NEW POSSIBILITIES OF MAGNESIUM UTILIZATION IN WASTEWATER TREATMENT AND NUTRIENTS RECOVERY

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ABSTRACT

New possibilities of nutrients removal by additions of magnesium compounds were studied in primary treatment and supernatant of side stream in wastewater treatment. The precipitation product from this method is magnesium ammonium phosphate (MAP) so called struvite. High efficiencies on NH₄-N and PO₄-P removals have been demonstrated up to over 90 % respectively in side stream from dewatering of digested sludge. In order to find out the nutrient removal efficiency in raw wastewater and the feasibility of MAP recycling in wastewater treatment, the postulations of combining MAP and nitrification-denitrification process, and MAP and partial nitritation-anammox process were carried out by experimental works in the laboratory at Land and Water Resources Department, KTH. It was found that 92-97 % of PO₄-P and 57 % of NH₄-N were removed from raw wastewater by Mg²⁺ addition at pH10 to pH10.5. The research work revealed that recycling of MAP by nitrification-denitrification and partial nitritation-anammox processes may be a feasibly process combination. In MAP and nitrification-denitrification process, the released ammonium was mostly oxidized to nitrate in nitrification phase and ready for denitrification. Based on presented results on MAP and partial nitritation-anammox process, it was found that the released ammonium was consumed by anammox bacteria.

Keywords: Ammonium, anammox, magnesium ammonium phosphate, nitrification, phosphate, struvite, wastewater.
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<th>Acronym</th>
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<tbody>
<tr>
<td>MAP</td>
<td>Magnesium ammonium phosphate</td>
</tr>
<tr>
<td>P</td>
<td>Phosphorus</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>SS</td>
<td>Suspended solids</td>
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<tr>
<td>VSS</td>
<td>Volatile suspended solids</td>
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<tr>
<td>K</td>
<td>Conductivity</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>CA</td>
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</tr>
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1. INTRODUCTION

Wastewater is increasingly making contribution for water sustainability. Since the shortage problem of water supplement is getting more intensive, wastewater reuse becomes more important for water resource replenishment. Water composition is not only vital for human health but also influences aquatic environments and ecosystems of surface and ground water. Wastewater technology is essential for recycling efficiency of wastewater.

Wastewater contains contaminants that are not desirable for aquatic environment; those elements would arouse aquatic problems. The most familiar case is the increasing stress from eutrophication. Eutrophication is an outcome when excess amount of nutrients are released and accumulated in water body. When water collects excess nutrients, nutrients will be absorbed by aquatic vegetation and bio-organism as food energy, so quantity of microorganisms and algae is growing up. As consequences dissolved oxygen in water is consumed, water is then full filled with nutrients and simultaneously aquatic ecosystem is unbalanced.

The most common nutrients in wastewater are phosphorus (P) and nitrogen (N), which are thought to be the main contributors for eutrophication. The removal of phosphorus and nitrogen can be classified as on-site wastewater treatment and municipal wastewater treatment. In central municipal wastewater treatment, phosphorus and nitrogen compounds are mainly removed by the combination of chemical precipitation and biological treatment. But facing to the arising stringent criteria, many intensive treatment technologies have been studied to enhance nutrient removal efficiency, for example ANAMMOX for nitrogen removal and dosing of magnesium compound for precipitating P and N.

Magnesium is one of the chemicals being studied due to its potential for P and N removal in municipal wastewater treatment. Magnesium is after sodium the most abundant positive ion in the sea. Magnesium compounds are widely used as coagulant to remove organic compounds in water treatment due to the high treatment efficiency at low costs. Based on this predominance, the adoption of magnesium precipitation to

\[
\text{Supernatant } \text{NH}_4^+\text{,HCO}_3^- \\
\to \text{Denitrification} \to \text{Nitritation/Anammox} \\
\to \text{Air Flocculation} \\
\to \text{Settling} \to \text{Aeration Tank} \\
\to \text{MgNH}_4\text{PO}_4 \\
\to \text{Addition } \text{Mg}^{2+},\text{PO}_4^{3-} \\
\to \text{To main stream}
\]

*Fig. 1 Combination of Partial Nitritation/Anammox and MAP (Hassanzadeh, 2005)*
Municipal wastewater treatment has been investigated typically in primary treatment process and in side stream, which normally contains returned sludge supernatant with high strength nutrient contents. The reaction mechanism is the same as other chemical precipitation process. The product from this method is magnesium ammonium phosphate (MAP) (MgNH4PO4), so called struvite. This formation has been used as a good fertilizer product since it comprises most elements that crops require. In research by Jaffer (2002), phosphate phosphorus (PO4-P) removal rate was up to 97% as MAP formation; and in research of Uludag (2009), PO4-P removal achieved 94% while ammonium nitrogen (NH4-N) removal achieved 92% from side stream.

Though the MAP precipitates is commonly used as slow released fertilizer in agriculture, parks and etc., the recycling of MAP connecting to biological treatment is of interest. The principle of this idea is to re-dissolve MAP precipitates in the circulation of wastewater stream connecting nitrification-denitrification process or anammox process, to enhance nutrient removal efficiencies and reduce the generation of carbon dioxide, meanwhile, enhancing the purity of biogas productions.

The possible pathways to dissolve MAP can be classified as chemical, thermal and biological. Biological dissolution has been studied only by introductory tests so far (Levlin & Hultman, 2008). It was shown that nitrification bacteria can dissolve magnesium ammonium phosphate. The mechanism was postulated to be similar as bacterial leaching of sulfide minerals. Thus, ammonium can be used as an energy source for the bacteria, hydrogen ions and nitrite/nitrate can be generated during dissolution of MAP in nitrification process. The produced nitrite/nitrate can be denitrified or used for instance to decrease hydrogen sulfide formation and diminish odor problems. The dissolution of magnesium and phosphate ions makes it possible to recycle magnesium and phosphate ions from the precipitation step.

The project addressed in this thesis work is to investigate the treatment efficiency by magnesium compounds, and the feasibility of biological dissolution of MAP by means of combining MAP with nitrification-anammox process (Fig 1) or combining MAP with nitrification-denitrification process (Fig 2). The laboratory research was

![Fig. 2 Combination of nitrification/denitrification and MAP (Hassanzadeh, 2005)](image-url)
carried out at lab scale. Firstly the N and P removal as MAP formation was observed; thereafter dissolution of MAP crystalline was tested by use of different dissolution pathways.

2. WASTEWATER TREATMENT TECHNOLOGIES (WWTs)

Wastewater is classified as industrial wastewater and municipal wastewater. Usually, industrial wastewater after pretreatment with compatible characteristics is discharged to the municipal sewer and will be treated in municipal wastewater treatment plant with municipal wastewater. Main contaminants in wastewater are normally suspended solids (SS), biodegradable organics (soluble organics), pathogens, heavy metals and nutrients. All these components have to be reduced to an acceptable level in order to diminish the direct or indirect harms and impacts to human and environment before water can be reused or discharged to natural water body.

2.1. WWT Principle

Wastewater treatment system can be classified into two types: biological and physical/chemical. Wastewater treatment is a combination system of unit operations and unit processes designed to eliminate certain constituents in wastewater, where unit operations involve contaminant removal by physical forces, unit processes comprise biological and/or chemical treatment processes (Peavy et al., 1985). The treatment system may generally consist of 6 treatment steps (Fig. 3):

Preliminary treatment
Wastewater contains diverse suspended solids with wide various sizes, shapes and densities. Removal of these solids is the first step of wastewater treatment, because large objects or grit might damage facilities. This process comprises of unit operations such as screening, grinding and grit routings (Peavy et al., 1985; Mancl, 1996).

Primary settling
The effluent from preliminary treatment is retained in primary settling tank for up to a few hours, organic suspended matter is settled down or float to the surface. Mostly, the density of this material is quite similar with that of water, which means that enough time is required for separation. At the bottom of settling tank, the scraper is collecting settled

Fig. 3 Wastewater treatment system
sludge and conveying it to further treatment. This process plays a role on reduction of waste loading and receiving streams for secondary treatment (Peavy et al., 1985; Mancl, 1996).

**Secondary treatment**

The effluent from primary treatment contains 40%-50% of suspended solids and all of dissolved organics. Biological treatment is adopted to eliminate the dissolved organics. Microorganisms are used in consuming organics as food supply and converting them into biological cells or biomass. There are three approaches to implement secondary treatment: fixed film, suspended growth and sewage lagoon system.

Fixed film system is material such as rock, sand and plastic on which microorganisms can grow on. Organic matter and nutrients are absorbed from wastewater when it passes through the film of microorganisms fixed on. Therefore the film of microorganisms grows and thickens.

Suspended growth systems mix microorganisms in wastewater. Microorganisms grow in quantities with absorbing organic matters and nutrients from wastewater. Thereafter they settle out as sludge. Some of them are returned back into the treatment system.

Sewage lagoon systems allow the natural degradation of waste by retaining wastewater in a shallow earthen basin for a certain long enough period. Oxygen is provided artificially in the course of natural purification process (Mancl, 1996; Hassanzadeh, 2005.).

**Effluent disinfection**

Disinfection of effluent is an essential process when a portion of effluent may come in contact with humans. As similar as disinfection of ground water, chemical oxidants are generally the most effective disinfectants with required much higher dosage than those for ground water, for instance chlorination (Peavy et al., 1985).

**Advanced wastewater treatment (tertiary treatment)**

Effluent from secondary treatment might not always fulfill discharge criteria. This is normally reflected by the presence of undesirable loading of nutrients in effluent, for instance nitrogen and phosphorus compounds. Additional treatment, usually referred to as advanced wastewater treatment, is adopted. In this process nitrogen and phosphorus are removed to an acceptable level. Remained dissolved organic solids are removed in further stages (Peavy et al., 1985).

