to fulfill the local law requirements and avoid eutrophication problems.

- The $pK_s=13.26$ (Regy et al, 2002) for MAP at pH close to 9.2

In these pictures (Fig.1, 2) the struvite crystals were formed with MgO as the magnesium source (zoom x 176) (Mrowiec et al., 2003). Usually, the structure is ortoromboedric but needle like structure has also been observed. Needle like structure is harder to precipitate as the ortoromboedric structure is more compact. If there is an upwards flow as in the crystallization reactors the needle like structure can be blown away easier.

Both, ammonium and phosphate are contaminants for water. Therefore, the struvite crystallization can be designed differently depending on our goals and the type of water to treat. Struvite precipitation can be used as a complementary treatment for many industrial effluents with a high ammonium concentration. Although struvite based anaerobic pre-treatment is very effective for ammonium removal usually for high concentrated leachates a secondary treatment is needed to satisfy law regulation before the discharge. Finally, struvite precipitation is usually used to reduce the phosphates concentration down to the lowest levels but it also reduces the ammonium concentration. Depending on the kind of effluent needs to be treated a more specific removal, focused either on phosphates or ammonium can be applied.

Struvite or MAP's formation reaction is:



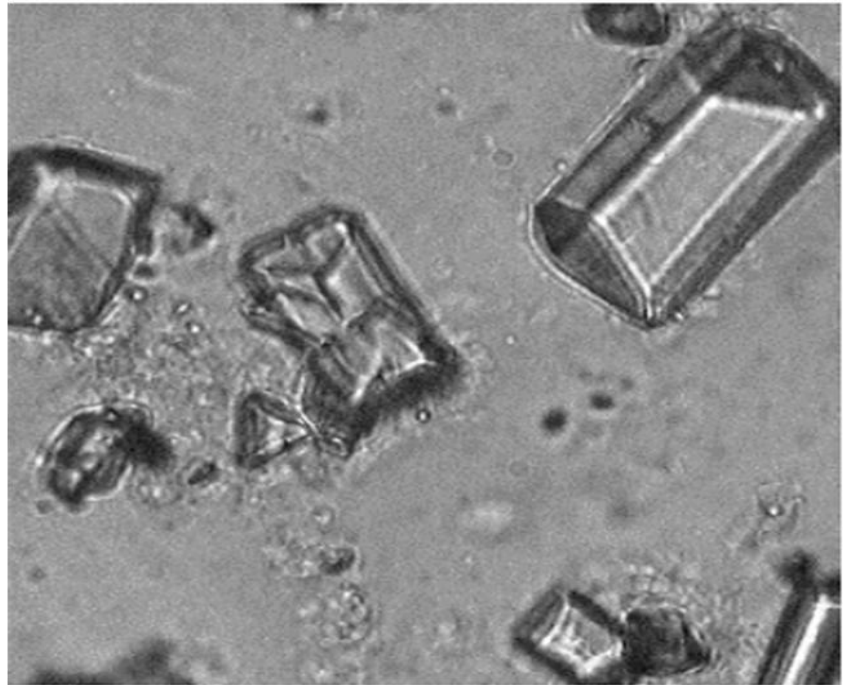


Fig. 1. Usually the struvite crystallizes in an ortoromboedric structure (Pastor, 2006).

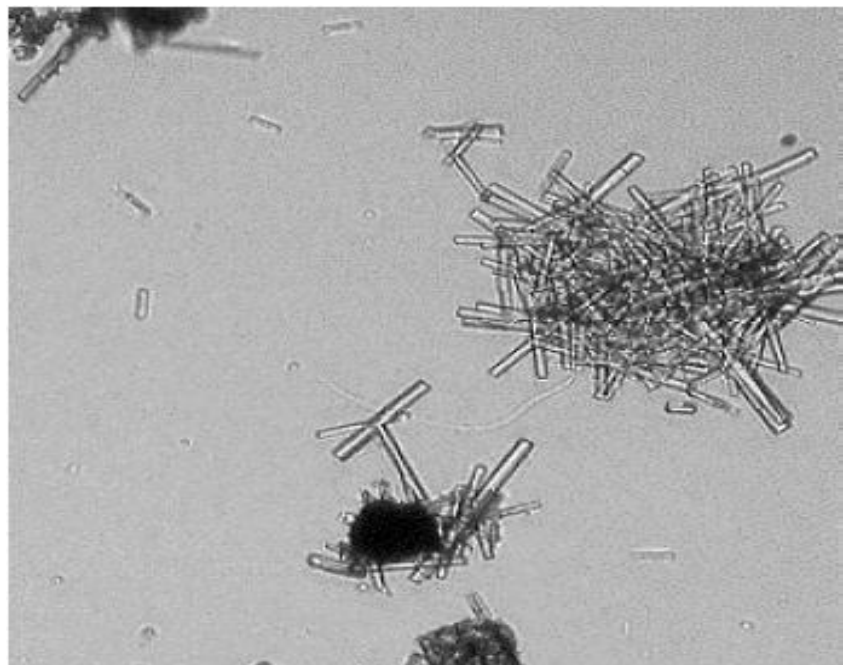


Fig. 2. Needle like structure of precipitated struvite (zoom x 176) (Suschka, 2001).

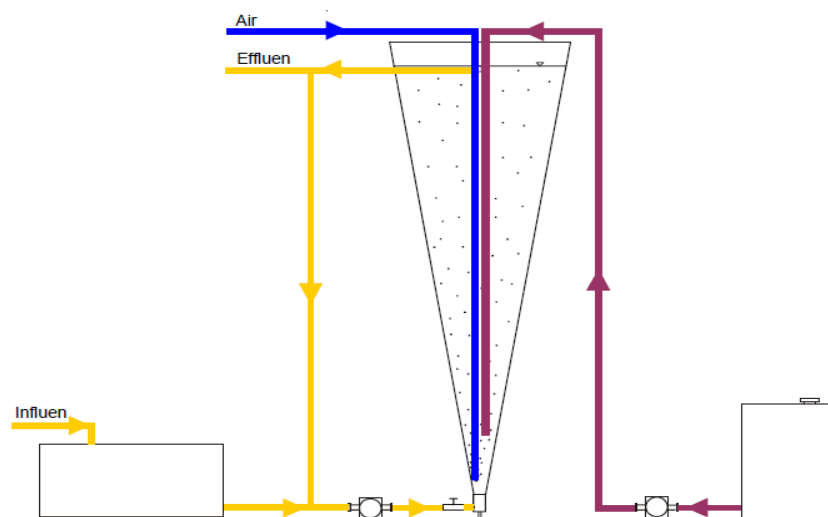


Fig. 3. Struvite precipitation reactor model.

1.1. Current different technologies for map precipitation

The most used reactors in the industry for struvite precipitation are the fluidized bulk reactors and stirred tanks, being the last ones the easiest to set and control (Ueno and Fujii, 2001; Battistoni et al, 2002). On the other hand, the fluidized bulks are harder to control because they need a continuous flow to keep the bulk fluidized. There are a couple of processes developed by companies such as the Crystalactor developed by DHV, Netherlands and the Phosnix process developed by Unitika Ltd in Japan.

Different examples of each type of reactor can be found in the biography. In (Fig. 3) sewage from digested sludge and the chemicals were supplied from the bottom with an upward flow. The cone shape allows a lower flow in the top of the cone where the nucleation can happen. In the bottom, a higher turbulence ensures a better mixing of the inflows. Moreover, the recirculation of the reactors outflow must be carefully established not to break the clusters of crystal that are already formed. The model that was studied during the experiments had a volume of 100 L. The air stripping was the only system used to mix the sample. Also anaerobic experiments were carried out. (Mrowiec et al., 2003).

Figure 4 is an example of a fluidized bed reactor used at the University of British Columbia, Canada. The variation in the reactor diameter with the increase of height keeps certain turbulence along the reactor. Thus, it ensures the mixing in the different stages. As the flow is going upwards the flow speed slows down due to diameter increase. This way, as the former example the particle size in each stage was also indirectly controlled. The particles were kept in the reactor until harvest.

There are different reactors developed by the industry to precipitate struvite. However, they are mainly based in the previous basic fluidized bulk models:

- The Phosnix (Unitika Ltd.) Process (Fig. 5) is based on this kind of reactors as well. NaOH and MgCl are added to set the needed parameters. An upwards blown air mixes the reactor helping to keep it homogeneous. The product is discharged from the reactor when it has arrived certain concentration and particle size. Afterwards, it is dewatered

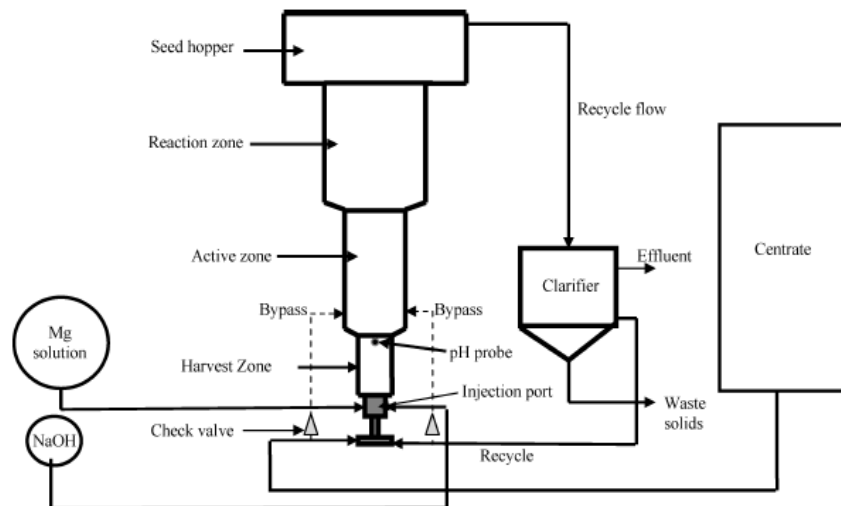


Fig. 4. Phosphorus recovery in secondary wastewater treatment plant (Fattah, 2008).

with a residual moisture of 10% (Morse et al, 1998). Phosphate removal efficiencies are reported in the range of 88-97%

- The Rem Nut Process (Liberti et al, 2001):

Rem Nut process is a system based on two selective ion exchangers, for ammonium and phosphate. (Fig. 6) The inflow to the system comes from the already treated outflow from the activated sludge treatment, after the settler. This method is based on the ion exchange by selective membranes. The effluent's ammonium and phosphate concentration will be reduced and a concentrated outflow will be sent to the struvite precipitation reactor.

In this study (Liberti et al, 2001) different schemes were proposed, one of them with struvite reaction (Fig.7). Also, iron phosphate was regarded as another option for phosphorus removal.

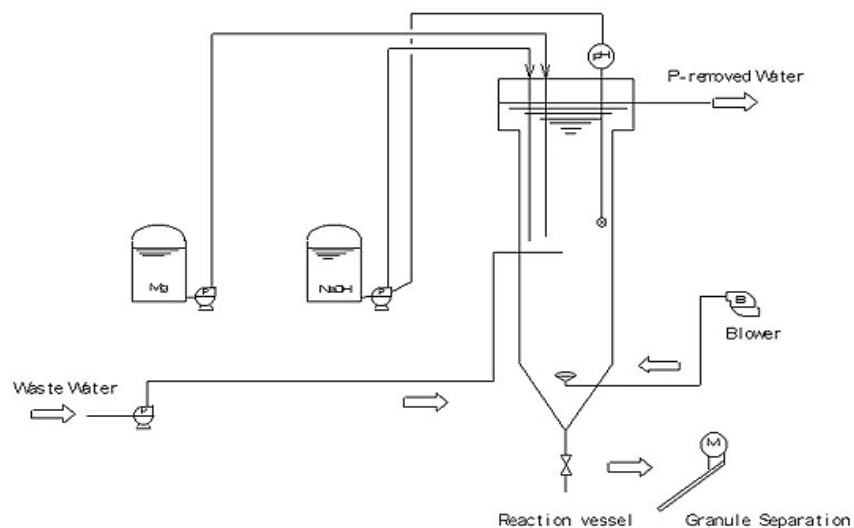


Fig. 5. Phosnix process.

Rem Nut process is an expensive process compared to normal precipitation and also has the inconvenience of finding high effective materials for ion exchange.

1.2. Different line designs incorporating the struvite process

Regarding the line designs to integrate a struvite precipitation process two main groups can be distinguished: a side stream location for the struvite reactor of the biological treatment and a complementary treatment afterwards in the polishing step. The side stream disposals take sludge form the anaerobic stage from the activated sludge treatment. In this step the phosphates are release by the cells in order to use the energy store in the polyphosphates to assimilate the volatile fat acids (VFA) and grow. Thus, a high phosphates concentration can be expected. The tertiary-treatment based processes treat the effluent from the secondary settler and precipitate the still remaining phosphates as struvite.

The phosphate concentration is higher in the anaerobic tanks than in the outflow but the flow that is pumped into the crystallization reactor is smaller because it's a side stream (Fig. 8) than the flow treated if the reactor is placed after the biological treatment. On the other hand, the phosphate concentration in the side-stream is higher than the concentration found after the biological treatment. There exist a compromise between the concentration and the flow. Thus, the decision for the line design may depend on the reactor and the parameters that are chosen. Anyhow, regarding the literature (Woods et al, 1994) the global removal is similar.

Another difference among different treatments is the reaction itself. Nowadays, there are different techniques that can be applied. Among these ones the chemical and the biological treatments can be distinguished. In the chemical process (Fig. 9) a chemical reaction is the main force that separates the phosphates from the influent. The phosphate molecules are bound to another compound, in this case to Fe^{3+} and then usually are precipitated as different insoluble salts. However, in a biological process the phosphates are assimilated by the biomass and hence eliminated from the main flow. Then, the active sludge is separated in a clarifier.