**Sludge treatment**

Sludge is concentrated solids generated from wastewater treatment. The sludge always contains much undesirable hazardous components. It must be stabilized and disposed properly for preventing disease diffusion in environment. Mostly, sludge is thickened by a thickener for volume reduction right after the wastewater treatment. Such concentrated sludge is then stabilized by biological degradation for example anaerobic/aerobic digestion, so that the degradable organic material is rendered inert prior to disposal. Stabilized sludge is further disposed ultimately by incineration, land-filling or reused as fertilizer (Mancl, 1996).

### 2.2. Nutrient removal

Nutrients are the essential constituents for the growth and reproduction of plants, animals and humans. The largest proportion of nutrients is used in agriculture as fertilizer. They are dissolved in soil phase and absorbed by crops roots, while some of them are transported into adjacent water body by agricultural runoff. The common nutrients in
wastewater are nitrogen (N) and phosphorus (P) compounds. They are mainly supplied from human activities. Excess of nutrients causes eutrophication (Gustafsson et al., 2007). Although the nutrient loading of wastewater is not as large as the one contributed by agricultural runoff and other sources, the nature of aquatic environment makes them amenable to control techniques (Peavy et al., 1985).

**Nitrogen removal**

Nitrogen is the main constituent of proteins and many biological compounds. In raw municipal wastewater, nitrogen concentration is in the range of 15-50 mg/L. It mainly exists in the form of organic nitrogen (approx. 20 %) and ammonia (NH3) (approx. 80 %). Organic nitrogen exists in both soluble and particulate forms. Both of them are transformed to ammonium by microorganisms in biological treatment. Ammonium (NH4+) results from bio-decomposition of proteins. During the release of soluble organic nitrogen, complex organic matter is broken down by bacterial decomposition and hydrolysed to ammonium (Eq. 1). When oxygen is present, ammonium is oxidized to nitrite (NO2-) and then to nitrate (NO3-) (Eq. 2; Eq. 3). These processes can be expressed as:

\[
\begin{align*}
\text{NH}_4^+ & \leftrightarrow \text{NH}_3 + \text{H}^+ & (1) \\
\text{NH}_4^+ + 3/2\text{O}_2 & \rightarrow \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O} & (2) \\
\text{NO}_2^- + 1/2\text{O}_2 & \rightarrow \text{NO}_3^- & (3)
\end{align*}
\]

Conventionally, the reduction of organic nitrogen is not benefited much by primary sedimentation, particulate organic nitrogen rarely settle out in this process, but in secondary treatment, nitrogen removal is increased more than 50 %. In primary and secondary treatment, 25 % to 75 % of organic nitrogen can be removed, of which part is transformed to ammonium. The common technology for nitrogen removal in wastewater treatment plant refers to biological nitrification-denitrification. Soluble organic nitrogen and partial particulate organic nitrogen are transformed into ammonium and other inorganic forms in this phase (George et al., 2003).

**Nitrification/ Denitrification**

Biological nitrification is an aerobic autotrophic process in which *Nitrosomonas* consume ammonia nitrogen as energy source. Ammonium is then oxidized to nitrite (Eq. 4). Afterwards, nitrite is oxidized to nitrate by *Nitrobacter* (Eq. 5). Biological nitrification is functioning when ammonia removal requirement exists without the demand of complete nitrogen removal.

*Nitrosomonas*:

\[
\begin{align*}
\text{NH}_4^+ + 1.5\text{O}_2 + 2\text{HCO}_3^- & \rightarrow \text{NO}_2^- + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} & (4)
\end{align*}
\]

*Nitrobacter*:

\[
\begin{align*}
\text{NO}_2^- + 0.5\text{O}_2 & \rightarrow \text{NO}_3^- & (5)
\end{align*}
\]

Once ammonium is oxidized with bicarbonate utilization, nitrate and carbonate acid are generated. In this case, no external carbon source is required in the process. Produced energy is used for microorganisms’ growth (George et al., 2003).

During the biological denitrification process, heterotrophic bacteria use oxygen from nitrite and nitrate, and transform nitrite to nitrogen gas (N2) (Eq. 6 & 7). Methanol is often provided as external carbon source supplement for the reaction. This process must be performed in an anoxic environment. The reactions upon the methanol supplement are performed as below (Hassanzadeh, 2005):
The combination of two reactions can be expressed as:

\[ \text{NO}_3^- + \frac{5}{6} \text{CH}_3\text{OH} \rightarrow \frac{1}{2} \text{N}_2 + \frac{5}{6} \text{CO}_2 + \frac{7}{6} \text{H}_2\text{O} + \text{OH}^- \]  

The kinetics of biological nitrification and denitrification are affected by several environmental factors, such as ammonia concentration, pH-value, temperature, and dissolved oxygen (DO) level. Because the activity of bacteria is quite depending on pH value, the optimum pH level has been observed at the range of 6.8 to 8.0. The DO content in treatment process drives the rate of nitrifier growth and nitrification reaction. A high concentration of DO promotes the growth of \textit{nitrosomonas} and \textit{nitrobacter} species in the nitrification process. A high concentration of DO inhibits the denitrification process, because denitrification reaction is proceeding in anoxic environment. Once oxygen exists, it is used as electron acceptor instead of nitrates. denitrification process is thus inhibited (Hassanzadeh, 2005).

Nitrogen content with a high concentration range from 300 to 1500 mg N/L in wastewater is referred to as “High strength nitrogen wastewater”. This high strength nitrogen can be removed by some new biological treatment processes: SHARON (Single reactor system for High activity Ammonium Removal Over Nitrite), ANAMMOX (ANAerobic AMMonium OXidation), CANON (Completely Autotrophic Nitrogen removal Over Nitrite) and OLAND (Oxygen Limited Autotrophic Nitrification and Denitrification system). The different mechanisms of nitrogen removal are described in Figure 4.

As Figure 4 shows, the SHARON process converts ammonium nitrogen to nitrite and subsequently reduces nitrite to nitrogen. This is a cost-effective treatment for nitrogen removal, taking place in single and completely mixed reactor tanks without retaining biomass by use of return sludge. High temperature around 35°C is kept during reaction procedure to ensure only nitrite is formed in the reactor. Comparing SHARON process, ANAMMOX process is new pathway much simpler for nitrogen removal. Within this process, ammonium and nitrite are transformed straightly into nitrogen gas at anaerobic condition (Hassanzadeh, 2005).
ANAMMOX (Anaerobic AMMonium Oxidation process) is a biological nitrogen removal process which seems to be the most profitable among the new treatment pathways. In this process, ammonium and nitrite are converted directly to nitrogen gas under anaerobic condition, where ammonium acts as electron donor and nitrite as electron acceptor. The anammox process is totally autotrophic, so there is no extra methanol or carbon source needed for bacteria activities. The reaction can be described by the formula:

\[ \text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \]  (9)

There are generally three genera of anammox bacteria: Brocadia, Kuenenia and Scalindua. Their activations are depending on the pH level and temperature. Anammox bacteria are active in the range of pH 6 to 8 with optimum value 7 and within temperature 6-43°C with best at 37°C. Anammox stoichiometry might be presented based on mass balance over anammox abundance culture (Cema et al., 2005):

\[
\begin{align*}
\text{NH}_4^+ + 1.32\text{NO}_2^- + 0.066\text{HCO}_3^- + 0.13\text{H}^+ & \rightarrow \\
0.26\text{NO}_3^- + 1.02\text{N}_2 + 0.066\text{CH}_2\text{O}0.5\text{N}_{0.15} + 2.03\text{H}_2\text{O}
\end{align*}
\]  (10)

As formula shows, part of nitrite is to be oxidized to nitrate as electron donator which is necessary for cell growth. The ratio between ammonium and nitrite should be 1:1.32, which can be achieved by partial

![Diagram of Partial nitritation-Anammox process](Atkins, 2007)

**Fig. 5 Partial nitritation-Anammox process (Atkins, 2007)**

**Partial nitritation-anammox**

- Biological treatment
- Sludge treatment
- Supernatant 500-2000mg N/l
- Sludge disposal

![Diagram of Wastewater treatment with Anammox treatment for side-stream](Atkins, 2007)

**Fig. 6 Wastewater treatment with Anammox treatment for side-stream (Atkins, 2007)**
nitritation process (Fig. 5). In partial nitritation process is usually followed by the anammox process. Partial ammonium is oxidized to nitrite and subsequently nitrite and ammonium are converted to nitrogen gas during anammox process. The operation conditions of the anammox process is not critical but the process would also be constrained if nitrite concentration is higher than 20 mM, if nitrite concentration retains over 5 mM up to 12 hours, anammox process is totally inhibited. Besides, the presence of oxygen influences the anammox process. It was found by Third (2003) that anammox process was completely inhibited even at oxygen concentration as low as 0.5 % air saturation, but by Joss et al (2009), nitrite oxidation and anammox reaction occurred simultaneously at continuously dissolved oxygen supplement less than 1 mg O₂/l.

Figure 6 presents the application of anammox process in wastewater treatment. Anammox process is used in side stream for the supernatant with high nitrogen content from anaerobic sludge digestion and dewatering. The supernatant normally contains concentrated nitrogen from 500-2000 mg N/l. Ammonium nitrogen in supernatant is efficiently diminished through anammox process combined with partial nitritation (Fig. 5).

Another benefit from the adoption of anammox process is the remarkable reduction of greenhouse gas. 95 % of overall CO₂ emission from wastewater treatment plant is reduced through anammox process where anammox bacteria consume CO₂ as energy source (Van Loosdrecht, 2004).

**Phosphorus removal**

Another major cause of eutrophication in receiving water is phosphorus. Typical forms of phosphorus in wastewater involve orthophosphates, polyphosphates and organic phosphates. Orthophosphates are presented in soluble form by PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, H₃PO₄ and ready for biological absorption without degradation. In ordinary primary and secondary wastewater treatment, phosphorus removal is deficient since the majority of phosphorus is in soluble form. Only 5 %-10 % of phosphorus is removed through primary sedimentation. Subsequently 10 %-20 % of phosphorus is removed by secondary biological uptake without mineral addition (George et al., 2003). As documented, the addition of chemical compounds in primary and secondary treatment has a positive influence on the effectiveness of phosphorus removal. The removals of phosphorus with addition of chemical compounds are up to 70-90 % and 80-95 % (Table 6) in primary and secondary treatment respectively (George et al., 2003).

![Fig. 7 Interpretation of biological phosphorus removal (Levlin, 2008)](image-url)
New Possibilities of magnesium utilization in wastewater treatment and nutrients recovery

**Chemical precipitation**

Phosphorus removal can be accomplished by the combination of chemical precipitation and biological method. Chemical precipitation is commonly done by addition of iron (Fe) or aluminum (Al) compounds, for instant ferric chloride and aluminum sulfate. These metallic ions can be added before primary sedimentation for precipitating phosphorus in raw wastewater. Their mechanisms can be written as:

**Aluminum:**

$$\text{Al}_2\text{(SO}_4\text{)}_3\cdot14\text{H}_2\text{O} + 2\text{HPO}_4^{2-} \rightarrow 2\text{AlPO}_4\downarrow + 2\text{H}^+ + 3\text{SO}_4^{2-} + 14\text{H}_2\text{O} \quad (11)$$

**Iron:**

$$\text{FeCl}_3 + \text{HPO}_4^{2-} \rightarrow \text{FePO}_4\downarrow + \text{H}^+ + 3\text{Cl}^- \quad (12)$$

Aluminum and iron treatment lead to the reduction of pH value. The optimum pH for aluminum treatment is approximately 5.5-6.0 and for iron treatment near 5.0 although with a good function up to pH 8. Another chemical compound often applied for coagulation is lime. Lime treatment (Eq.13&14) takes place in alkaline environment and the optimum pH is 10-11 (George et al., 2003).

**Lime:**

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad (13)$$

$$5\text{Ca(OH)}_2 + 3\text{HPO}_4^{2-} \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH}\downarrow + 3\text{H}_2\text{O} + 6\text{OH}^- \quad (14)$$

**Biological phosphorus removal**

Right after primary settling, water is let into biological compartment. Biological phosphorus removal can be implemented by modified operation of the activated sludge process. It always contains an anaerobic-aerobic sequence. Phosphates in wastewater are accumulated by bacteria within their cells and then can be removed in activated sludge. During the first anaerobic phase, release of phosphate occurs, and the concentration of phosphate increases continuously in the anaerobic stage. During the aerobic phase, the released phosphate is assimilated and stored as polyphosphate in bacteria cell, presenting a net removal with metabolism. Then, the biomass can be separated and recycled along with sludge settling (Eugene & Weiner, 2000). This metabolism mechanism is illustrated in Figure 7.

![Diagram](image_url)

*Fig. 8 Utilization of magnesium compounds in WWT*
3. ADOPTION OF MAGNESIUM SALTS IN WWT

Magnesium is one of the most important rock-forming minerals and constitutes 2% of earth’s crust. It is also the second most abundant element after sodium in sea water and is usually presented in soluble form of magnesium chloride (MgCl₂). It is one of the chemical compounds that give the rise to hardness of water (Shand, 2006). Yet, magnesium is a non-expensive chemical, being used in water and waste water treatment process with a large commercial potential. Since the 60’s of last century, magnesium salts have been investigated. It has been demonstrated that the effectiveness of magnesium compounds used in wastewater treatment is remarkable within a certain alkaline pH range. The removal of suspended solids (SS), organics and turbidity in wastewater have been found to be higher than those by conventional chemical precipitation. Besides, magnesium compounds are quite effective in inactivating fecal bacteria in wastewater (Diwani & Rafie, 2003). Moreover, magnesium compound was found to be a good reagent in phosphorus and nitrogen recycling. Usually, phosphorus and nitrogen are presented in soluble forms as phosphate (PO₄³⁻) and ammonium (NH₄⁺) in wastewater, phosphate and ammonium are precipitated easily by magnesium compounds for instance magnesium chloride (MgCl₂) in specific pH value 9.0-11.5 (Diwani & Rafie, 2003). This technique allows not only to remove but also to recover nutrients.

The main mechanism of magnesium treatment is not differed from other mineral precipitation but gives higher treatment efficiency and nutrients removal. The precipitate generated by the addition of magnesium salts is magnesium ammonium phosphate (MAP), so called struvite. The reaction can be described by following formula (Buchana, 1994):

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} \rightarrow \text{MgNH}_4\text{PO}_4 \]  

In the research of Diwani & Rafie (2003), bitterns as the source of Mg²⁺ were used as coagulants in municipal wastewater treatment. The removal of suspended solids and turbidity exceeded 99%, while COD (organic matter) removal reached 90%. These can be compared with those by other mineral flocculations, for instance iron, which gives 60-75% for SS removal and 50-80% for COD removal (George et al., 2003). The application of magnesium salts in wastewater treatment process can be modified based on chemical precipitation in WWT (Fig. 8).

As Fig.8 shows, magnesium salts are added into the main stream of wastewater before primary sedimentation and into the supernatant from activated sludge outlet (side stream). To implement the formation of MAP, relevant factors which would affect the reaction are necessary to
be considered. Particularly pH is one of the most important factors since MAP formation occurs under alkaline condition. The optimal pH range for MAP formation is pH 9.0-11.5. It was indicated that MAP precipitation starts slightly at approximately pH 7.9-9 (Doyle et al., 2000), becomes significant over pH 10.5, and is completed during pH 11-11.5. A good clarification of wastewater is usually reached in this range (Dziubek & Kowal, 1984).

Another main factor that affects the implementation of MAP formation is the molar ratio of Mg: N: P. MAP formed as hard crystalline deposit when molar ratio of Mg: NH₄: PO₄ was greater than 1:1:1, especially when the molar ratio of Mg: PO₄ was larger than 1.05:1, MAP precipitation occurred (Jaffer et al., 2002).

The solubility of MAP is also pH dependent since magnesium ammonium phosphate is obtained at high pH values 9.0-11.5. This implies MAP precipitates are soluble under acidic circumstance, with tendency of higher dissolution rate at lower pH value. As recorded, solubility of MAP it is barely soluble when pH range is up to 9.0-10.7 (Nelson et al., 2003).

4. MATERIALS AND METHODS

4.1. Materials

Various materials used in the research work include municipal wastewater, activated sludge, anammox bacteria and several chemical compounds.

Municipal wastewater before primary treatment (raw wastewater) was taken from KTH-IVL wastewater treatment pilot plant-Hammarby Sjöstadverket with initial magnesium ions approx. 5 mg/l and calcium ions approx. 26 mg/l (Levlin & Hultman, 2008). pH value of raw wastewater was 7.63 and concentration of suspended solid (SS) was 0.448 g SS/l wastewater. Phosphate phosphorus concentration was 4.15 mg/l and ammonium nitrogen 39.26 mg/l. Chemical oxygen demand (COD) of wastewater was 1015 mg COD/l.

Chemical reagents required were: Magnesium chloride hexahydrate (MgCl₂•6H₂O), calcium chloride dihydrates (CaCl₂•2H₂O), sodium hydroxide (NaOH), sodium nitrite (NaNO₂) and sulfuric acid (H₂SO₄).

Struvite crystalline from PHOSNIX with “the lake Shinji Eastern Clarification Center of Shimane prefecture”, Japan, has the formula MgNH₄PO₄•6H₂O and was used to test MAP solubilization at concentration 2 g/l.

Activated sludge with nitrification bacteria was taken from Hammarby Sjöstadverket. Initial pH value of activated sludge was 7.25, suspended solid was 3.2 g/l, total nitrogen was 38.5 mg/l and total phosphorus was 2.0 mg/l.

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<th>Main phosphates</th>
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<tr>
<td>3</td>
<td>H₂PO₄⁻</td>
</tr>
<tr>
<td>4</td>
<td>H₃PO₄⁻</td>
</tr>
<tr>
<td>5</td>
<td>H₂PO₄⁻</td>
</tr>
<tr>
<td>6</td>
<td>H₃PO₄⁻</td>
</tr>
<tr>
<td>7</td>
<td>50% H₃PO₄⁻; 50% HPO₄²⁻</td>
</tr>
</tbody>
</table>
24.6 mg/l.

Kaldnes ring was one of the components in the research. It is small plastic ring with diameter 9 mm and a cross inside. Anammox bacteria are attached on inner wall of rings (Fig. 9). Kaldnes rings were adopted to complete the anammox process.

4.2. Methods

This project consisted of 3 batch of experiments on laboratory scale (Append. I). First, precipitation of MAP was carried out for investigating the phosphorus and nitrogen removal from raw wastewater. Secondly, solubility of struvite was tested under different pH conditions. Finally, the feasibility of biological dissolutions of struvite by nitrification and anammox bacteria were investigated as central research. The 3 batch experiments established by different methodologies are described as below:

4.2.1. Precipitation of MAP

Precipitation of MAP was done by addition of magnesium chloride hexahydrate (MgCl₂•6H₂O) into raw wastewater, followed by flocculation and sedimentation.

‘Modde’ model was used for experimental design. Modde refers to as “modeling and design” and is a program for generation and evaluation of statistical experimental designs. The basic idea is to vary all relevant factors simultaneously over a set of planned experiments and then connect the results by means of a mathematical model. This model is then used for interpretation, evaluation and optimization by experimental results through 3-D graphical means.