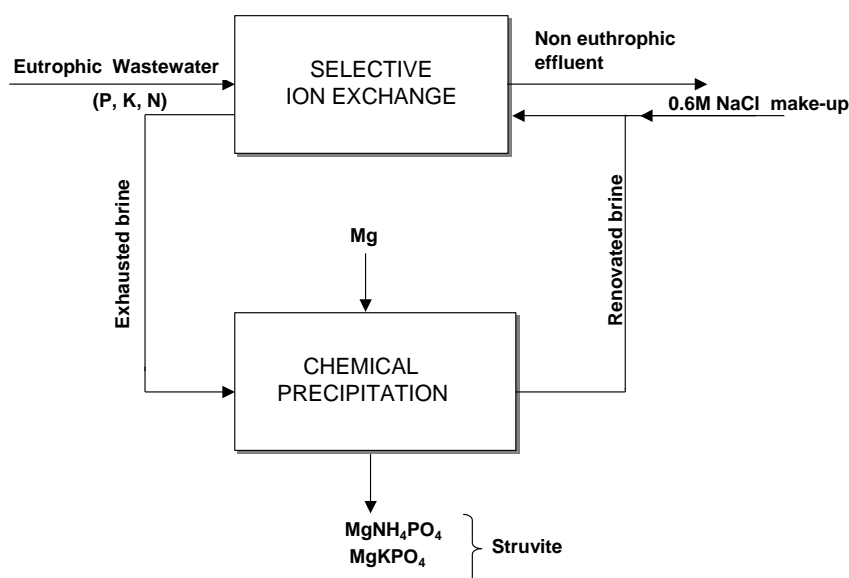


Fig. 6. Rem Nut process.

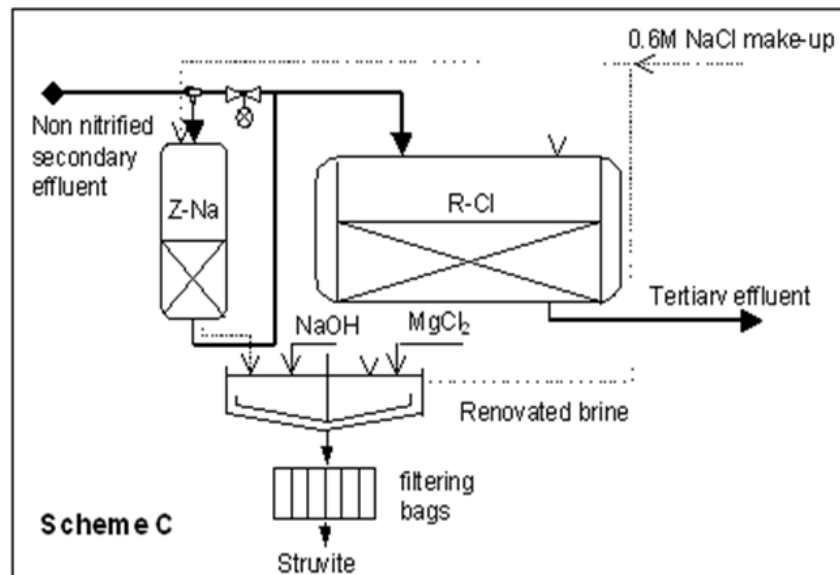


Fig. 7. Scheme including the struvite precipitation.

1.2.1. Possible designs for plant-lines with struvite dissolution process

Struvite can be sold as a fertilizer directly so it may be a revenue or at least reduce the operational costs as well as removal of the still present ammonium and phosphates. To produce as much fertilizer as possible as much available phosphates have to be recycled because is the limiting compound in the waste water. Reuse of the phosphate rich leachate of the dewatered sludge for this aim is an effective idea (Fig. 10). Another interesting option would be to try a possible biological dissolution.

This way, the magnesium and the phosphates could be recycled and the struvite's precipitation reaction could be used also to reduce effectively not only the phosphates but also the ammonium. This could be possible because dissolving the struvite higher concentrations of ammonium and magnesium could be reached. Actually, investigating this possibility was one of basic aims of the experiments that were conducted

For the dissolution the more feasible process was thought to be the biological dissolution. Besides, to dissolve the MAP chemically pH round 3 was needed and this was supposed to be more expensive than a possible biological process. Regarding the basic equipment a biological reactor and a separation device: settler, membranes etc. are needed and need to be integrated in the process.

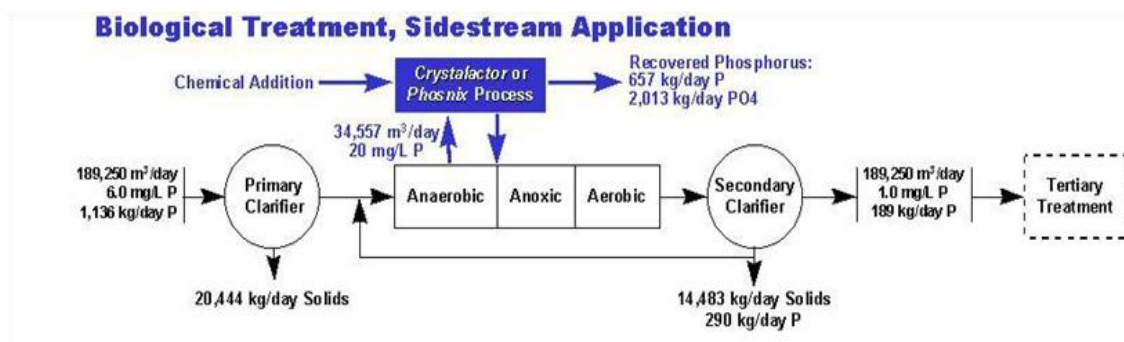


Fig. 8. Side streams schemes.

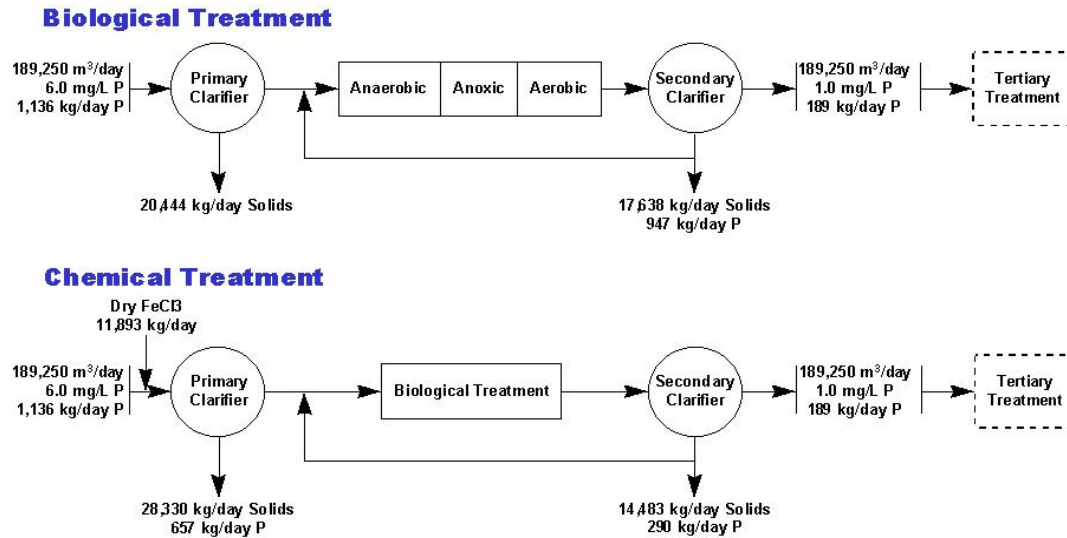


Fig. 9. Biological and chemical treatments.

1.2.2. Economy of the process

Even though the struvite fertilizing properties are proved to be effective there is a cost of raw chemicals that are needed, basically MgO or another source of magnesium and NaOH. However, the biological dissolution of struvite gives a chance to reduce this cost and makes the process more feasible. The profit of selling the fertilizer should be taken in account to make these processes economically possible.

‘While the use of struvite for the removal and recovery of phosphates and ammonium is technically feasible for the treatment of high strength wastewater, it is not adopted economically since the high cost of magnesium compounds’ (Giesen, 1999).

For facilities close to the coast, the option of taking the magnesium directly from the seawater is an interesting idea which needs further studies. The concentration of the magnesium in the sea, even if is not a really salty sea, is much higher than the concentration needed for the WWT concentration. Hence, the volume of seawater needed is not big compared to the volume treated.

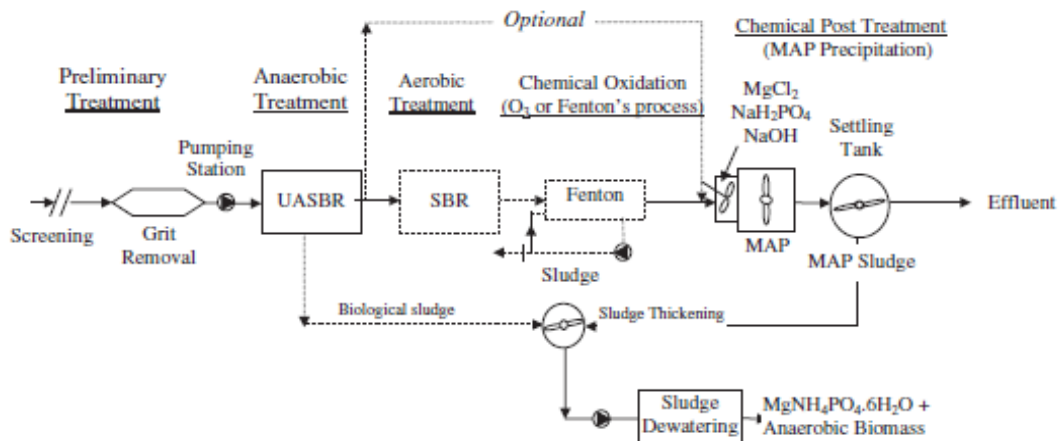


Fig. 10. Possible design of a plant with the MAP precipitation.

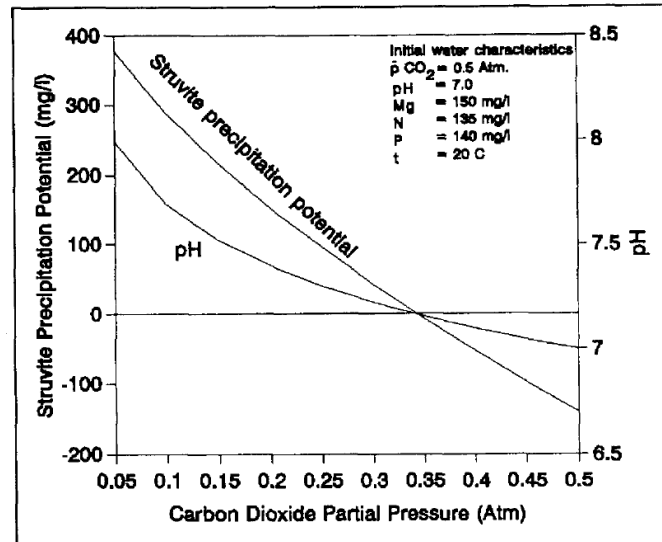


Fig.11.
Struvite precipitation potential in equilibrium with CO₂ (Loewenthal, 1994).

1.3. Struvite solution by bacteria activity

The possibility of achieving a high MAP dissolution is an attractive idea that would allow a recycling of magnesium and the phosphates. This fact will allow a more versatile process. Therefore, it could not only reach higher concentrations of magnesium and phosphate to reuse it, in fact, will be able to eliminate higher concentrations of contaminants but also will reduce the cost of the process.

A biological reactor was used to try to dissolve the struvite. For separating the sludge a settler by gravity was used.

The use of two bacteria was studied: anammox and nitrification bacteria.

1.3.1. *Anammox*

The anammox bacteria are a new technology for ammonium removal. They consume less oxygen than the denitrification bacteria. Moreover, they oxidize the ammonium to nitrite but instead of oxidizing it to nitrate as the common process the nitrite is directly reduce to nitrogen. This can happen because the nitrites react with some amines that are also formed in the process avoiding the nitrate formation and thus saving some oxygen. Even it's a promising technology the anammox bacteria are stuck in rings. Therefore, the contact between these bacteria and the struvite may not be as good as it should. As the contact is not that good as free bacteria in a water solution the efficiency of the dissolution a priori may be less comparing with a better liquid-solid contact.

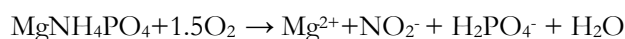
1.3.2. *Nitrification bacteria*

High rates of ammonium removal can be achieved by air stripping. The ammonium removal by air stripping of landfill leachate was studied (Cheung et al, 1997) and their results show that for an influent ammonium concentration between 309 and 368mg/L a 65-74% was removed just by air stripping with a retention time of one day. This fact may indicate that an air stripping reactor would help the struvite solution due to the lack of ammonium in the reactor forcing the struvite to get dissolved. Furthermore, this air stripping can lead to a continuum ammonium release from the struvite that can be taken up by the nitrification bacteria.

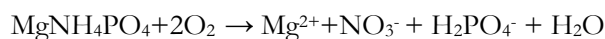
The bacteria may also be able to oxidize the ammonium directly from the struvite resulting in a combination of both processes to dilute the struvite.

In this case ammonium is the energy source for bacteria and the hydrogen ions produced facilitates the dissolution. Reactions based on nitrification, nitrification and deammonification can be written (Hassanzadeh, 2005).

Nitrification:



Nitrification:



Deammonification:



1.3.3. *Possible products of the dissolved solution*

Dissolved phosphate can be reused or stored and be sold to the phosphate industry to produce fertilizers or detergents. However, the ammonium that was dissolved and not assimilated by the bacteria can't be stored because it's oxidized into nitrite within one day.

With some treatment to purify the effluent and the addition of potassium this solution could be sold as a liquid fertilizer for hydroponic grows.