15 experiments were designed by Modde with different combinations of 3 parameters, which are considered as most influencing for MAP formation in experiments: Mg²⁺ dosage, pH level and Ca²⁺ dosage. There were mainly three variables for each parameter: 1) Mg²⁺ dosage: 5 mg/l, 10 mg/l, 15 mg/l, 2) pH level: 9.5, 10.5, 11.5, 3) and Ca²⁺ dosage: 10 mg/l, 20 mg/l, 30 mg/l. MgCl₂•6H₂O was used as Mg²⁺ source for the MAP formation combining the addition of calcium chloride dehydrate (CaCl₂•2H₂O). Sodium hydroxide (NaOH) was added for pH adjustment.

All experiments were performed in parallel with 1 liter wastewater for each. The planned amount of MgCl₂•6H₂O and CaCl₂•2H₂O were added into water sample as coagulants at beginning of experiment, meanwhile NaOH was added to raise pH to a specific level. Right after, flocculation was performed by “Kemira minifloculator” for 30 minutes under 20 rpm/min and subsequently sedimentation occurred for 1 hour.

Several measurements were performed to wastewater decantate after sedimentation: pH, Conductivity (K), Alkalinity, SS, Volatile suspended solid (VSS), Chemical oxygen demand (COD), the concentration of Total phosphorus (Pₜₒₜ), Total nitrogen (Nₜₒₜ), Nitrate nitrogen (NO₃⁻), Nitrite (NO₂⁻), Soluble phosphorus (PO₄³⁻) and Ammonium (NH₄⁺).

4.2.2. Solubility of struvite at different pH values

The solubility of struvite was tested by acidic dissolution of struvite at different pH values. Sulfuric acid (H₂SO₄) at pH 2, 3, 4 and distilled water at pH 6.3 were used as dissolvent. The used struvite was crystalline from Japan with a concentration of 2 g/l. Two groups of samples with different ratios between struvite and sulfuric acid were: Group A: struvite/ H₂SO₄ = 2:1; Group B: struvite/H₂SO₄ = 1:2. Dosages of struvite were based on stoichiometry of the reaction formulae:
MgNH₄PO₄ + H⁺ $\rightarrow$ Mg²⁺ + NH₄⁺ + HPO₄²⁻ (16)  
MgNH₄PO₄ + 2H⁺ $\rightarrow$ Mg²⁺ + NH₄⁺ + H₂PO₄⁻ (17)  
MgNH₄PO₄ + 3H⁺ $\rightarrow$ Mg²⁺ + NH₄⁺ + H₃PO₄ (18)

Under different pH conditions, different phosphate compounds would be released (Table 1). Struvite as used was assumed to have the formula MgNH₄PO₄•6H₂O at temperatures 25°C. At heating to 100°C the used struvite was transformed to MgNH₄PO₄•H₂O and Mg₂P₂O₇ at 600°C, struvite gradually lost its crystal water and ammonium content. Ammonium was removed as ammonia. Ultimately pH, conductivity and NH₄⁺ concentration were measured after 24 hours for evaluation of struvite solubility.

4.2.3. Biological dissolution of struvite

This experiment consisted of three sub-experiments by use of different biological bacteria:

- **Nitrification sludge with aeration**: An important constituent of this activated sludge was nitrification bacteria with initial pH 7.25 and 3.2 g SS/l. 1 g of struvite was added into a 1 liter nitrification sludge and dissolved by nitrification bacteria. Simultaneously, the reaction was aerated continuously at oxygen concentration 3 mg O₂/l. The reaction lasted for 1 month.

- **Anammox bacteria with aeration**: 70 pieces of kaldnes ring with attached anammox bacteria were mixed with 200 mg of struvite in 1 liter sludge supernatant, while it was aerated with the oxygen concentration 3 mg O₂/l for partial nitritation. The reaction lasted for a month.

- **Anammox bacteria without air supplement**: 70 pieces of kaldnes ring with attached anammox bacteria were mixed with 200 mg of struvite in 1 liter water, meanwhile, 15 mg/l NO₂-N/l was provided by addition of sodium nitrite into sample, to accomplish transformation of nitrite and released ammonium to nitrogen gas. The reaction lasted for one month.

Along with the operation of biological dissolution of struvite, parameters including pH, conductivity and alkalinity were measured. In parallel, concentration of P₉, N₉, PO₄³⁻, NO₂⁻, NO₃⁻ and NH₄⁺ were measured for evaluating dissolution feasibility.

4.3. Measurements

**pH-value**

pH is a numerical expression of hydrogen ions concentration in water. It is defined as the negative base₁₀ logarithm of H⁺ concentration in mole/litre according to the following equation (Eugene & Weiner, 2000):

$$\text{pH} = -\log_{10}[H^+]$$ (19)

pH was measured by a pH meter.

**Conductivity (K)**

Conductivity is the ability of how well a solution can conduct electricity. Conductivity measurement is widely used in detection of contaminants in water. Logically high conductivity is resulted from high concentration of ions. The units of conductivity are Siemens/cm (S/cm), formally called mho/cm. It covers a wide range of water conductivities from pure water at less than 0.1 μS/cm to values over 1 S/cm in concentrated solution. It is described by the following equation (Emerson, 2004).
\[ \lambda = z \times F \times u \] (20)

Where:
- \( \lambda \) is molar ionic conductivity (Sm²/mol)
- \( z \) is ion charge
- \( F \) is Faraday’s constant (96500 C)
- \( u \) is electric mobility

Conductivity was one of the most representative indicators of nutrient content in water in this project. It was measured with conductivity meter at 25°C in the range 0-2000 \( \mu \)S/cm.

**Alkalinity**

Alkalinity is an indicator of the total dissolved inorganic carbon in water, which includes bicarbonate (HCO\(_3\)) and carbonate (CO\(_3^{2-}\)) anions. Alkalinity is determined by measuring how much acid is titrated to reduce the pH value to 5.4. The most important elements that influence alkalinity of water are bicarbonate (HCO\(_3\)), carbonate (CO\(_3^{2-}\)) and hydroxyl ion (OH\(^-\)). Their total concentration is presented as alkalinity. Other factors that might cause alkalinity are phosphate ion and dissolved ammonia. (Eugene & Weiner, 2000). Alkalinity is usually defined in following equation [other references] (Gustafsson et al., 2007):

\[
\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + 2[\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] - [\text{H}^+] \quad (21)
\]

In alkalinity measurement, 10 ml sample is titrated with 20 mmol/l HCl to decrease pH value to 5.4. The volume of consumed hydrochloric acid is recorded for alkalinity calculation (Eq. 22):

\[
\text{Alkalinity} = \frac{V_{\text{HCl}} - V_{\text{water}}}{V_{\text{HCl}}} \times C_{\text{HCl}} \quad \text{mmol/l} \quad (22)
\]

Where:
- \( V_{\text{HCl}} \) is consumed HCl volume (ml)
- \( C_{\text{HCl}} \) is the concentration of hydrochloric acid (mmol/l)
- \( V_{\text{water}} \) is volume consumption of HCl to reduce 10 ml distilled water to pH 5.4 (ml)

**SS, VSS**

Suspended solid (SS) is the small particles that retain suspended in water. They are usually organic and mineral particles that presented as colloids. Volatile suspended solid (VSS) is the loss of solids when SS is ignited over 530°C. This solid mostly consists of organic materials and also crystalline and absorbed water. In another word, it is a parameter that measures biomass growth in full-scale biological wastewater treatment systems. Both of SS and VSS are statistical indicator of water quality (Eugene & Weiner, 2000).

SS/VSS was measured by filtering certain volume of sample with 55 g/m² glass fiber, and then would be ignited in 105°C and 530°C oven respectively for 1 hour and dried in desiccator for 20 minutes. SS and VSS are calculated through equations:

\[
SS = \frac{m_{\text{sample,105\(^\circ\)C}} - m_{\text{glass fiber}}}{V_{\text{sample}}} \times 1000 \quad \text{g/l} \quad (23)
\]

Where:
- \( m_{\text{sample,105\(^\circ\)C}} \) is weight of remained solid and glass fiber after 105°C (g)
New Possibilities of magnesium utilization in wastewater treatment and nutrients recovery

\[
m_{\text{glass fiber}} \quad \text{is weight of glass fiber before filtration (g)}
\]

\[
V_{\text{sample}} \quad \text{is volume of filtrated sample (ml)}
\]

\[
\text{VSS} = \frac{m_{\text{sample,530°C}} - m_{\text{sample,105°C}} - m_{\text{glass fiber}}}{V_{\text{sample}}} \times 1000 \quad \text{g/l}
\]  \hspace{1cm} (24)

Where

\[
m_{\text{sample,530°C}} \quad \text{is weight of remained solid and glass fiber after 530°C (g)}
\]

\[
m_{\text{sample,105°C}} \quad \text{is weight of remained solid and glass fiber after 105°C (g)}
\]

\[
m_{\text{glass fiber}} \quad \text{is weight of glass fiber before filtration (g)}
\]

\[
V_{\text{sample}} \quad \text{is volume of filtrated sample (ml)}
\]

COD

Chemical oxygen demand (COD) is defined as the chemical oxygen consumed when organic matter is oxidized to carbon dioxide and water by chemical oxidants. Normally in aquatic parameters, COD presents as indicator of organic material quantity in water. It analyzes both chemically and biologically oxidizable organic matters. Its unit is mg/l COD (Eugene & Weiner, 2000). The measurement was done by spectrophotometer with 620 nm wavelength and high range COD concentration.

\textbf{\textit{P}tot, \textit{N}tot, P\textit{PO}_4^{3-}, \textit{NO}_2^-, \textit{NO}_3^-, \textit{NH}_4^+ \textit{measurements}}

The concentrations of these chemical compounds were measured by Aquatec®, which is an automated system for water analysis. The main types of determination were ammonium, nitrite, nitrate, and phosphate. Samples for total phosphorus and total nitrogen analysis were treated by addition 4 M sulfuric acid plus potassium-per sulfate solution and digestion solution, and subsequently steamed in Autocave at 100°C before analysis. The analysis of different compounds were carried out under different wavelength and concentration respectively: \textit{P}tot-P (690 nm, 0-5 mg/l), \textit{N}tot-N (540 nm, 0-5 mg/l), \textit{PO}_4^{3-}-P (690 nm, 0-10 mg/l), \textit{NO}_3^-\textit{N} (540 nm, 0-5 mg/l), \textit{NO}_2^-\textit{N} (540 nm, 0-1000 μg/l), \textit{NH}_4^+\textit{N} (590 nm, 0-10 mg/l).

![Mg dosage and pH value in corresponding experiment](image)

*Fig. 10 Experiments with different Mg dosages and pH values*
5. RESULTS

5.1. Precipitation of magnesium ammonium phosphate (MAP)

After 15 experiments with corresponding magnesium dosage and pH values (Fig. 10), all required analyses were performed.

Removal degree of SS, COD, PO₄³⁻-P and NH₄⁺-N from 15 experiments were applied into Modde program as response factors. They were analyzed by response surface modeling to evaluate the optimal experimental conditions (section 6).

According to the numerical results (Appendix 1), the highest SS removal rate was up to 92 % at pH range 10.5-11 while optimal total COD removal rate was up to 83.9 % between pH 10-10.5, whereas soluble COD increased. The removal of VSS reached 91 % (Fig. 11).

Due to the addition of calcium chloride and sodium hydroxide, pH of wastewater increased from original 7.63 to 9.5-11.5, meaning that alkalinity of water increased in accordance with increase of [OH⁻]. The alkalinity of all water samples after reaction was 10-30 times higher than original ones. The same tendency occurred to the conductivity.

It was shown that conductivities after reaction were generally 200-600 μS/cm higher than those in raw wastewater.

There were significant reductions in phosphorus concentration. P_{tot} removal reached 83 % while PO₄³⁻-P removal reached 97 %. But

Table 2. SS removal rates and NH₄⁺-N productions at pH 2 (Group A&B)

<table>
<thead>
<tr>
<th>Group A (struvite/sulfuric acid = 2:1)</th>
<th>SS removal (%)</th>
<th>NH₄⁺-N (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite at 25°C</td>
<td>99.60</td>
<td>115.50</td>
</tr>
<tr>
<td>Struvite at 100°C</td>
<td>99.70</td>
<td>45.35</td>
</tr>
<tr>
<td>Struvite at 600°C</td>
<td>91.80</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group B (struvite/sulfuric acid = 1:2)</th>
<th>SS removal (%)</th>
<th>NH₄⁺-N (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite at 25°C</td>
<td>99.80</td>
<td>30.40</td>
</tr>
<tr>
<td>Struvite at 100°C</td>
<td>99.40</td>
<td>10.44</td>
</tr>
<tr>
<td>Struvite at 600°C</td>
<td>99.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Fig. 11 Removal rates of different components in the experiments
Table 3. SS removal rates and NH\textsubscript{4}+-N productions at pH 3 (Group A&B)

<table>
<thead>
<tr>
<th></th>
<th>SSremoval (%)</th>
<th>NH\textsubscript{4}+-N (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group A:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite at 25 C</td>
<td>92</td>
<td>15.12</td>
</tr>
<tr>
<td>Struvite at 100 C</td>
<td>100</td>
<td>5.89</td>
</tr>
<tr>
<td>Struvite at 600 C</td>
<td>90.79</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Group B:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite at 25 C</td>
<td>100</td>
<td>4.40</td>
</tr>
<tr>
<td>Struvite at 100 C</td>
<td>100</td>
<td>1.28</td>
</tr>
<tr>
<td>Struvite at 600 C</td>
<td>73.68</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Nitrogen removals are not as high as phosphorus. The highest removal rate presented in all experiment results was 48% for N\textsubscript{tot} removal and 57% for NH\textsubscript{4}+-N removal (Fig. 11). There was also some increase of NH\textsubscript{4}+-N content in some experiments, as represented in appendix 1.

5.2. Acidity solubilization of struvite

At the start of experiment, SS, conductivity and pH values of initial samples were measured before reaction. Initial SS was the weight of used struvite. pH values and conductivity were measured by pH meter and conductivity meter respectively. Ammonium concentration at the beginning was zero. The removal of SS and NH\textsubscript{4}+-N concentrations were measured after 24 hours and compared with initial data.

At pH 2, pH of solutions in group A increased slightly 0.1-0.25 after 24 hours, whereas conductivity of different samples decreased 4000-5000 μS/cm. pH in group B didn’t change much but slightly raised by approx. 0.01, and conductivity was reduced 1000-1500 μS/cm. Suspended solids removal and ammonium productions are presented in table 2.

Removal rates of suspended solid at different H\textsubscript{2}SO\textsubscript{4} dosages were mostly over 99% at pH 2. But the differences of NH\textsubscript{4}+-N production were large. Generally there was no NH\textsubscript{4}+-N production from dissolutions of struvite preheated to 600°C, but from dissolution of struvite at 100°C and struvite at 25°C. NH\textsubscript{4}+-N released from struvite at 25°C were around three times higher than the one at 100°C in group A and B. This was also the same in samples at pH3 and pH4 as shown in table 3 and 4.

Table 4. SS removal rates and NH\textsubscript{4}+-N productions at pH 4 (Group A&B)

<table>
<thead>
<tr>
<th></th>
<th>SSremoval (%)</th>
<th>NH\textsubscript{4}+-N (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group A:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite at 25 C</td>
<td>88</td>
<td>1.34</td>
</tr>
<tr>
<td>Struvite at 100 C</td>
<td>93.65</td>
<td>0.50</td>
</tr>
<tr>
<td>Struvite at 600 C</td>
<td>89.47</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Group B:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite at 25 C</td>
<td>100</td>
<td>0.45</td>
</tr>
<tr>
<td>Struvite at 100 C</td>
<td>100</td>
<td>0.21</td>
</tr>
<tr>
<td>Struvite at 600 C</td>
<td>68.42</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Table 5. SS removal rates and NH$_4^+$-N productions at pH 6.38 (Group A&B)

<table>
<thead>
<tr>
<th></th>
<th>SSremoval (%)</th>
<th>NH$_4^+$-N (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>struvite/sulfuric acid = 1:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite at 25 °C</td>
<td>2.2</td>
<td>0.74</td>
</tr>
<tr>
<td>Struvite at 100 °C</td>
<td>2.26</td>
<td>0.48</td>
</tr>
<tr>
<td>Struvite at 600 °C</td>
<td>0</td>
<td>0.00</td>
</tr>
</tbody>
</table>

According to similar results shown in table 3 and 4, struvite was dissolved efficiently below pH 4 both in group A and B. So it was worth to test the solubility of struvite above pH 4, because struvite was going to be dissolved at pH value 6-8 in next biological experiments. Upon the pH range of MAP formation was starting at pH value 7.9-9 and the observation of MAP solubility at pH 5-7 was carried out. Distilled water in the same pH range was used, which pH value was 6.38. The ratio between struvite and distilled water was 1:1. The results showed that after 24 hours, MAP was rarely dissolved. The SS removal rate got only 2.2 %, ammonium released was 0.74 mg/L (Table 5), whereas pH climbed up to 6.9.

5.3. Biological solubilization of struvite

5.3.1. Dissolution of struvite by nitrification sludge with aeration

The outcome of pH and conductivity measurements indicated that struvite was dissolved during the operation. The pH of solution sample was decreasing from initial 7.25 to 5.37 after one month, and conductivity increased from 638 $\mu$S/cm to 1409 $\mu$S/cm. The reaction tendencies are shown in Fig. 12. The alkalinity of wastewater was decreasing in accordance with decrease of pH value (Fig. 13). According to the increase of conductivity, it can be concluded that Mg$^{2+}$, PO$_4^{3-}$, NH$_4^+$ were released from struvite, because the dissolution of struvite conducted a high concentration of ions in water. NH$_4^+$ was oxidized to NOx due to the aeration. Their concentrations were analyzed with Aquatic® equipment. The NO$_3$-N and N$_{tot}$ concentrations increased

Fig. 12 Conductivity and pH variations in nitrification sample
Nevertheless, the concentrations of NH$_4$-N and NO$_2$-N decreased constantly during the process (Fig. 15). Obviously, the reductions of NH$_4$-N and NO$_2$-N were caused by the aeration of water sample. Ammonium was oxidized to nitrite as shown in first two days. The NH$_4$-N concentration dropped remarkably in day 1, whereas, nitrite increased in day 1 and 2 and subsequently decreased sharply and was oxidized further to nitrate.

Another view was the release of phosphate. The initial PO$_4$-P concentration in raw wastewater was 12.64 mg/l and subsequently increased to 103.6 mg/l at the end of experiment, showing the increase of total phosphorus content. As figure 16 shows, the increase of total phosphorus was generally in accordance with the increase of PO$_4$-P. They increased rapidly in first 7 days, and increased steadily during following days.

**Fig. 13 The changes of alkalinity and pH value during experiment**

from 0.25 to 140 mg/l and 38.46 to 126 mg/l respectively, shown graphically in Figure 14.
5.3.2. Dissolution of struvite by anammox bacteria with aeration

The responses from analysis showed that pH was decreasing with reaction days from original 7.2 to 6.1 at the end of reaction. Meanwhile conductivity was going up from initial 768 μS/cm to end point 1393 μS/cm shown in Fig. 17. Alkalinity of water sample decreased from the beginning 4.7 mmol/l to 0.3 mmol/l at the end of experiment (Fig 18). But anyhow pH variations didn’t exceed the pH condition which microorganisms relied on.