There is always the option of precipitating these ions in the form of struvite changing the environment and adding some ammonium and optionally magnesium to help the reaction to happen, regarding the ions concentration optimum values. Anyway, if our aim is to produce struvite it would be more efficient if we precipitate it directly just to save the possible ammonium that might be needed.

Other salts similar to the struvite in structure are observed as $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ and are always present in a minor proportion

1.3.4. *Struvite's characteristics and benefits as a fertilizer*

MAP is a well proved slow released fertilizer that is already being used in some countries as Japan, where it is used among others, in rice crops. A priori, the kind of inflow of the waste water plant could seem to be determinant to ensure that no heavy metal ions still remain in the struvite after the reaction, within the structure or just dragged with the MAP salt. It can be thought that if the inflow carries industrial waste water with heavy metals then this process might not be convenient due to the presence of these metals in the fertilizer. Despite this warning, the struvite content of metal ions is lower than in the minerals that are usually used as a phosphate source (Pastor, 2006). Furthermore, benefits for the product sales can be read in (Ueno and Fujii, 2001).

As mentioned before, struvite is a slow release fertilizer that can last long in the ground. A fact that proves the quality of the MAP is that currently the struvite produced in Japan by the Unitika Ltd. is being sold to fertilizer producing companies in the United States of America (Pastor, 2006).

For a complete fertilizer the NPK, nitrogen phosphorus and potassium, concentrations should be adjusted with a potassium salt or substitute the ammonium with the potassium ion: the salt $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ can also be formed. This adjustment issue will raise the final cost of the fertilizer. Some crops need high amounts of magnesium as the sugar beet (Pastor, 2006).

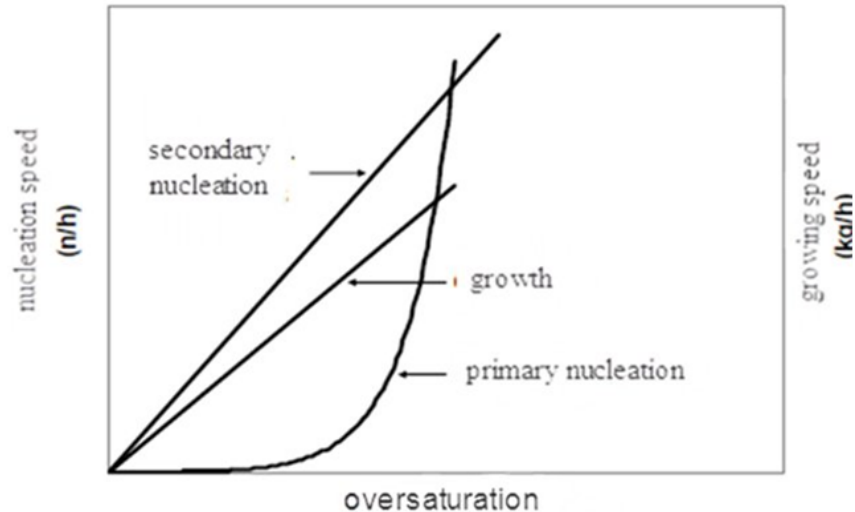


Fig. 12. Nucleation and growing speed.

It was shown in an experiment conducted by El Diwani, et al, (2006) that the use of struvite as a fertilizer rises the NPK uptake of the plant. This study was made on bean plants. It is shown that the nutrients uptake for struvite based fertilizer was even higher than the recommended dose during the whole experiment. Dry and wet weight was measured and the struvite based fertilizer plants were heavier than the plants without struvite dosage.

Another study that shows the effectiveness of struvite as a slow release fertilizer that can be used directly for agricultural purposes for both foliar and soil applications (Mrowiec et al., 2003).

These kind of slow releasing fertilizers are appropriate for long term harvests that don't need a constant care as woody landscape, parks of the municipality or golf courses. With this kind of fertilizer a constant amount of nitrogen and phosphate is ensured to be supplied to the crops.

Struvite could be used as a solid substrate in where the roots grow for example in hydroponic system crops. The slow struvite release in a moisture environment or in a gel could favor the ions release. If it is successfully integrated in gels it may be applied to crops landed in semi desert areas. This way, a constant care could be avoided.

MgKPO₄ might be used as well combined with other compounds to complete the fertilizer's requirements. This salt is usually present during struvite precipitation.

1.4. Parameters for MAP precipitation.

Struvite precipitation is controlled by pH, oversaturation, temperature and impurities as calcium. (Regy et al, 2002).

For the crystal precipitation of MAP two different stages can be differentiated, the nucleation and the growth of the core. The purity and uniformity of the crystals are an interesting fact if we want to sell it afterwards.

The design of such a reactor is a complicated issue that needs more than the equilibrium data. From the equilibrium data the total crystal mass that will theoretically be formed can be obtained but the shape and amount of crystals cannot be exactly predicted (Fig 11 and 12). Therefore, small plant experiments should be done before designing a large scale

reactor and take the kinetic data of the reaction into account. The crystal nucleus population and their growth also need to be studied.

Different molar ratios between Ca and Mg and their interferences have been studied. It seems that depending on which is the major ion in the solution calcium phosphate, hydroxyapatite or struvite are formed.

1.4.1. **Solubility**

The struvite solubility product can be defined as:

$$K_{ps} = \frac{a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}}{\gamma_{Mg^{2+}} [Mg^{2+}] \gamma_{NH_4^+} [NH_4^+] \gamma_{PO_4^{3-}} [PO_4^{3-}]}$$

K_{ps} for pH 9.5 is $10^{-13.26}$ (Regy et al., 2002). This data was taken from a solution Mg: NH₄: PO₄³⁻ = 0.1:0.1:0.01 mmol/L

Oversaturation of the solution

The oversaturation is the driving force of the appearance of the crystal cores and their growth. For the crystallization this force is the difference between the chemical potential in the solution and in the solid, where in equilibrium state both potentials will be the same. (Pastor 2006)

The chemical potential for the solid phase is represented as the chemical potential of the solution in equilibrium:

$$\mu_e = \mu_0 + RT \ln(a_e) \rightarrow \text{for several ions } \mu_e = x\mu_{Ae} + y\mu_{Be}$$

Thus,

$$\mu_e = x\mu_{A0} + RT \ln(a_{Ae}) + y\mu_{B0} + RT \ln(a_{Be})$$

μ_e is the chemical potential in equilibrium

μ_0 is the standard chemical potential for each ion

a_e is the ionic activity in the solution in equilibrium for each ion.

T in kelvin

For a oversaturated solution of one ion:

$$\mu = \mu_0 + RT \ln(a) \rightarrow \text{for several ions } \mu = x\mu_A + y\mu_B$$

Thus,

$$\mu = x\mu_{A0} + RT \ln(a_A) + y\mu_{B0} + RT \ln(a_B)$$

a is the activity of the solution of each ion

The driving force for precipitation:

$$\Delta \mu = x(\mu_A - \mu_{Ae}) + y(\mu_B - \mu_{Be}) + z(\mu_C - \mu_{Ce}) = RT \ln \left(\frac{a_A^x a_B^y a_C^z}{a_{Ae}^x a_{Be}^y a_{Ce}^z} \right) = RT \ln \left(\frac{a_A^x a_B^y a_C^z}{K_{ps}} \right) = S$$

S, oversaturation

If the oversaturation is not too high the approximation of $\gamma_e \approx \gamma \approx 1$ can be applied. Thus, the $\Delta \mu$ result in:

$$\Delta \mu = RT \ln \left(\frac{a_A^x a_B^y a_C^z}{a_{Ae}^x a_{Be}^y a_{Ce}^z} \right) \approx RT \ln \left(\frac{C_A^x C_B^y C_C^z}{C_{Ae}^x C_{Be}^y C_{Ce}^z} \right) \approx RT \ln \left(\frac{C_A^x C_B^y C_C^z}{K_{ps}} \right)$$

There is already software available to calculate the struvite precipitation potential in the market for plants and to simulate different operational simulations.

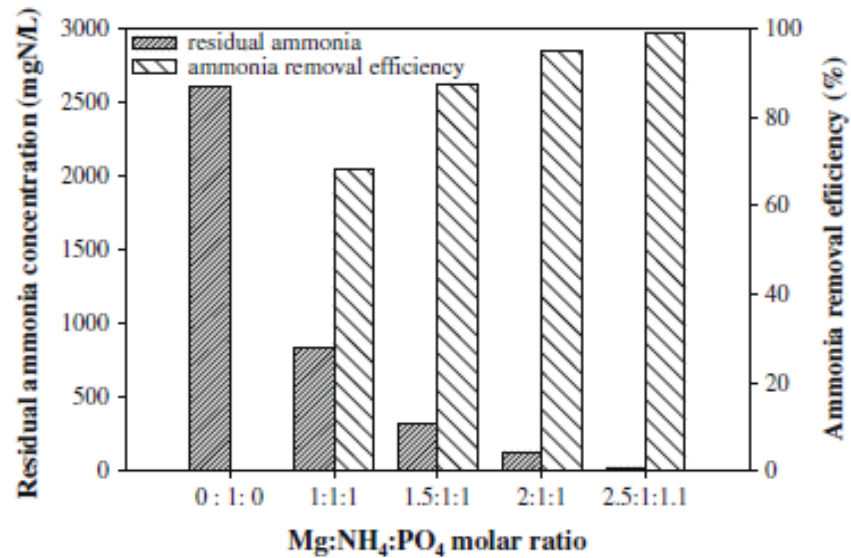


Fig. 13. Residual ammonium concentration and removal efficiency during MAP precipitation at different Mg: NH₄: PO₄³⁻ molar ratios. (Di Iaconi et al, 2010).

1.4.2. Kinetics of precipitation

To study the kinetics both processes of the precipitation should be analyzed: the crystal core formation and the granulation of the clusters. The driving force for both is the chemical potential difference between the actual and the equilibrium state.

The primary nucleation, the initial core formation is almost exponential. On the other hand, the secondary nucleation and the growth of the formed nucleus curves are similar to a first order polynomial.

Another parameter affecting the kinetic is the mixing of the reactor. Its homogeneity and the local effects that may occur mainly in the inflow pipe where local high saturation may be observed are facts to take into account. To avoid these problems the mixing speed should be higher than the reaction velocity. (Pastor, 2006)

- Nucleation:

The nucleation is the stage when the crystal cores are formed. It is in this stage where the amount of crystals will be defined. Indirectly, the size of the crystals will also be defined because the rest of the still present oversaturation will be used to make the crystals larger.

- Growth:

The growth of the crystal cores is a diffusion based material transport process towards the particle surfaces. Once the particles are in contact with the surface they need to be clustered around the crystal's structure. This reaction occurs in a limited velocity. Depending on the reaction and the conditions in which the reaction is happening the limiting speed can be the diffusion through the liquid phase toward the interface or the precipitation and the particle growing.

- Agglomeration:

Agglomeration of already existing particles to form a bigger one might happen but this is a process that not always occurs.

To allow it some circumstances are needed:

1. Appropriate turbulence and mixing favorable properties.
2. Proper parameters such as density or viscosity
3. Crystal size
4. Crystal population density
5. Oversaturation and growth velocity
6. Cohesion forces among crystal particles (influence of impurities, ionic strength...)

1.4.3. *Precipitation mechanism*

According to the results of the study by Chimenos et al, (2003) a proposal of mechanism is made. In this work struvite was precipitated using low concentrated MgO as magnesium source. The X-ray results show that the core of the supposed to be struvite particles was rich in magnesium and oxygen but not in ammonium or phosphates. Thus, the cores were still MgO. On the other hand, the more external layers were rich in magnesium, ammonium and phosphates indicating that the struvite precipitation has happened. The proposed mechanism is the following one:

- The low grade MgO particles are placed into the solution. In contact with water the MgO is hydrolyzed. Thus, the magnesium concentration in the interface increases.
- The diffusion from the magnesium into the liquid starts. Depending on the initial salt's magnesium concentration this process of hydrolyzing and diffusion may be slow. As a result, this step is mentioned to may be the controlling process of the reaction. The purest the magnesium the faster the dissolution and thus the diffusion through the liquid.
- The phosphate and ammonium in the liquid in contact with the magnesium reacts and form struvite. As the magnesium diffusion is not too high due to the low initial concentration this reaction takes place almost in the interface instead of in the bulk. The concentration in the

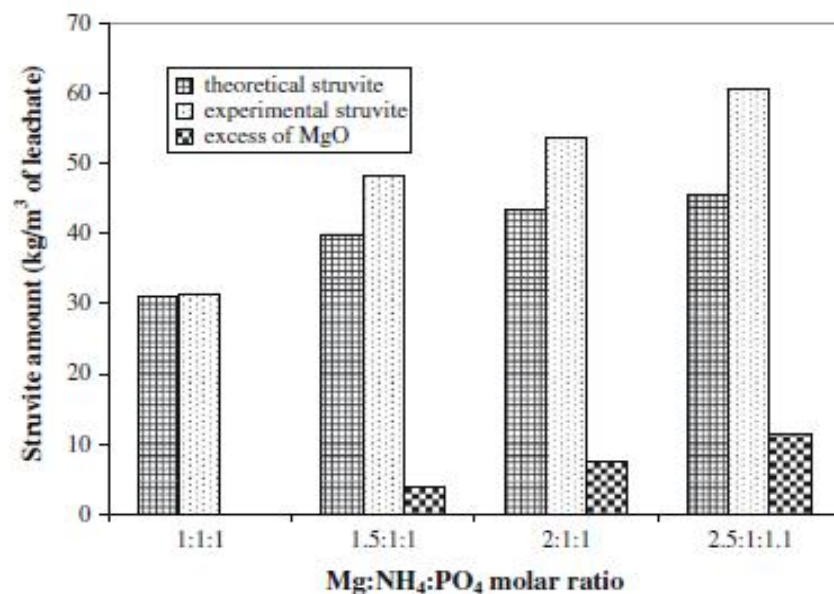


Fig. 14. Experimental and theoretical amount of struvite for each investigated molar ratio.

interface of ammonium and phosphate drop down so the diffusion of these species starts towards the interface.