Fig. 19 shows the variation tendency of nitrogen concentration during reaction. It shows that NH₄-N and NO₂-N contents generally decreased. On the first day, NH₄-N concentration decreased to 0 from initial 25.65 mg/l (results from measurement, not shown on graph), and NO₂-N contents jumped up from 0.02 mg/l to 0.35 mg/l simultaneously. This was caused by the oxidation of ammonium to nitrite by aeration. This situation was just reversed in next two days. NH₄-N content increased up to 0.25 mg/l again which was released from struvite, meanwhile NO₂-N depleted to 0.004 mg/l, due to the oxidation and transformation to nitrate. During the rest of operational days, NH₄-N content increased or decreased intermittently but did not overall exceeded 0.25 mg/l, and NO₂-N decreased steadily. The total nitrogen content increased

---

![Nitrogen concentration as function of time](image1)

**Fig. 15 Reduction of ammonium and nitrite nitrogen concentrations**

![Phosphorus concentration as a function of time](image2)

**Fig. 16 Growth of phosphate phosphorus and total phosphorus contents**
constantly with the growth of NO$_3$-N from 0.068 mg/l to 110 mg/l and 23 to 97 mg/l respectively (Fig 20). As another indicator of struvite dissolution, PO$_4$-P concentration raised 5 times of original after 20 days. Figure 21 presents P$_{tot}$ and PO$_4$-P varieties.

### 5.3.3. Dissolution of struvite by anammox bacteria without aeration

The experiment was the same as 5.3.2-struvite dissolution with anammox bacteria, but without air supplement. So results of this experiment were similar as those in 5.3.2. As Fig 22 reveals, conductivity raised from 141 μS/cm to 469 μS/cm against pH reduced from 7.2 to 5.9. Alkalinity didn’t change significantly even if it fluctuated in mid-term. Alkalinity was approximately constant and reduced from 0.48 mmol/l to 0.47 mmol/l shown in Fig. 23. Concentrations of NO$_2$-N and NH$_4$-N were decreasing constantly whereas NO$_3$-N increased which represented the highest proportion of total nitrogen content in the sample (Fig. 24). Figure 25 presented that phosphate was released steadily and enhanced the total phosphorus concentration in the water sample.

---

**Fig. 17 Changes of pH and conductivity in aerated anammox sample**

**Fig. 18 pH and alkalinity tendency during experiment period**
Nitrogen concentration as a function of time

Fig. 19 Ammonium and nitrite nitrogen variations

Nitrogen concentration as a function of time

Fig. 20 Increase of nitrogen concentration

Phosphorus concentration as a function of time
(Aerated Anammox)

Fig. 21 Growth of phosphate phosphorus and total phosphorus contents
Fig. 22 Changes of pH and conductivity in anoxic anammox sample

Fig. 23 pH and alkalinity tendency during experiment

Fig. 24 The variation of nitrogen concentrations versus time
6. MODELING, EVALUATION AND DISCUSSION

The experimental results indicated that phosphorus and ammonium were removed successfully completely or partially removed from raw wastewater and recycled in biological dissolution. Nevertheless, some deficiencies should be considered.

Precipitation as MAP

Over a dozen experiments of MAP precipitation indicated high removal rates of SS, COD, PO$_4^{3-}$ and NH$_4^+$. This was due to the additions of magnesium and calcium chloride and adjustment of pH value by NaOH. The optimum conditions for obtaining high removal rates of all SS, COD and phosphorus and nitrogen were multiple factors dependent. The most significant factors were pH and magnesium contents. With obtained data, the optimization of experimental conditions was evaluated by Modde with surface response modeling method (Fig 26 and 27). The

![Fig. 25 Increase of phosphate phosphorus and total phosphorus contents](image)

![Fig. 26 Evaluations for SS and COD removals](image)
ruby area in graphs represents the optimal removal efficiency in corresponding conditions. As Fig 26 shows, the optimal SS and COD removal rates were respectively 92 % and 84 % under approx. pH 10.5 and 15 mg/l for Mg$^{2+}$ dosage. They were the same as obtained in practical works. The optimum magnesium dosing and pH range from modeling evaluations for NH$_4$-N and PO$_4$-P removal were 15 mg/l and pH 10.5-11 respectively (Fig 27). Under these conditions, optimal NH$_4$-N removal rate would achieve 67 %, which is 10 percentages higher than obtained result (57 %), PO$_4$-P removal arrives 100 % in the model, which was 97 % from empirical results in this case.

The large contrast between ammonium and phosphate removal in this case can be explained by the kinetics of MAP formation related to their molarities ratio. The molar ratio among ammonium and phosphate in raw waste water and magnesium dosage in project were [Mg$^{2+}$]:[NH$_4^+$]:[PO$_4^{3-}$]=0.29:1:0.02. These are extremely deviating from the stoichiometry of MAP formation (Eq. 15). Molar ratio among all compounds should be theoretically Mg:NH$_4$:PO$_4$=1:1:1. Obviously in this practical study, phosphate concentration was inadequate to support ammonium precipitation as MAP.

Since MAP formation was the major mechanism of ammonium nitrogen removal in primary treatment, phosphate concentration was one of important factors to promote the removal efficiency other than magnesium. The lack of phosphate content induced low ammonium removal rate. Replenishment of phosphate phosphorus to wastewater is necessary in research.

The magnesium concentration was another factor leading to the deficiency of MAP formation. In the investigation that had been carried out by Uludag et al., (2009), NH$_4^+$ and PO$_4^{3-}$ removal achieved 92 % and 94 % respectively while molar dosage of magnesium was 1.5 to 2 times of ammonium molar concentration, where 1.8 was the best. For phosphate removal, magnesium molar dosage was found by Fujimoto et
al (1991) at least 1.05 times of phosphate molar concentration to guarantee 95 % phosphate removal. To guarantee both phosphate phosphorus and ammonium nitrogen removals as MAP precipitates above 90 %, their molar ratios ought to be $\text{Mg}:\text{NH}_4:\text{PO}_4 = 1.8:1:1.7$. This is due to the possibilities of formation species of magnesium and phosphate other than MAP, for instance $\text{MgHPO}_4\cdot 3\text{H}_2\text{O}$, $\text{Mg(OH)}_2$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{CaHPO}_4$ and etc. Compared with those in this experiment, magnesium and phosphate concentration needed to be replenished. Due to the limitation of lab condition, magnesium dosage couldn’t be well prepared based on MAP stoichiometry.

Though ammonium nitrogen removal rate reached 57 % as highest value, there were still some interesting outcomes for instance $\text{NH}_4$ concentrations increased in some experiments (Append. II). The main reason would be the hydrolysis of urine and proteins, as we know they are the major constituents of municipal wastewater. When the observation turned to soluble COD removal, the increase of soluble COD was found. This may cause an increase of BOD, but it can be removed in next biological treatment step, so it is not taken into account in this research.

**Dissolution of MAP**

Generally, solubility of MAP was mainly pH dependent. Chemical dissolution of MAP showed that MAP was slowly dissolved in distilled water and dissolved rapidly below $\text{pH } 4$. This contrast was depending on the different concentrations of hydrogen ion in solutions. Since phosphate ions and ammonium ions were constantly released and hydrogen ions were consumed, alkalinity of solution increased as the result as described by Eq. 21, so that pH value rose. Biological dissolution efficiency of MAP depend not only pH value but also the size of particle surface. That means the area of contact surface of particles with bacteria determines the dissolution rate of particles, larger contact surface area conducts the higher dissolution rate, in another word, higher dissolution rated can be conducted by smaller particle, on which surface can be covered by more bacteria. Besides, the dissolution rate might be affected by the age of MAP particles. The solubility of particles is decreasing with on going time. In this thesis work, particles used have been stored for two years before experiments, so the solubility of particles has decreased, and low dissolution rate of particles in the result was due to the small area of contact surface of particles, meaning that particles should be finer.

**Dissolution of MAP with nitrification sludge**

There were not many research works concerning biological dissolution of MAP, so the direct comparison with references is limited. As illustrated objective and mechanisms of biological MAP dissolution, nitrification bacteria were the main driving force of operation. Since pH of aquatic circumstance is very important for their living and activities, they are working between pH 6-8 and most active at pH 7. The pH captured from nitrification dissolution of MAP was represented in reduction tendency. This was because hydrogen ions were continuously released (Eq. 4), and another possibility was the production hydrogen sulfide alongside nitrification. This tendency was affecting the nitrification rate, because pH value has ever been below 6, as a result the activities of nitrification bacteria slowed down.

The supplement of oxygen with 3 mg O$_2$/l was the assistance of nitrification process, when activities of nitrification bacteria slowed down, released ammonium could be oxidized with extra aerated oxygen to
guarantee that nitrification process wouldn’t be interrupted. Comparing with similar experiment reported by Levin & Hultman (2008), ammonium concentration in this research dropped mostly 99.99% reversely increased 10% in research by Levin & Hultman (2008). The probable reason is the aeration supplement.

Dissolution of MAP with anammox bacteria and continuous aeration

MAP dissolution by anammox bacteria with continuously aeration (CA) and without aeration (NA) respectively, are interesting subjects. In the results, nitrite and ammonium contents stayed less than 1 mg N/l whereas nitrate contents kept increasing during CA experiment. Anammox process could be influenced by:

1) Oxygen concentration. Oxygen concentration is a sensitive element in nitritation-anammox process, because anammox process would be constrained by oversized oxygen content. Joss et al., (2009) showed that at low oxygen concentration at ≤1 mgO2/l nitritation and anammox process occurred simultaneously, because while outer layer of sludge floc depleted oxygen diffusing into floc for nitritation, the inner part remained anaerobic. But in this experiment, oxygen supplied was kept 3 mg O2/l; this oxygen density would boost up oxidation of NH4 to NO3 with shortened retention time of NO2 for anammox process.

2) Nitrite oxidizers. According to stoichiometry molar ratio between ammonium and nitrite (Eq. 10), the standard ratio should be as high as NH4:NO2=1:1.3. But the actual ratio during experiment was mostly in ratio: NH4:NO2=1:0.03, this was a large deviation from stoichiometry. So nitrite concentration in reaction was too deficient to accomplish anammox process, in other words, oxidation of nitrite was too fast by aeration, at the same time the nitrate reduction was limited by the availability of organic substrate, anammox process is limited.

3) pH condition. The optimum pH condition for anammox bacteria activities is around pH 6.7-8.3 (Egli et al., 2001). In this experiment, pH value was mainly between 6.2 and 7.2. Though anammox bacteria are still acting at this condition, but at least their activities were slowed down. The dissolution rate was affected with the changes of activities of bacteria.

4) Struvite dissolution speed. Like demonstrated in acidic solubilization of struvite, struvite was dissolved slowly in the range of pH6-7 and with a long time consuming. As a result ammonium was slowly released with very small quantity. So the dissolution of small quantity of struvite in laboratory scale was hard to observed, but it would be more visible with batch studies in pilot plant for long time (half years) monitoring.

Dissolution of MAP with anammox bacteria at anoxic condition

This was simulating anammox process without supernatant from digested sludge, but with distilled water. This was no doubt inducing the low content of NO2 even if it was provided by addition of NaNO2. As shown by presented results, phosphate phosphorus and nitrate nitrogen were continuously increasing, the postulation of MAP dissolution by anammox bacteria was tenable. Because according to Eq. 10, nitrate nitrogen is one of the components resulting from anammox process and accumulating in solution. But the process was extremely active only in first 3 or 4 days (Fig 24). This was resulted by pH changes and nitrite contents in sample. The influence from pH and NO2 concentration has been discussed in previous MAP dissolution by anammox bacteria with aeration.
1) pH condition is the important factor which affected the activity of anammox bacteria. pH value of sample dropped from 1st day from 7.2 to 6.1 after 4 days. Obviously, anammox bacteria worked actively in first 4 days and conducted the efficient anammox reaction, whereas, low reaction efficiencies were induced during the rest of reaction period after 4 days.

2) The concentration of nitrite nitrogen is important for accomplishing anammox process. According to stoichiometrical ratio between $\text{NH}_4\text{NO}_2=1:1.3$, the amount of added $\text{NO}_2^-$ in sample should be 1.9 mmol/l in order to react with total amount ammonium released from 200 mg MAP in this research. But the actual molar amount of added nitrite was 0.87 mmol/l. This was deficient to accomplish this postulation. But due to the dissolution rate of MAP, 0.87 mmol/l $\text{NO}_2^-$ seemed to be sufficient according to the representation of Fig. 24, the production of nitrate wasn’t stopped during reaction.

Combined system for precipitation and dissolution of MAP

MAP can be precipitated by adding magnesium salts and increasing the pH value. The high removal of suspended solids, phosphorus and COD around 80-90% is in agreement with literature and higher compared with traditional precipitation agents (Table 6). It could also be expected that part of influent COD in particle form should be hydrolyzed due to high pH-value and therefore be transformed to soluble COD and that organic bound nitrogen should be transformed to ammonium, thus explaining negative reduction of ammonium in some experiments.

What was not expected from the study was the high ammonium removal in some experiments up to 57%. As the phosphate concentration is not high enough to remove such a high percentage of ammonium, other removal mechanisms may have occurred (excluding possible experimental errors). One possibility may be transfer of ammonia to the air due to the use of high pH-value but not in agreement with negative ammonium removal at similar pH values. Ammonium may also have been adsorbed on sludge (similar to ion exchange by clinoptilolite) and should be subject for further studies.

7. Conclusion

Literature studies and experimental works were performed to evaluate the possibilities to combine precipitation of MAP (struvite) with dissolution by biological means (nitrification or deammonification bacteria) and/or chemicals for recycling of magnesium and phosphate ions back to the precipitation step. The experiments were performed in laboratory scale and some experiments were evaluated by multivariate analysis. Main results of the study were:

- Magnesium compounds are abundant in nature and can be obtained as dolomite, rest products from industry or from brines from desalting plants.

<table>
<thead>
<tr>
<th>Treatment process</th>
<th>Phosphorus removal %</th>
<th>SS removal %</th>
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<tr>
<td></td>
<td>without with</td>
<td>without with</td>
</tr>
<tr>
<td>Primary</td>
<td>5-10 70-90</td>
<td>40-70 60-75</td>
</tr>
<tr>
<td>Secondary</td>
<td>10-20 80-95</td>
<td>70-95 85-95</td>
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</table>

*Table 6. Efficiency of phosphorus and SS removals with and without chemical addition (George et al., 2003)*
Addition of magnesium compounds to influent wastewater can give a removal efficiency of suspended solids, COD and phosphorus above 80% at alkaline pH-values between 10 and 11.

The alkaline pH-value gave rise to some dissolution of suspended nitrogen (to ammonium) and COD.

The removal of total phosphorus reached 83% and typically removal of phosphate reached 97%.

The removal of total nitrogen could reach 40% and in some cases a high removal efficiency (up to 57%) of ammonium was obtained and could not be explained only by MAP precipitation and other removal mechanisms were suggested (transfer to air or adsorption).

MAP can be dissolved by acids at pH-values below about 4.

Biological dissolution can be obtained at neutral pH-values by addition of nitrification or deammonification bacteria.

The mechanism for biological dissolution is probably the use of ammonium as an energy source combined with hydrogen ion production during the bacterial metabolism (similar to bacterial leaching of sulfide containing ores).

Combined MAP precipitation of the influent followed by bacterial dissolution and recycling of magnesium and phosphate back to the precipitation step seems to an interesting new process variant.

A suggestion was given to combine MAP precipitation with chlinoptilolite or other adsorption materials for improving ammonium removal efficiency before a following biological step.

From the results, it can be concluded generally that the use of magnesium in wastewater water treatment promotes not only organic material removals but also enhance nutrient removal especially phosphorus and nitrogen removal. Particularly for phosphorus removal, dosing of magnesium is necessary since phosphorus removal is sparingly undertaken in ordinary treatment.

There are increasing debate and resistance to use sludge as fertilizer for agriculture, because sludge normally contains many hazardous from wastewater for instance heavy metal. The extraction of phosphorus recycling from wastewater to agricultures in is increasing, which urges the enhancement of recycle efficiency. By the comparison of phosphorus removal rates between magnesium compounds and ordinary chemicals, it is obvious that magnesium compounds have the predominance in phosphorus recycling. The dissolution efficiency of MAP makes it amenable to be advanced fertilizer in soil phase prior to other complexes, for instance iron phosphate is insoluble in soil phase. Magnesium compounds with phosphorus may have a better acceptance for meeting goals of recycling phosphorus to productive land compared with present use of iron salts as coagulants.

8. RECOMMENDATIONS FOR FURTHER STUDIES

The introductory studies in laboratory scale together with literature studies suggest that precipitation by magnesium compounds is an interesting possibility to replace iron or aluminum salts as precipitation agents in wastewater treatment. However, further studies should be performed before implementation in full-scale can be justified. Some suggestions for further studies are (Fig. 28):
• Laboratory scale experiments of the combination of use of magnesium and iron compounds for precipitation.
• Laboratory scale experiments to evaluate the effects on ammonium removal of combined MAP precipitation with clinoptilolite addition.
• Use of supply of nitrate after biological dissolution of struvite together with soluble COD to accomplish denitrification in the main stream
• Use of produced carbon dioxide from digester or biological step to neutralize alkaline sludge before digestion or high pH value in the influent to the biological step in the main stream
• Mechanisms and kinetics of dissolution of MAP by nitrification and/or anammox bacteria.
• Possibilities to use manganese dioxide for biological oxidation of ammonium in digester supernatant or struvite to nitrite and nitrate (anaerobic nitrification)
• Removal of ammonium from MAP before digestion:
  - Dissolution of MAP by acids (biologically produced) or mineral acids of precipitated primary sludge in order to get a concentrated solution of magnesium phosphate and ammonium ions
  - Oxidation of the concentrated solution by use of nitrification or deammonification to remove ammonium and have the possibility to recycle magnesium and phosphate ions to the precipitation step (with possibilities of combined treatment with digester supernatant)
  - Hydrolysis of precipitated sludge by use of anaerobic biological treatment and/or chemicals (as NaOH) to produce soluble organic material in a concentrated form
  - Heat treatment of precipitate to remove ammonium, production of a rest product containing MgO and CaO in addition to magnesium and calcium phosphates, and use the energy of organic material for energy supply

Fig. 28 General concept of MAP precipitation and recirculation of magnesium and phosphate ions from primary treatment step
- Combination of (1) and (3) for use of a treatment step with nitrification and heterotrophic denitrification and also for alkalinity balance
- Combination of (1) and (4) to obtain an ammonium rich stream for further treatment

- Theoretical analysis of a system with combined MAP precipitation, bacterial dissolution and recycling.
- Performance in pilot plant of magnesium compounds addition after laboratory and theoretical studies as a step for full-scale implementation.
- Value of magnesium phosphate containing end product for use as fertilizer.
9. References


Other references:

APPENDICES I-EXPERIMENTAL INSTRUCTIONS

Precipitation of magnesium ammonium phosphate (MAP)

Precipitation of magnesium ammonium phosphate may be described by the formula:

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} \rightarrow \text{MgNH}_4\text{PO}_4 \]

The optimum value for precipitation is around pH10. The precipitate is an interesting substance as a product containing phosphorus from wastewater.