- A struvite superficial layer is formed surrounding the MgO. This layer stops the further MgO dissolution and the reaction is stopped due to the lack of magnesium.

This mechanism is proposed regarding the results and it also can explain why a higher than the stoichiometric magnesium concentration is needed to reach good reaction efficiency.

As a result, can be mentioned that the dissolution rate of MgO is smaller than the struvite precipitation rate. Regarding this study some research should be made to investigate the influence of the MgO particle size. The smaller particles the more contact of surface per unit of mass of magnesium oxide. Thus, the magnesium dissolution will be improved. On the other hand, having a solid surface where the struvite can be crystallized may increase the reaction rate. It seems that there could be an optimum particle size and concentration for the MgO. Maybe, a potassium based compound could be combined with the MgO to fulfill the NPK requirements of a fertilizer.

Another issue that can be interesting to study is the combination of MgCl which is more soluble than the MgO. This way, a higher magnesium concentration in the liquid could be allowed and also provide solid particles to help the process of nucleation of the struvite. Again the use of sea water, rich in magnesium is an interesting option maybe in combination with some magnesium based salt.

The results of the study (Di Iaconi et al., 2010) show that the theoretical weight expected during the precipitation process, regarding the decrease of ions between the inflow and the outflow was lower than the experimentally measured weight. This fact supports the idea of magnesium oxide that is not dissolved remains as MgO. During these experiments excess of magnesium was loaded.

1.4.4. *Reactive molar ratios*

It was gathered from biography that to achieve an appropriate reaction yield the ions concentration should be higher than the stoichiometry concentrations: $[Mg][NH_4][PO_4]=1:1:1$ is not enough if we are looking for a successful phosphate removal. Depending on our goal we can use different molar ratios. For WWT, as both ammonium and phosphate lead to eutrophication processes the molar ratio between ammonium and phosphate should not be established far from 1.

Moreover, if we are looking for an ammonium reduction we can increase a little the phosphate concentration from the stoichiometric requirements and if we are more focused on the phosphate removal the ammonium concentration can be removed. Furthermore, the ion that can be increased without any eutrophication hazard to force a high precipitation rate is the magnesium. It has been reported in different studies that an increase of this ion improves the struvite precipitation (Uludag-Demirer et al, 2005). Another authors mention the molar ratio of $[Mg][NH_4][PO_4]=1.6:0.6:1$ as the optimum one (El Diwani et al, 2007).

A lack of magnesium is a common factor that raises the operational costs. It must usually be added to the waste streams of different flows to allow the struvite precipitation. The location of these facilities close to the sea might be an interesting solution due to the high magnesium concentration in it. Other study that supports the fact that high magnesium concentration favors the struvite crystal aggregation is

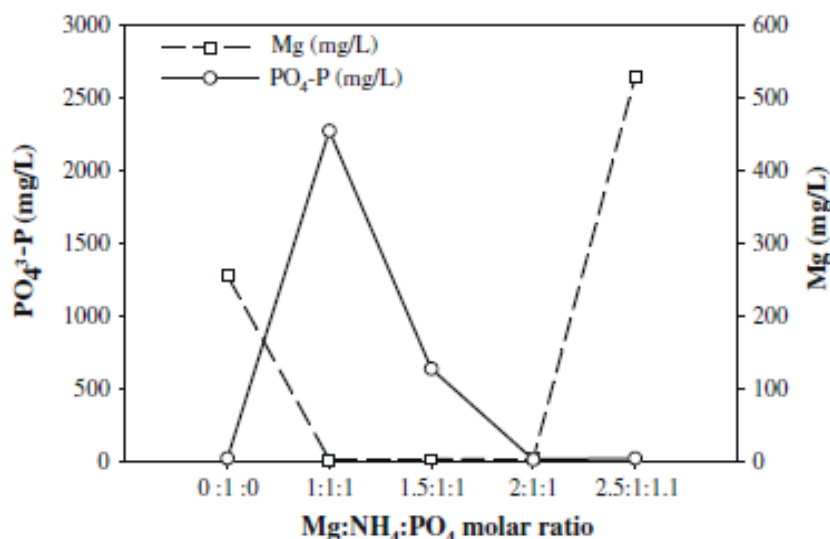


Fig. 15. Residual magnesium and phosphate concentrations during MAP precipitation as a function of molar ratio (Di Iaconi et al, 2010).

(Bouropoulos and Koutsoukos, 2000). There are different magnesium sources that are available in the market. $\text{Mg}(\text{OH})_2$, MgO , MgCl_2 .

General advantages of MgO:

“There are many advantages in using MgO as raw material, namely, magnesium oxide has minimal environmental impact, has low solubility and is essential for plant, animal and human growths; also, it has a high alkalinity, more than other alkalis, which helps to neutralize acids and precipitate metals requiring less $\text{Mg}(\text{OH})_2$ to neutralize the same amount of acid; $\text{Mg}(\text{OH})_2$ is a weak base and its dissolution is not exothermic, reaching a maximum pH of 10 which is in order with the Clean Water Act basic limits; the sludge formed by the reaction is conducive to crystal growth and is not light, fragile, or gelatinous like that formed by other alkalis” (Chimenos et al, 2003).

“It has been found that the low-grade MgO needed is greater than the stoichiometric value for the full removal of ammonium and phosphate as MAP compounds” (Chimenos et al, 2003).

Depending on the wanted final concentrations, either MgO , $\text{Mg}(\text{OH})_2$ or MgCl can be used. The most soluble compound is the MgCl . A combination of a couple of them could be the best solution.

Other solids might be formed besides the struvite (Uludag-Deminer, 2005). Thus, the optimum amount of magnesium depends on the different ions of the solution and the complex compounds that can be formed consuming as well a part of the magnesium present in the solution. (Uludag-Deminer, 2005).

The degree of saturation of the three ions, the amount of calcium, ionic strength of the solution and temperature are direct parameters that affect the reaction and determine it. More studies should be done in concern for the importance of this parameter for struvite precipitation, especially when the Mg^{2+} and PO_4^{3-} concentrations are rather high. The less ionic strength in the solution the less magnesium concentration is needed.

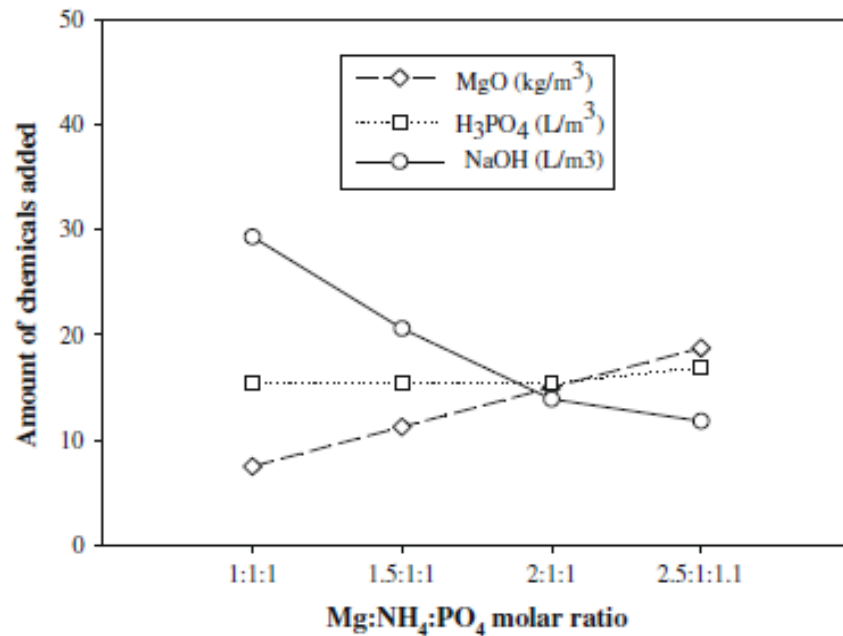


Fig. 16 Amount of chemicals added from Di Iaconi et al, (2010).

Besides, to find the parameters to establish the optimum efficiency practical studies are recommended to optimize a specific reactor. According to the biography, in several experiments, concentrations close to $[\text{Mg}][\text{NH}_4][\text{PO}_4]=1.8:1:1$ have been used. Being this one a molar ratio that is generally regarded sometimes as the optimum one or at least an initial value to start optimizing the reaction with practical experiments.

Ammonium elimination based on struvite precipitation is a successful technique with an ammonium removal up to 95% (Uludag-Deminer, 2005). However, to achieve such a high removal loadings over the stoichiometric concentrations seem to be necessary. Another author, under stoichiometric conditions has only achieved at pH 9.3 an 86% of its removal (Altinbas et al, 2002).

Regarding the biography (Uludag-Deminer, 2005) an ammonium removal above 95% was observed when the Mg^{2+} concentration was close to 0.06M. Anyhow, the concentrations needed depend on the type of water we are working with and the rest of the reaction parameters. As the struvite formation reaction is directly linked to the magnesium availability, so is the ammonium removal. Just changing the Mg^{2+} concentration a decrease on NH_4^+ was reported as the Mg^{2+} concentration increases, (Uludag-Deminer, 2005).

Using clean water and chemical reagents was found that when the molar ratio N:P is increased from 1 to 5, the P-removal efficiency increased from 70 to 96% (Fattah et al, 2008).

Di Iaconi et al, (2009) conducted a study of MAP precipitation with stoichiometric molar ratio. It was shown an ammonium removal of 67%. In this stoichiometric test the magnesium concentration in the outflow was very low, a fact that shows that there was a lack of magnesium: 2mg/L while there was still phosphates in the solution 2274mg/L. While the magnesium concentration was increasing in other experiments the percentage of ammonium removal was also increased.

Table. 1. Amount of chemicals consumed at each molar ratio. Table from (Uludag-Demir et al, 2005).

| | | | | | | | | |
|---|---|--|---------|--------------|----|--------------|----------------------------------|------|
| Combined wastewater from bovine and leather tanning factories | MgCl ₂ ·2H ₂ O | Mg:N:P = 1:1:1 | 200 | 4.1 | 82 | NI | 9.0 | [12] |
| | Na ₂ HPO ₄ | | | | | | | |
| Sidestreams from AD treating sludge from biological phosphorus removal in WWTP | Mg(OH) ₂ | Slurry, 55% (w/w) Mg(OH) ₂ | 790 | 61 (ortho-P) | 6 | 94 (ortho-P) | 8.5 (Mg(OH) ₂ slurry) | [16] |
| | | Mg:P = 1:1.3 | | | | | | |
| Swine waste | MgCl ₂ | Mg:TP = 1.6:1 | | 572 (SP) | | 91 (SP) | 9.0 (1 M NaOH) | [5] |
| Anaerobic supernatant from a centrifugation sludge section of a civil biological nutrient removal plant | No chemicals added | – | 1090 | 58.2 | NI | 80 | 8.78 (by aeration) | [17] |
| Effluent from the biologically (UASBR) treated opium alkaloid wastewater | MgCl ₂ ·6H ₂ O | Mg:N:P = 1:1:1 | 98 | 0.3 | 65 | NI | 9.2 | [7] |
| | Na ₂ HPO ₄ | | | | | | | |
| Effluent from the anaerobic treatment of the baker's yeast industry | MgCl ₂ ·6H ₂ O | Mg:N:P = 1:1:1 | 735 | 5.8 | 84 | NI | 9.2 | [7] |
| | Na ₂ HPO ₄ | | | | | | | |
| Effluent from the anaerobic treatment of domestic wastewater + 2% leachate | MgCl ₂ ·6H ₂ O | Mg:N:P = 1:1:1 | 60–92 | 8.2 | 77 | NI | 9.2 | [9] |
| | Na ₂ HPO ₄ ·2H ₂ O | | | | | | | |
| Effluent from the anaerobic treatment of landfill leachate | MgCl ₂ ·6H ₂ O | Mg:N:P = 1:1:1 | 2240 | 11.2 | 85 | NI | 9.2 | [9] |
| | Na ₂ HPO ₄ ·2H ₂ O | | | | | | | |
| Wastewater from the cochineal insects processing | Low grade MgO | 24 g/L | 2320 | 3490 | 89 | 100 | 8.5–9 (MgO) | [31] |
| Supernatant from an anaerobic digestion of sludge from a sewage treatment plant | MgSO ₄ ·7H ₂ O | Mg:P = 1.1:1 | 441–602 | 198–242 | NI | 92 | 8.4–8.5 | [32] |

TP, total phosphorus; SP, soluble phosphorus; AD, anaerobic digester; WWTP, wastewater treatment plant; NI, not investigated.

When the molar ratios were $\text{Mg:NH}_4\text{:PO}_4^{3-} = 2:1:1$ the ammonium removal was 95%. The results showed that there is a strong dependence on the magnesium concentration at least until $\text{Mg:NH}_4=2:1$ is reached.

During the experiments (Fig.13 and Fig.14) looking at the decrease in phosphate and ammonium concentration the theoretical mass of struvite removed was calculated. The experimental weight was in all the experiments larger than the theoretical one. These results can be explained due to MgO that remains undissolved as has been presented in the mechanism before and also due to other precipitates that have been formed.

Different waste waters treated with the struvite reaction process under different conditions give an idea of the different applications and versatility of this treatment (Table. 1)

1.4.5. pH influence

Regarding the MAP composition there is not only one chemical group that is affected by the pH. The struvite is composed of proton donating, NH_4^+ and proton accepting, PO_4^{3-} species so the solubility of the mineral does not necessarily vary monotonically with pH.

| References | pH |
|----------------|------------|
| Buchanan, J.R | 9,0 |
| Momberg, G.A | 8,0 – 10,6 |
| Booram, C.V | 10,3 |
| Ohlinger, K.N | 10,3 |
| Stumm & Morgan | 10,7 |
| Snoeyink, V.L | 10,7 |

*Fig. 17
Different
optimum pH
values.*

NH_4^+ concentration decreases from 99 to 64% when pH increases from 7 to 9. On the other hand, initial pH adjustments up to 8.50 don't result in a drop of ammonium concentration. Thus, the pH variations under lower values than the pK_a -limit seems not to affect the ammonium concentration. This is a fact that agrees with the theory.