Material and methods

- Raw wastewater before addition of coagulants was taken from pilot plant. Some initial characters were documented (Levlin & Hultman, 2008): Mg\(^{2+}\): 5 mg/l wastewater; Ca\(^{2+}\): 26 mg/l wastewater based on drinking water composition.
- Chemicals: magnesium chloride hexahydrate (MgCl\(_2\)•6H\(_2\)O) was added as coagulant and with combined addition of calcium chloride dehydrate (CaCl\(_2\)•2H\(_2\)O). Sodium hydroxide (NaOH) was used for pH adjustment before the experiment.
- Flocculation and sedimentation were performed.

Procedure

15 experiments were arranged by use of Modde program. All experiments were established in parallel. From each, the following procedure was obeyed:

- 1 liter of completely mixed wastewater was filled into a 1 liter beaker.
- 5/10/15 mg Mg\(^{2+}\)/l were added into wastewater depending on different planned dosage compositions.
- pH value of each wastewater sample was adjusted by addition of NaOH to value 9.5/10.5/11.5 respectively.
- After pH adjustment and addition of chemical compounds. The water sample was rapidly mixed with a speed of 350 rpm/minute for 1 minute. Subsequently, the sample was flocculated at speed of 20 rpm/minute for 30 minutes. At the end of flocculation period, 200 ml sample was taken out for analysis.
- After flocculation, water sample was left for sedimentation of suspended solid up to 1 hour. Afterwards, clear supernatant (decantate) was abstracted; part of it was filtrated and stored for analysis.

Analysis for different samples

SS, VSS, total-COD, pH, alkalinity, conductivity, soluble-COD, P\(_{\text{tot}}\), N\(_{\text{tot}}\), PO\(_4^{3-}\), NH\(_4^+\).

Acidic solubilization of struvite

Struvite (MAP) has the formula MgNH\(_4\)PO\(_4\)•6H\(_2\)O. The molecular weight is approximately 245 g/mole. The dissolution can be described as depending on pH-value and dissolved phosphate might be present in the form of hydrogen phosphate, dihydrogen phosphate or phosphoric acid (Eq. 16, 17 & 18).

The necessary amount of sulfuric acid for dissolution of magnesium ammonium phosphate, were based on the formulae for dissolution of 1 mole magnesium ammonium phosphate and the main phosphate species
at a certain pH value. Main dissolved phosphates in the treatment of MAP at different pH level were approximately as in table 1.

**Material and methods**

Struvite at different temperatures were prepared:

- MgNH₄PO₄•6H₂O at room temperature 25°C.
- MgNH₄PO₄•6H₂O was heated to 100°C. The expected composition would be MgNH₄PO₄•H₂O with molecular weight 155 g/mol.
- MgNH₄PO₄•6H₂O was heated to 600°C. Mg₃P₂O₇ was obtained with a molecular weight of 236 g/mol.
- Sulfuric acid (H₂SO₄) at pH 2, 3, 4 was used.
- Vibration facility was used for improving reaction efficiency.

**Procedure**

- Preparation of struvite at temperature 100°C and 600°C.
- Struvite (MgNH₄PO₄•6H₂O) within beaker was placed separately into 100°C preheated oven and 600°C preheated oven for 1 hour.
- 1 h after, struvite from 100°C and 600°C respectively, were placed into desiccator for cooling.
- Group A samples were prepared: Different amount of struvite at room temperature was added to corresponding dosage of sulfuric acid at pH 2, 3, 4 respectively, with ratio of struvite/sulfuric acid= 2/1. The same processes were performed to struvite at 100°C and 600°C (totally 9 samples were prepared in this group).
- Group B samples were prepared as same procedure as Group A, but the ratio between struvite/sulfuric acid was 1/2 (totally 9 samples were prepared).
- All samples from Group A and B were placed on vibration facility, which kept samples shaking at speed of 150 Mot 1/min for 24 hours during dissolution process.

**Analysis**

SS, conductivity, pH value, NH₄⁺-N

**Biological solubilization of struvite**

**Dissolution of struvite by nitrification sludge with aeration**

Nitrification bacteria can dissolve struvite both due to use of ammonium as an energy source and the hydrogen ion production in nitrification. When struvite is constantly dissolved under pH 6-8, released ammonium is absorbed and used as energy source by nitrification bacteria. This function was illustrated in previous chapter 2.1 on nitrification process. The reaction with nitrification and nitritation bacteria can be written:

\[
\text{MgNH}_4\text{PO}_4 + 2\text{O}_2 \rightarrow \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NO}_3^- \quad (25)
\]

**Materials and Methods**

- 1 liter nitrification sludge from Hammarby Sjostadsverk was used as dissolution media.
- 1 g struvite was added for dissolution by sludge.
- Sample was aerated at oxygen concentration 3 mg O₂/l.

**Procedure**

- 1 liter nitrification sludge was filled into the bottle. Simultaneously 1 g struvite (MgNH₄PO₄•6H₂O) was added into sludge.
• Prepared sample was aerated with oxygen concentration 3 mg O₂/l and kept reacting for 1 month.

• During reaction period, water samples were collected every day in the first 3 days, and then were collected every 3rd or 6th day for analysis. Samples were stored in freezer for analysis.

• Analyses were performed for taken samples: pH, conductivity, alkalinity, PO₄³⁻, NH₄⁺-N, Pₜ₀₅, Nₒ₅, NO₃⁻-N, SS and VSS of initial sludge were measured in addition.

**Analysis**
pH, conductivity, alkalinity, PO₄³⁻, NH₄⁺-N, Pₜ₀₅, Nₒ₅, NO₃⁻-N, NO₂⁻-N.

**Dissolution of struvite by anammox bacteria with aeration**
Anammox is capable for transforming ammonium and nitrite to nitrogen gas under anoxic condition. This function is accomplished by partial nitrification and anammox steps. In partial nitrification step, ammonium is partially oxidized to nitrite. Produced nitrite acts as electron acceptor and reacts with remaining ammonium, producing nitrogen gas. Based on this concept, the hypothesis about potential of struvite dissolution by anammox bacteria is researchable. Once ammonium is released from struvite, it is oxidized partially by aeration so nitrite is obtained. Thereafter, nitrite is reacting with remaining ammonium and nitrogen gas is produced. The mechanism can be described by the formulae:

\[
\begin{align*}
\text{MgNH}_4\text{PO}_4 + 1.5\text{O}_2 & \rightarrow \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NO}_2^- \\
\text{NO}_2^- + \text{NH}_4^+ & \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

**Materials and Methods**

• 1 liter decantate from nitrification sludge was abstracted and used in experiment.

• 70 pieces kaldnes ring reacted with 200 mg struvite (MgNH₄PO₄•6H₂O) in water.

• Sample solution was aerated with oxygen concentration at 3 mg O₂/l.

**Procedure**

• 1 liter supernatant from nitrification sludge was filled into bottle, simultaneously 200 mg struvite (MgNH₄PO₄•6H₂O) and 60 pieces of kaldnes ring with anammox granule were added into water.

• Prepared sample was aerated with oxygen concentration at 3 mg O₂/l and kept reacting for 1 month.

• During reaction period, water samples were collected every day in the first 3 days, and then were collected every 3rd or 6th day for analysis. Samples were stored in freezer for analysis.

**Analysis**
pH, conductivity, alkalinity, PO₄³⁻, NH₄⁺-N, Pₜ₀₅, Nₒ₅, NO₃⁻-N, NO₂⁻-N.

**Dissolution of struvite by anammox bacteria without aeration**
The concept of this experiment is the same as 5.3.2. The main difference is that this experiment was operated under anoxic conditions without air supplement. So that NO₂⁻ was provide by the chemical compound NaNO₂. Once ammonium is released from MAP, it will be transformed to nitrogen gas with nitrite by anammox bacteria.

\[
\begin{align*}
\text{MgNH}_4\text{PO}_4 + \text{H}^+ & \rightarrow \text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-} \\
\text{NH}_4^+ + 1.32\text{NO}_2^- + 0.066\text{HCO}_3^- + 0.13\text{H}^+ & \rightarrow \\
0.26\text{NO}_3^- + 1.02\text{N}_2 + 0.066\text{CH}_2\text{O}_{0.4}\text{N}_{0.15} + 2.03\text{H}_2\text{O}
\end{align*}
\]
Materials and Methods

- 200 mg struvite (MgNH₄PO₄•6H₂O) and 70 pieces kaldnes ring were mixed in distilled water.
- 60 mg NaNO₂ was added as nitrite source.
- Sodium hydrogen carbonate (NaHCO₃) was used for pH adjustment.
- Sample was shaken in vibration machine at 150 Mot 1/min.

Procedure

- 1 liter distilled water was filled into a bottle. 200 mg struvite and 60 pieces of kaldnes ring were added into distilled water.
- 60 mg NaNO₂ was added into prepared sample, and then the bottle was sealed with a cap.
- Sample was placed on vibration facility and was kept shaking at 150 rpm during the whole experiment process (1 month).
- 50 mg NaHCO₃ was added once when sample pH dropt below 6.
- Water samples were collected every day during first 3 days, and then were collected every 3rd or 6th day. Samples were stored in freezer for analysis.

Analysis

pH, conductivity, alkalinity, PO₄³⁻, NH₄⁺-N, P₂₅₅, N₂₅₅, NO₃-N, NO₂-N
### APPENDICES II - Mg$^{2+}$ DOSAGE AND pH VALUES VERSUS OBTAINED RESULTS

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<th>Mg</th>
<th>pH</th>
<th>SS</th>
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