According to Altinbas et al, (2002) the optimum pH to maximize NH_4^+ recovery, of high ammonium content wastewaters, was 9.2 and the MAP precipitation starts being very effective over a pH higher than 8.5 for a successful reaction. The optimal pH values for struvite precipitation is ranged between 9 and 10.7

Besides, PO_4^{3-} concentration increases in the same range of pH (Uludag-Demirer et al, 2005). Therefore, the pH is the main factor to optimize

The struvite precipitation is strongly dependent on the pH but the pH should be adjusted regarding our goals. For struvite precipitation there is a disagreement among authors but according to biography a value about $\text{pH}=9.6$ is said to be the optimum one (El Diwani et al, 2007). During

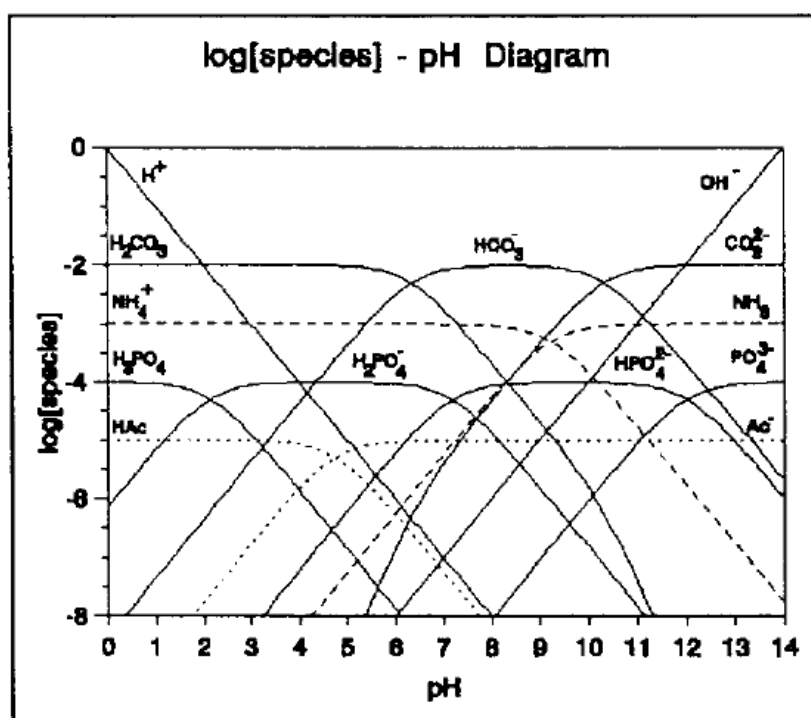


Fig. 18. Concentration of species with pH.

these experiments the pH was raised at first with the MgO and then it was set to the value of 9.5 with NaOH. The first crystals were observed at pH=7.5-8. Theoretically, the pH should be as high as possible up to the pH that drops down the ammonium concentration due to the reaction of ammonium into ammonia gas, around pH=9.2. Regarding the concentration/pH diagram plotted (Fig.18) the concentration of the ammonium does not drop until pH=9.2. If our goal is to eliminate as much ammonium as possible the pH can be set above this value. As a result, both effects: the proton losing of ammonium to ammonia and the struvite reaction will be summed.

There are studies that set the pH lower than these values from (Fig. 17) close to 7.5 and still achieve a 90% of phosphorus removal (Fattah et al, 2008). However, molar ratios were kept much lower for the P. N:P =[50-200] and Mg:P=5. Regarding the income data: phosphate was in the range [39-88] mg/L and ammonia-nitrogen [410-907] mg/L.

pH was the optimum set for struvite precipitation in (Mrowiec et al).

Different ways of increasing the pH are:

- Mg(OH)₂ or MgO.
- CO₂ stripping.
- NaOH.
- Lime or caustic.

The required pH can be achieved by the addition of different compounds or techniques: MgO, NaOH, CO₂ stripping, lime or caustic. The addition of Ca compounds interferes in the struvite reaction due to calcium phosphate formation. A study by Fujimoto et al., (1991) shows that the addition of sodium hydroxide was more effective in term of struvite formation than the addition of calcium oxide or magnesium hydroxide.

- Influence of air stripping on pH.

Air (CO₂) stripping is another way to increase the pH until the operation levels but it required longer residence time. If the acidity or alkalinity is usually high increasing the pH with this method can take too much time.

Air stripping results in an increase of pH due to CO₂ dissolution giving a oversaturation state where the magnesium ammonium and phosphate are forced to precipitate in form of struvite.

If the equilibrium pH after the reaction is above 9.2, the pKa for ammonium, the ammonium removal can be due to the sum of two different effects: the struvite formation and the deprotonation of the ammonium nitrogen to ammonia.

A decrease in equilibrium pH as the Mg²⁺ was added in the form of MgCl₂.6H₂O was observed regardless of the initial pH. This fact is due to the added acidity originating from the Cl⁻ ions into the system. Therefore, there is no need to consider the removal of NH₄⁺ as NH₃ for reactors dosed with MgCl₂.6H₂O. (Uludag-Demirer, 2005).

1.5. Phosphates

Phosphorus is a basic compound for all living species. It is basic for ATP synthesis, the basic energy unit for cells. In bones it is present bounded to calcium as hydroxyapatite and the human body is in an approximately concentration of 1.2 g/Kg. Phosphorus is also basic for plants and this is, indeed, the main use of phosphorus in the industry; as a basic compound for fertilizers.

The population increase or the desertification of some areas are facts that are forcing the optimization of the cultivable land. Therefore, the use and production of the fertilizers has increased to respond to the arising demand. As a result, the phosphorus cycle (Fig. 19) has been modified by human being by taking the inorganic phosphorus contained in some minerals to increase the fertilizers potential. Thus, the phosphate based mineral seams or deposits are getting more valuable. Currently around 140 million tones of phosphate rock are extracted every year in the world (Rana, 2004). The phosphates are obtained from the rock mineral, thus, is a limited resource that will be finished within 150-200 years. A consequence of this mineral exploitation is the higher phosphorus concentration in lakes and streams that may result in eutrophication and therefore, waters pollution.

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Phosphorus in water streams comes from farming activities (use of fertilizers and animal dungs) and human wastewater, which is the larger runoff. More accurately, urban residents discharge 2-3g phosphorus/capita/day. Hence, to avoid this problem new techniques that could fulfill the more strict law regulations should be applied. Besides, a phosphorus concentration higher than 100µg/L can lead to an eutrophication environment (Rana, 2004).

The increasing phosphorus discharge to wastewaters and on the other hand, the stricter final discharge concentrations are increasing a efficiency gap that the new techniques need to fill. In this contest, the struvite formation and as a consequence the phosphorus reuse is regarded as an interesting option. Besides, the recovered phosphorus in form of struvite does not need further treatments and it can be directly sold or used as a fertilizer.

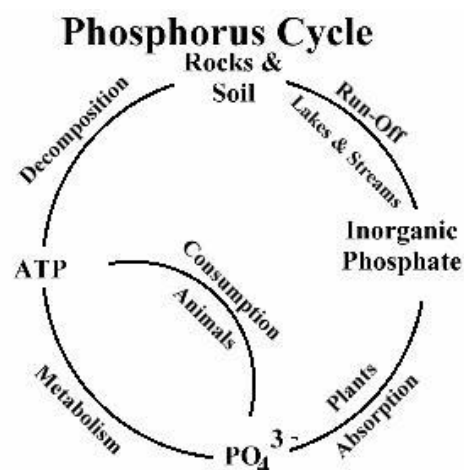


Fig. 19.
Phosphorus cycle.

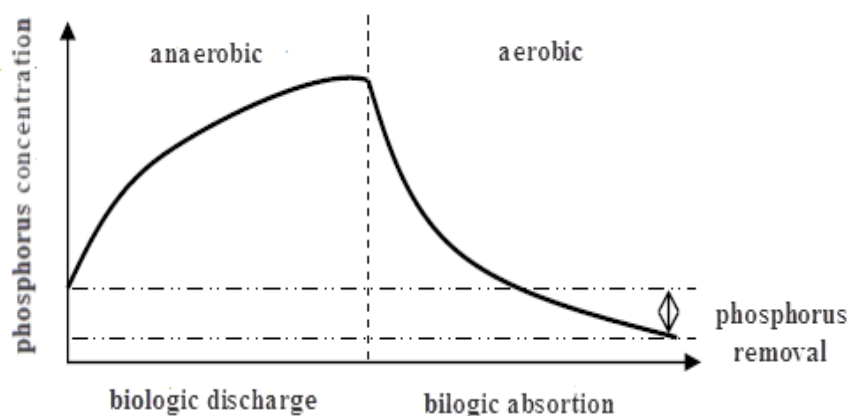


Fig. 20. Phosphorus concentration during biological treatment.

1.5.1. *Eutrophication*

In this global contest, reducing and recycling the phosphate is an interesting economical and also more environmentally conscious issue. The phosphate capacity to result in the eutrophication process is high comparing to other ions like ammonium and it needs to be removed before pumping it into rivers or any water disposal.

1.5.2. *Current treatments for phosphate removal*

The biological and chemical treatments are the most used ones. It is common also at a combination of both of them to achieve a lower concentration in the effluent.

The phosphorus, rather than the ammonium is considered the main factor that contributes to the eutrophication. In this way, it is really interesting to reduce its content (Schindler et al., 2008).

The removed phosphate is however not recycled or obtained. Usually, the phosphate is mixed with some metals and toxic compounds that cannot be allowed in fertilizers or different products or also are difficult to separate. In this field, the struvite is also an advantage: even it is formed in heavy metals containing waters the concentration of these metals in the struvite is much lower than the content of the metals of the ground itself. So it doesn't suppose significant hazard at all.

Biological treatment

The phosphates are taken up by the biomass and removed after as they are still in the cells in form of sludge. An anaerobic area is needed to allow the process and to achieve the needed phosphate removal.

Usually the phosphate removal due to the normal bacteria, nitrification-denitrification bacteria, goes from 20 to 40% (Pastor, 2006). That is why, for this process specific bacteria are grown, PAO: polyphosphate accumulating organisms. In this process the bacteria are changed from a first anaerobic environment into a second tank under aerobic conditions. Under an anaerobic environment the organic material is degraded by acidogenic bacteria into VFA, volatile fat acids. These organic acids are assimilated by the accumulating bacteria and stored as poly-hydroxybutyrate (PHB) and other poly-hydroxy-alkanoates (PHAs). These accumulating bacteria can't gain any energy under anaerobic condition so they use their own energy, stored as polyphosphates in the bacteria to

collect the fat acids. Is under this condition when the phosphates are released from the cells. In this stage, the concentrations of ammonium and phosphates can raise up to 1000 mg/L (Pastor, 2006).

In a second step and under aerobic conditions, the accumulating bacteria can use the stored organic acids and as a result the biomass of this type of bacteria grows exponentially. Furthermore, they use the excess of energy to store back the phosphates again as polyphosphates ensuring the energy for the anaerobic stage.

The total phosphorus removal is the difference between the initial and final concentrations, before and after both stages (Fig. 20). The removal is due to the cell growth and storage after the biomass rise.

On average and under good operational conditions this process can reduce the phosphorus concentration down to 1 mg/L but usually this removal levels are hard to achieve due to the lack of VFA available in the anaerobic stage.

These PAO, phosphate accumulating organisms, can't be mixed with denitrification bacteria because there will be a competition for these VFA and usually the denitrifiers win. Therefore, the PAO should not be mixed.

There are some researches about the possibility to ferment the biomass of PAO produced during the phosphorus biological treatment to provide VFA to the anaerobic stage decreasing the sludge produced volume. Moreover, producing in the plant VFA their purchase would be reduced. Besides, this phosphate rich sludge will release the phosphate from the bacteria and it can be precipitated as struvite. (Yuan and Oleszkiewicz, 2010).

Most plants avoid anaerobic situations before the sludge disposal to inhibit the phosphates release again. Another option is to treat the phosphate rich sludge with lime to bind it and precipitate it as calcium phosphate but this way we make the phosphates unavailable for further utilities. (Rana, 2004).

Currently, sludge produced now contains more toxic substances than ever before. Since the sewage dumping is now forbidden more care is taking in how it should be treated. Besides, the phosphorus and ammonium content in sludge is increasing as well. Thus, this can be an interesting option to improve the plant's efficiency.

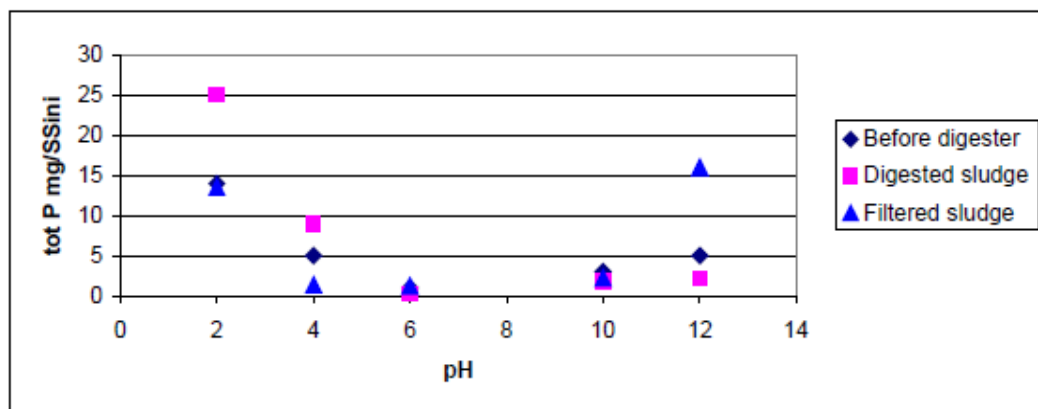


Fig. 21. Total phosphorus/ initial SS with pH.

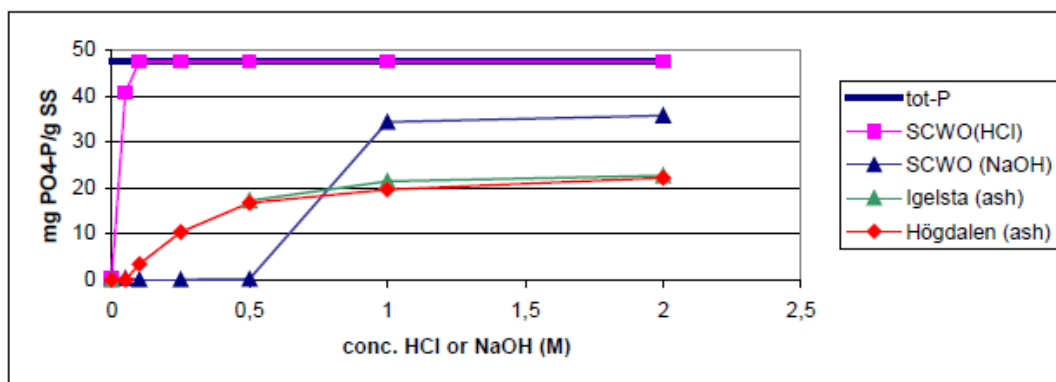


Fig. 22. Different phosphorus parameters.

1.5.3. Chemical release of phosphorus from sewage sludge

One of the possibilities to raise the concentration of recycled phosphates could be a phosphorus recovery from sewage sludge. The phosphorus recovery can occur immediately from sewage sludge by chemical methods. In this study sludge in an acid environment turn to be the most appropriate way to force the phosphate release from the biomass. Also alkaline environment is studied but the acid treatment is the most effective one.

This treatment can be regarded as a possible option as a pre-treatment for struvite precipitation, this way, increasing the phosphate concentration in the solution. It can be combined with other secondary treatments for the phosphate rich sludge that may result in an even higher phosphate concentration. This high phosphate content solution may be recycled and used for the ammonium removal.

In this study, the options of incinerating or supercritical water oxidation are mentioned before the acid treatment. Regarding the supercritical conditions that were applied, a temperature above 347°C and a pressure above 22.1 MPa were set to destruct organic material. They can be regarded as interesting options but they need a higher investment.

When sludge is acidified below pH 3 most phosphate salts are dissolved (Hansen et al., 2000). In addition, thermal hydrolysis releases parts of the biologically bounded phosphorus. The phosphate recovery from the biomass is mentioned to be about 70%.

One issue that has to be regarded is the different metals and heavy metals dissolved due to the low acid environment.

In (Fig.21) total phosphorus/ initial SS at different pH with different types of sludge can be observed. This information was obtained from Mrowiec et al.

At 0.1M acid was showed a 100% phosphorus release while under the alkaline conditions there was a slower release. The leaching with base showed at 1M approximately 70% phosphorus release.

A phosphorus release (mg phosphate/g SS) for residual sludge from SCWO treated with acid HCl or base NaOH together with leaching from ash (Fig. 22), which is only treated with acid (Mrowiec et al, 2003).

The experiments with pre-treated sludge show that a higher dose of base seems to be needed to achieve the same phosphorus removal as the one treated with acid (Mrowiec et al, 2003). Phosphates from the residue of supercritical water oxidation are shown to be easier to dissolve than

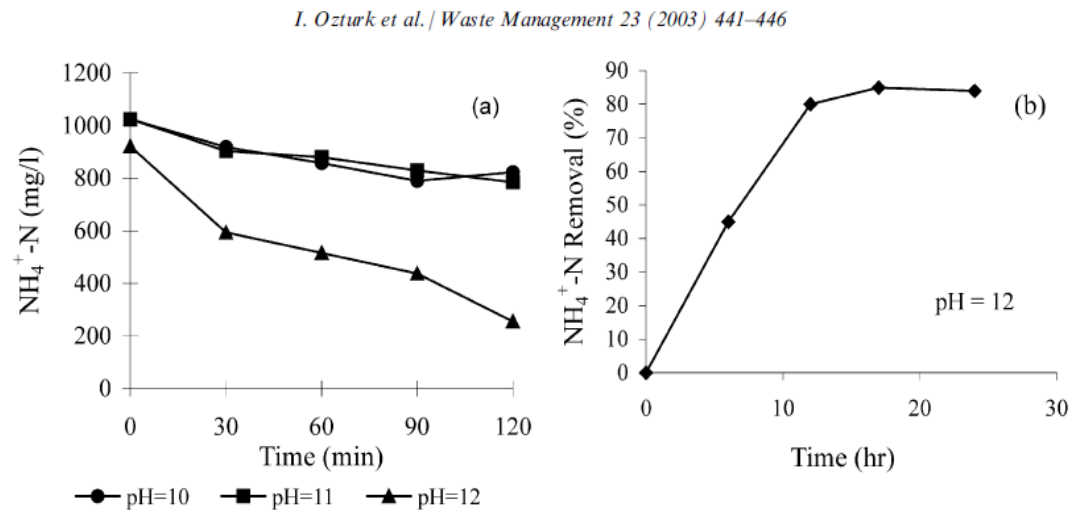


Fig. 23. Ammonium removal vs. time for different pH with long aeration time (Ozturk et al, 2003).

those from the leaching of ashes. Maybe is due to the fact that with the incineration process stronger bounds can be established among molecules.

The sludge volume after phosphorus recovery decreases up to 49% (Rana, 2004) approximately, always depending on the characteristics of the sludge.

Phosphates can be reduced by struvite precipitation from 100 mg/L to 2–3 mg/L with an ammonium removal at the same time (Rana, 2004).

1.5.4. Chemical treatments

Different chemicals can be added to precipitate the phosphorus as phosphate ions bounded to a metal ion. The usual ones are iron aluminum and calcium based compounds such as, ferric chloride, calcium phosphate.

The phosphate is removed within the sludge as a precipitated compound. These usual compounds avoid the eutrophication bounding the phosphorus to a metal but there is no possibility to reuse it. Hence, this is the main advantage of the struvite

1.5.5. Parameters

The inputs of P and also N come from completely different sources such as fertilizers from agriculture or industry. In addition, the demand of higher N content in fertilizers and the limited phosphorous from minerals have enhanced the importance of improving the removal and recycling of these minerals. Therefore, the importance of the removal of nitrogen and phosphate by struvite precipitation is regarded as an interesting option not only to remove phosphate but also to produce a directly reusable fertilizer.

1.6. Ammonium

Maximum ammonium removal was observed at pH 9.2 as well as TKN, Total Kjeldahl nitrogen, removal. With an influent of 2240 mg/L of ammonium and a molar ratio MAP=1:1:1. The ammonium removal efficiency was 85%. COD removal was 50%

Ammonia gas formation ($\text{pK}_a=9.2$) which is stripped due to the vigorous stirring in an experiment conducted by Chimenos et al, (2003). The removal due to air stripping depends a lot on the pH. There are some

studies that increase the pH up to 12 with a high removal of ammonium. The removal efficiency was 72% after 2 h of aeration at pH=12. On the other hand at pH=10 the removal in 2h was 20% (Fig. 23).

In this study the nitrogen removal was no further increased after 17-24 h. In this research the optimum time was concluded to be 17 h after which the pH starts to go down due to the CO₂ content in the air. The removal of ammonium by free stripping for 24 h was 95% for a lime dosage to increase pH of 8000 mg/L. (Ozturk et al, 2003).

The ammonium is changed to ammonia at pH higher than 9.2 so for pH higher than 9.2 a sum of two processes is observed. Both, the ammonium oxidation due to the dissolved oxygen to nitrite and the reaction of ammonium into ammonia take place at the same time.

1.7. Prevention of undesired precipitation of MAP

Forcing the precipitation reaction to happen before carrying the flows in long pipe networks can prevent further damages to the pumps and pipes. Thus, reducing the maintenance cost.

A struvite reactor with the influent from the dewatered sludge system allows recycling a high P, and N concentration back to the inflow.

2. METHODS

2.1. Nitrification bacteria

2.1.1. *Struvite dissolution by nitrification bacteria.*

Reactor:

1L of income and 0.5L of sludge were mixed in a bucket of 3L. The solution was kept mixing with a magnetic stirrer at room temperature, about 22°C. The reactor was loaded with 2.5090 g of struvite. The 3rd day sugar was added, 1.5750 g.

The pH was tried to be kept close to 7 and always between the values of 6 or 8 where the nitrosobacter bacteria are under less stressing conditions. The air was supplied with a small aquarium pump. In this experiment the air flow was not regulated.

Analytical procedure:

During the experiment samples were taken every day at the same time with a maximum difference of 2 hours, every 24h \pm 2h. The samples were filtrated and micro filtrated with a membrane filter with a diameter of 0.45 μ m. Then the samples were analyzed but for the phosphates. The rest of parameters were analyzed at the facilities laboratory with Dr. Lange. For the phosphate measurements the samples, after being micro filtrated were frozen and kept until the analysis at KTH laboratory with the Aquatech device.

2.1.2. *Ammonium removal with the final leachate from the struvite dissolution reactor.*

The struvite was dissolved in a biological reactor with nitrification bacteria. After the reaction, the final volume of the reactor was divided in two. One portion was just filtrated and the other one was flocculated and filtrated afterwards. Then, the effluent was mixed with influent in the calculated the proportion of 1.25 times volume of the effluent with the income. Hence, the stoichiometric requirements were satisfy. The mixture was intensively stirred for 10 minutes after which it was gently mixed for 30 minutes. Afterwards, the stirring was stopped and the precipitate was settled. The filtrated sample's volume was 85 mL and the

flocculated and filtrated sample was 200 mL. They were respectively mixed with 106 mL and 251 mL of income.

Once the mixture was done the pH was risen with NaOH while the mixture was being stirred until the value of 9.5 was reached.

2.1.3. *Influence of dissolved oxygen in struvite biological dissolution by nitrification bacteria.*

Reactors:

Three different reactors where prepared. One of them under anoxic conditions and the other two with an air pumping supply. It was tried to keep one aerobic reactor with a higher DO (dissolved oxygen) than the other one all the time in order to evaluate the influence of the dissolved oxygen influence. Besides, the DO is a difficult parameter to control. Thus, to try to keep it under constant range of values the mixing of the mixture was controlled. The air pumping was controlled with a valve. In addition, the aerobic reactor with the lowest DO dimensions were modify to fulfill this issue. Both bucket's volumes were the same but the diameter of the lowest DO content reactor was bigger so the height of the liquid was smaller. This way, the time of contact between the air bobbles and the liquid was also shorter. The reactions lasted for three days.

Three volumes of 0.6 L the same sludge were chosen. The air pumping pipes were glued to the bottom of the buckets. R1 was kept close to 5-6 mg/L. R2 was around 7 mg/L and R3 was placed without air supplement, close to 0.1 mg/L.

Analytic procedure:

The samples were taken and after microfiltration were frozen until the measurement of the parameters. The DO, conductivity and pH were measured in situ. Phosphates were measured with Aquatech at KTH laboratory.

2.1.4. *Maximum struvite that can be admitted by the reactor of nitrification bacteria*

Two equal reactors were prepared with the same sludge and air supplement. They were loaded with 5.0316 g and 7.5203 g of struvite. The reactors were running for 3 days.

The samples were micro filtrated and frozen until the analysis at the KTH laboratory. DO, Ec and pH were measured in situ.

The volume of the reactor was 1.2 L: 1 L of sludge was mixed with 0.2 L of income.

2.2. **Anammox bacteria**

80 anammox rings were placed in a bucket and mixed with 1L of income as well as with 2.5250 g of struvite. The rings were slowly stirred. The samples were microfiltrated and frozen afterwards.

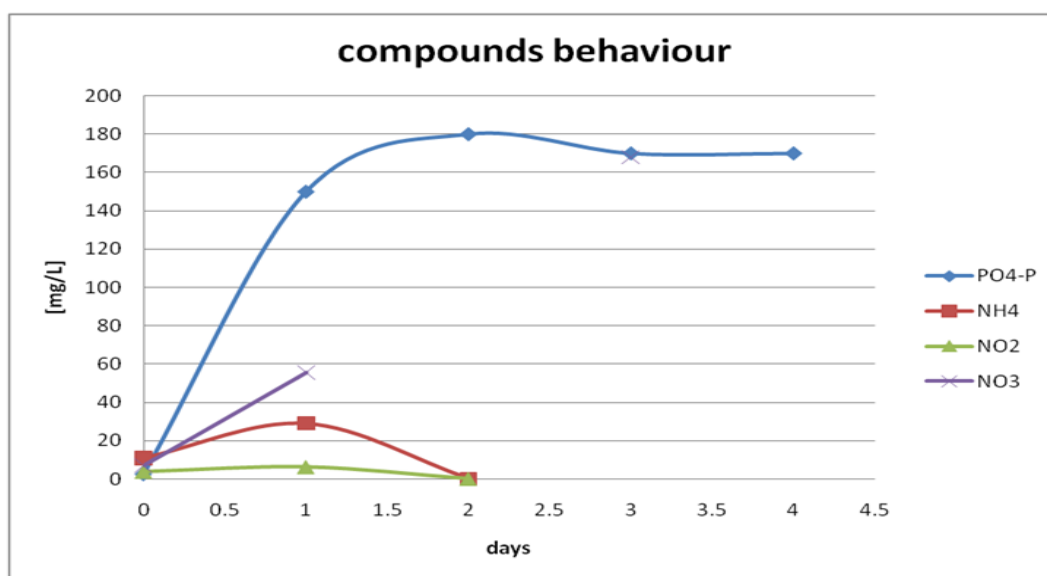


Fig. 24. Different concentrations plotted with time (days).

3. RESULTS

3.1. Nitrification bacteria

The obtained results for the conducted experiments by nitrification bacteria are presented in form of graphics.

3.1.1. *Struvite dissolution by nitrification bacteria:*

Different compounds concentrations were measured in the water solution during the experiments to try to identify and quantify the

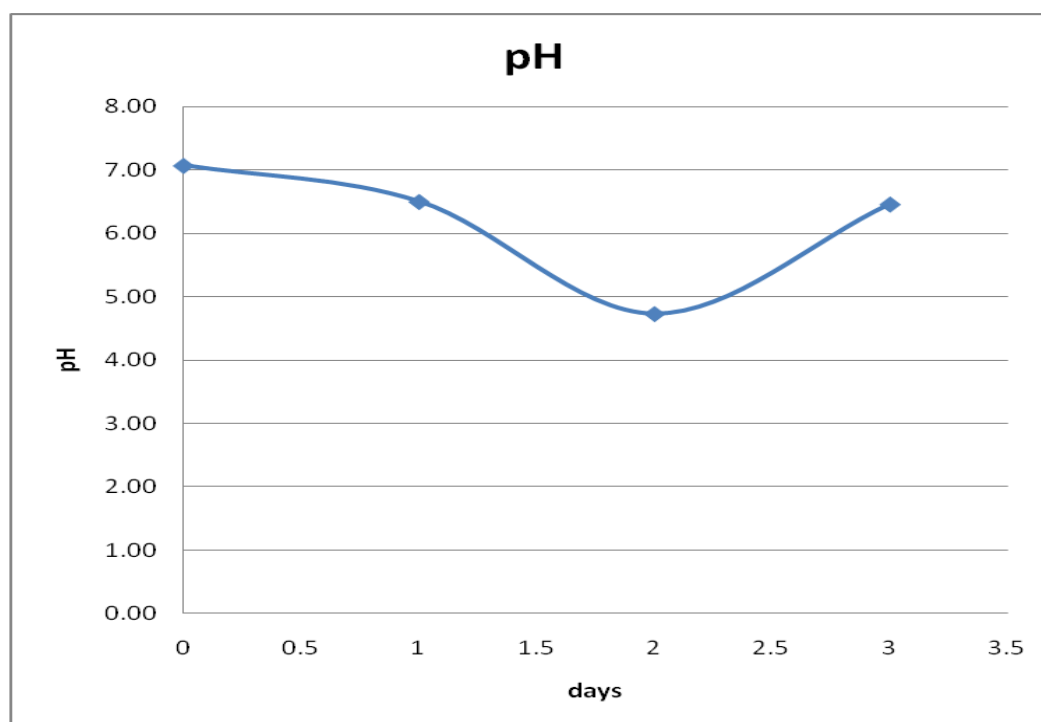


Fig. 25. pH was adjusted everyday to the value of 7. pH plotted with time (days).

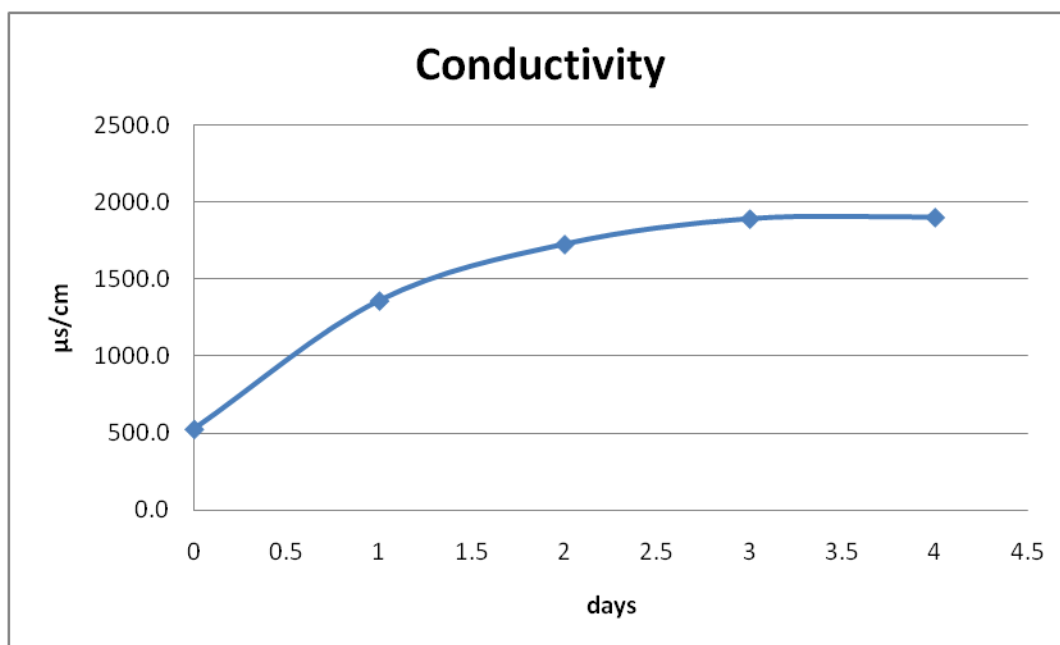


Fig. 26. Conductivity changes with time (days).

struvite dissolution (Fig.24). The phosphate concentration increased up to 150 mg/L in the first 24 hours. The maximum concentration was obtained in the second day with a concentration of 180 mg/L.

The pH was also measured as it is an indicator of the dissolution due to the bacteria activity and the influence of the ions on the pH (Fig. 25). In addition, the conductivity was measured during the experiments as representation of the increase in concentration of the ions in the solution (Fig. 26). Furthermore, the total hardness was measured as is directly related to the magnesium concentration (Fig. 27) and the same general relationship, increase with time, was observed.

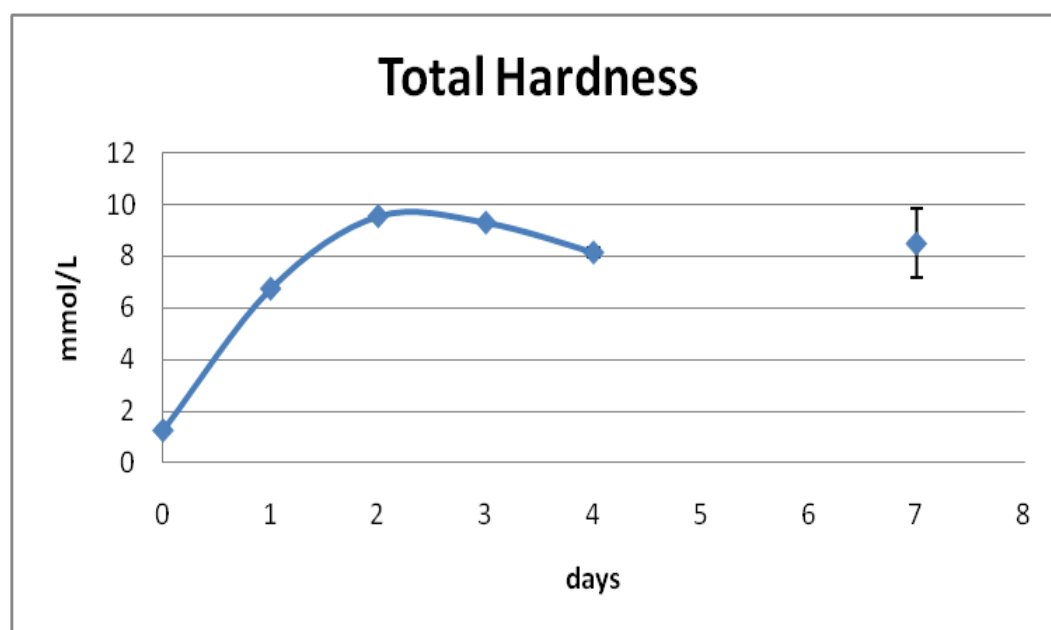


Fig. 27. Total hardness plot of the biological struvite dissolution with time (days).

Table 3. Ammonium removal

| | initial value mmol/L | final value mmol/L | removal % | mmol/L decrease |
|--|-------------------------|-----------------------|--------------|--------------------|
| [NH ₄] ⁺ filtrated | 1.011 | 0.989 | 2.21 | 0.022 |
| [NH ₄] ⁺ floculated | 1.014 | 0.983 | 3.08 | 0.031 |
| [PO ₄] ³⁻ filtrated | 0.212 | 0.001 | 99.52 | 0.211 |
| [PO ₄] ³⁻ floculated | 0.064 | 0.001 | 98.44 | 0.063 |
| [Mg] ²⁺ filtrated | 8.480 | 0.250 | 97.05 | 8.230 |
| [Mg] ²⁺ floculated | 17.650 | 0.640 | 96.37 | 17.010 |

3.1.2. **Ammonium removal with the final leachate from the struvite dissolution reactor.**

Results concerning the ammonium removal of the struvite reaction with the leachate from the biological dissolution are presented for both, filtrated and flocculated samples (table 3).

3.1.3. **Influence of dissolved oxygen in struvite biological dissolution by nitrification bacteria.**

The data for the three different reactors concerning the influence of the dissolved oxygen is plotted. (Fig.28).

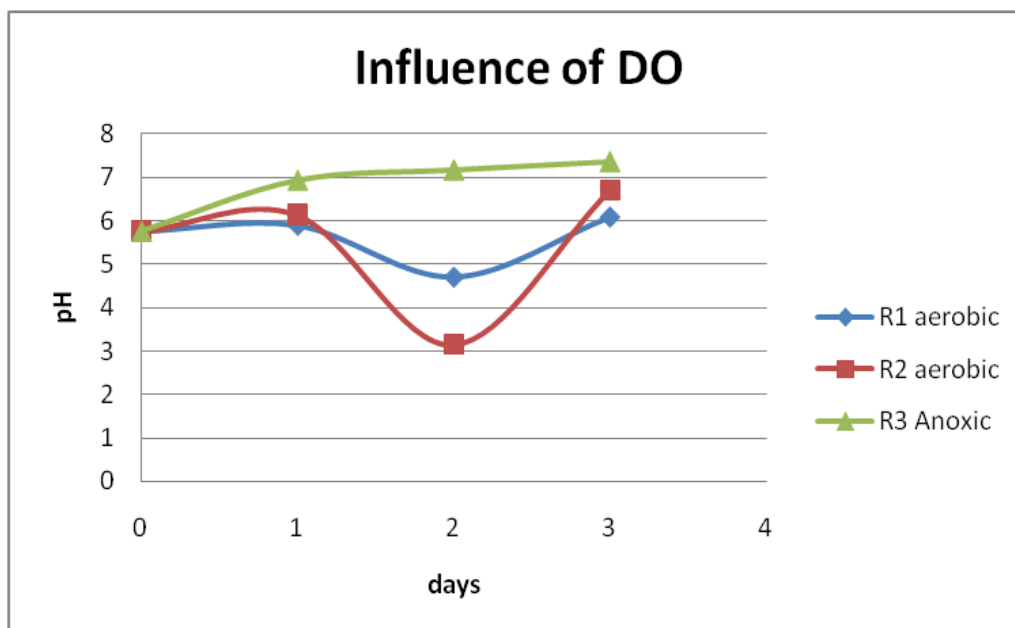


Fig. 28. pH changes for R1, R2, R3 with different DO content. R3 anoxic conditions. With time (days).

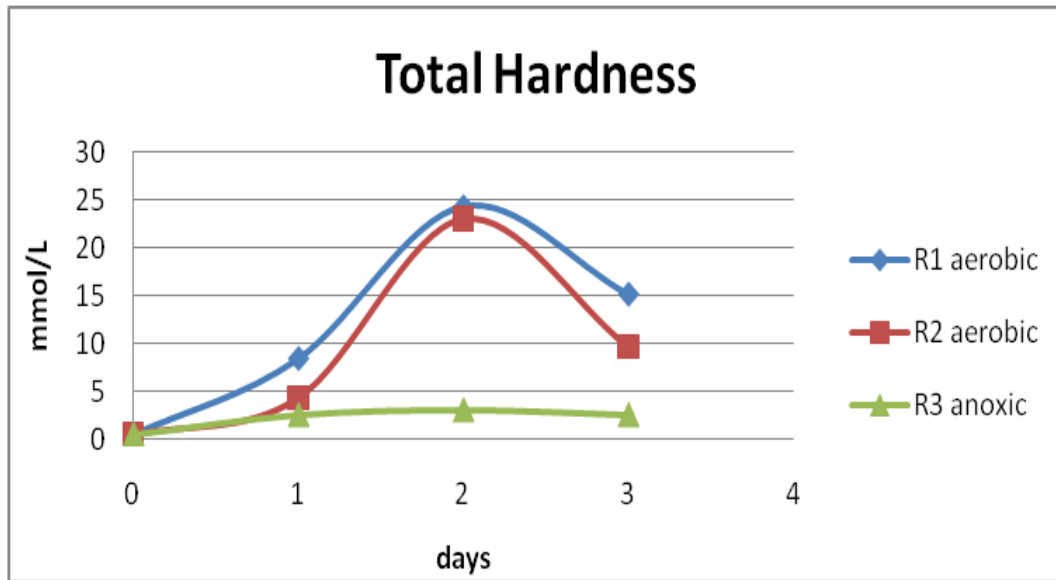


Fig. 29. Total hardness for R1, R2, R3. R3 under anoxic conditions. with time (Days).

The total hardness was measured under different oxygen conditions to quantify the increase in Mg^{2+} in the solution of each reactor (Fig. 29)

3.1.4. *Maximum struvite that can be admitted by the reactor of nitrification bacteria*

Conductivity was also checked to measure the ion increase in the solution. As in other experiments it is increasing with time. (Fig. 30).

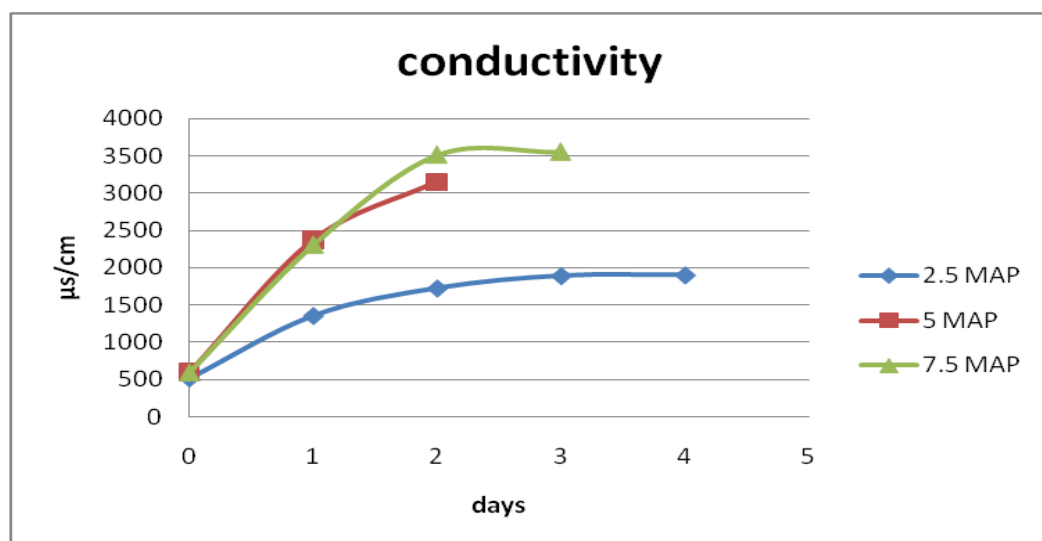


Fig. 30. Ec. For three different reactors with different struvite loads under same DO conditions with time (Days).

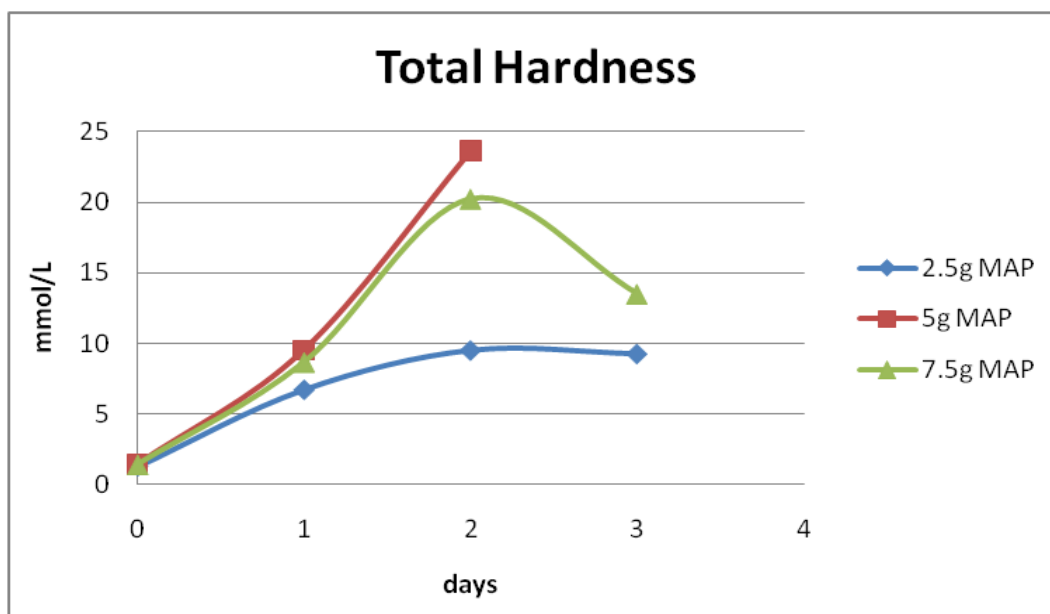


Fig. 31. Total hardness for the three reactors with time.

Also related to the maximum dissolution, data for the total hardness was recorded as another indicator of the biological activity (Fig. 31).

3.2. Anammox bacteria

3.2.1. Struvite dissolution by anammox bacteria

For the anammox bacteria the total hardness was also measured (Fig. 32).

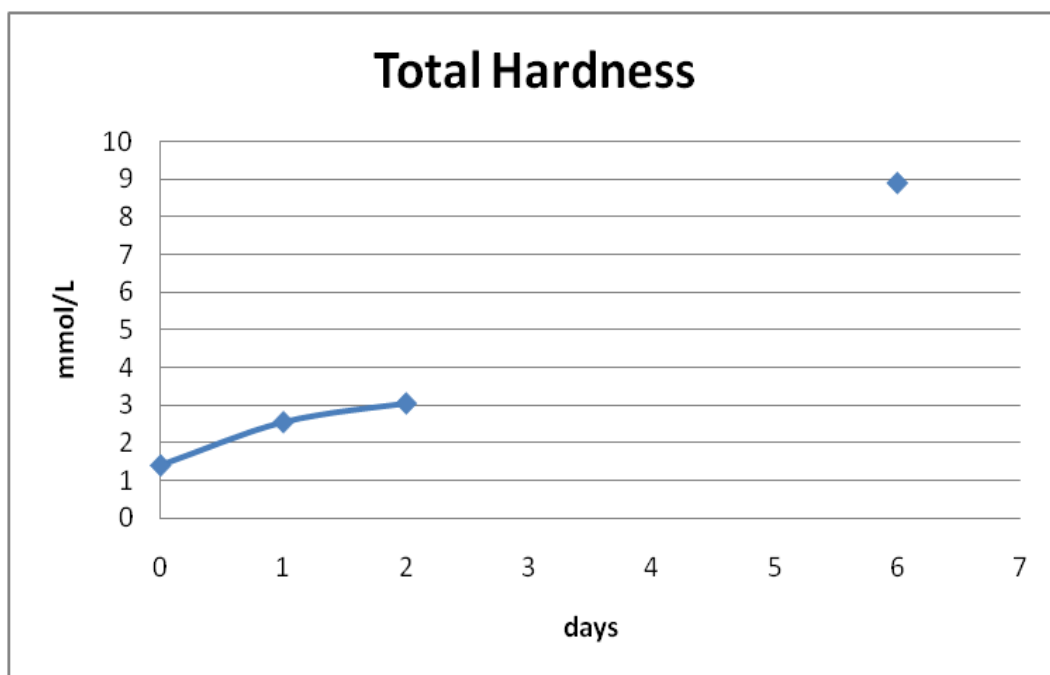


Fig. 32. Total hardness with time (days).

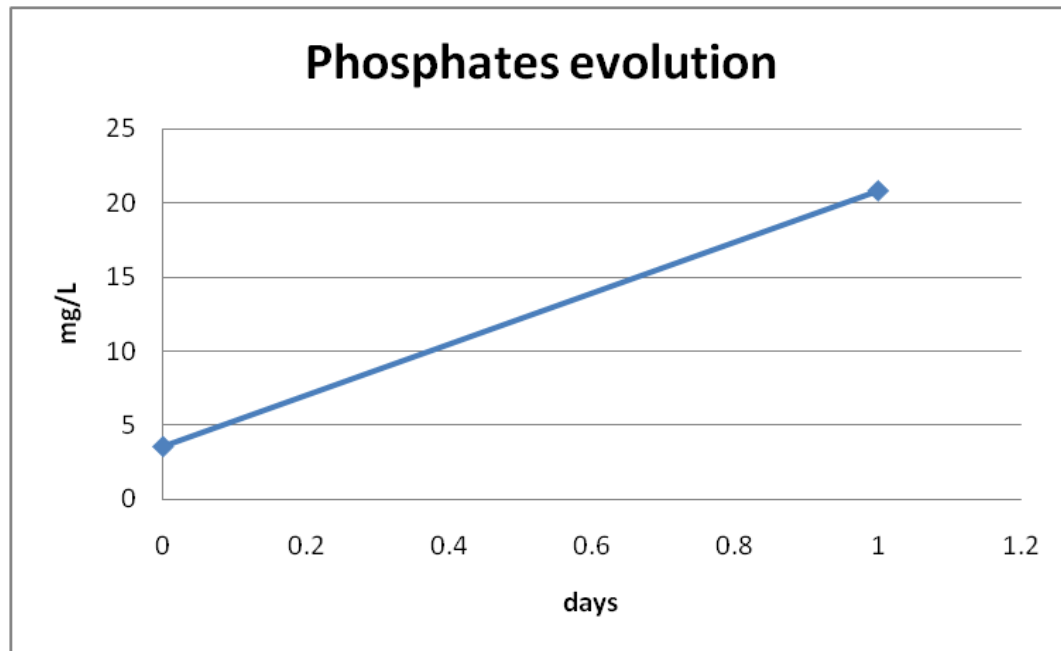


Fig. 33. Phosphates concentration with time (days).

For the anammox bacteria the phosphate concentration for the first days was obtained (Fig. 33).

4. DISCUSSION AND CONCLUSION

4.1. Nitrification bacteria

4.1.1. *Struvite dissolution by nitrification bacteria.*

An initial experiment was conducted to investigate the feasibility of biological struvite dissolution.

The sludge was mixed with influent to reduce the viscosity and also to provide some substrate to keep the biomass alive.

The third day, the phosphates drop can be explained due to the load of sugar (Fig. 24). As a result, the bacteria oxidized the supplied organic matter. Also, some of this energy is saved as polyphosphates in the cell.

There is an increase in the ammonium concentration (Fig.24) between the first and the second day. This was maybe due to the bacterial activity that is dissolving the struvite. Regarding the phosphate increase we can assume that a fast dissolution has happened and that the bacterial activity could not assimilate such a high amount of ammonium. Thus, more concentrated sludge should be used for further experiments. The pH (Fig. 25) was dropping down as a result of the dissolution by the bacteria activity. It was adjusted everyday to a neutral level, pH 7. Thus, the conditions were more comfortable for the bacteria and helped the dissolution. The total hardness and the conductivity are indirect indicators of the dissolution as they measure the ions concentration in the solution (Fig. 26, 27). Regarding these figures, how the dissolution is happening within the first two days can be evaluated

4.1.2. *Ammonium removal with the final leachate from the struvite dissolution reactor.*

The low ammonium removal (Table. 3) can be explained due to the unexpected low phosphate concentration that was observed. Regarding

the amount of phosphates and ammonium that has reacted we can assume that they reacted between them as well as with magnesium to form struvite. The rest of the magnesium that has been consumed can have reacted with organic material or at least consumed because the color of the supernatant that was observed after the MAP precipitation was much clearer than the initial mixture color. Regarding the samples after the struvite precipitation almost all the suspended solid were dragged while the struvite was precipitating. The high phosphate elimination rate indicates that a more concentrated leachate from the biological dissolution reactor should be as effective as these ones. Thus, a higher ammonium removal could be achieved by this method just supplying a more phosphate concentrated solution.

4.1.3. *Influence of dissolved oxygen in struvite biological dissolution by nitrification bacteria.*

After being running the reaction for one day and after arrival to the facility the air pumps were disconnected. Regarding the pH evolution similar values were taken for the three reactors so it seems that there was no air supplement and an anoxic reaction was happening (Fig. 28). On the other hand, when the air pumps were working a significant different pH values were obtained. The pH for the anoxic condition reactor was increasing constantly. However, for the aerated reactors the pH had dropped.

In the R2 more foam was observed due to the more narrow dimensions of the reactor. Thus, the bubbles were in contact with the solution for longer time.

It seems that the DO, dissolved oxygen, concentration was too high to measure any difference. In the first day, under anoxic conditions R1 was the most dissolved one but if we look at the total hardness figure the second day with the air supplement both R1 and R2 arrive at the same dissolution rate (Fig. 29). We can assume that the DO was not a limiting factor in these experiments. For further studies a better way to control the oxygen dosage is recommended. The DO values should be lower to see at which values oxygen starts to be a limiting factor.

4.1.4. *Maximum struvite that can be admitted by the reactor of nitrification bacteria*

Even the load of the reactors were different there is no difference almost between the 5 g and the 7.5 g reactors the first two days in the volume of 1.2 L (Fig. 30, 31). This may indicate that there is a maximum in the struvite dissolution that this sludge can admit. There was a leaching in the third reactor so the third day couldn't be measured because all the liquid was poured out.

A retention time of 2 days seems to be the optimum one. If the reaction is kept longer the phosphate concentration starts to decrease.

4.2. **Anammox bacteria**

4.2.1. *Struvite dissolution by anammox bacteria.*

The contact between the rings and the struvite is not that good as it is with the sludge; this fact influences the dissolution efficiency (Fig. 32). In addition, the rings density looks quite low for such a volume. As a result the dissolution was not as high as expected.

The dissolved oxygen was high compared to the optimum one for the anammox bacteria so the effectiveness of the anammox was not also at its maximum. Anyway the achieved dissolution was much lower than the results obtained with the nitrification bacteria. It was decided that the

next experiments should be focused on the nitrification bacteria. The phosphate increase in solution the first day was much lower than with the nitrification bacteria (Fig. 33).

5. CONCLUSION

The biological dissolution of struvite seems to be an interesting option for struvite precipitating plants. Not only for wastewater treatment plants but also for landfill leachate or any high ammonium concentrated waste water treated by struvite precipitation. This dissolving option opens new possibilities for the wastewater treatment based on struvite precipitation.

This way, the costs of the raw chemicals needed would be reduced due to the fact that magnesium and phosphates can be recycled. Also higher concentrations of magnesium and phosphates can be achieved. As a consequence of the costs reduction it may be applied in more places, smaller plants or farming activities achieving a higher phosphorus and ammonium removal.

Further studies should be conducted in order to specify the parameters and the feasibility of this future option.

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