

# WASTEWATER TREATMENT – NEW CHALLENGES

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**Abstract** Wastewater treatment is based on environmental concern that has gradually changed in focus from treatment of main wastewater stream to avoid negative effects on the recipient, taken care of the produced sludge, and consideration of emissions into the air. Today, wastewater treatment still must consider environmental effects based on emissions to receiving water, for sludge disposal, and into the air. Wastewater treatment is in this way regarded as a “get-rid-of-problem” but insights has led to evaluate wastewater as a resource that can give different products. A new attitude is then to consider wastewater treatment as an industry for producing valuable products but still maintain old requirements on environmental protection. In this paper approaches will be discussed to find ways to look on wastewater treatment as a factory for recovery of products and at the same time fulfill environmental requirements. Special emphasis is laid on the use magnesium compounds.

**Keywords** Anammox, biogas, energy, magnesium, reuse, recovery, wastewater

## INTRODUCTION

Today more than 80% of the population in Sweden is connected to central wastewater systems. The roots were the supply of water for fire protection (most used building material for houses was wood) and the growing insight of use of clean water to avoid water borne diseases. Thus, an infrastructure was built in Sweden based on transport of water into an urban city or municipality and a corresponding transport of wastewater and storm water out from the urban area. Although transport and corresponding construction works were dominating activities for central water and wastewater systems up to about 1970 increased efforts were made for water treatment and especially for wastewater treatment.

Wastewater treatment works were gradually built-up in Sweden during the last hundred years. Focus up to 1930 was mechanical treatment to remove particles. Later on biological treatment was gradually introduced based on oxygen depletion in the recipient and also due to hygienic reasons. The use of phosphate containing detergents led to eutrophication of lakes and for protection of the lakes chemical precipitation was generally introduced with large installations from 1970-1980 (Hultman & Moore, 1982). Later on at around 1990 and forwards many plants installed biological nitrogen removal.

The improved wastewater treatment led to production of large sludge quantities. Due to contaminants of metals, pathogens, and organic micro-pollutants some doubts were given to sludge disposal for agriculture use, especially from food production industries. Therefore, sludge disposal became an increasing problem for municipal wastewater treatment plants.

Wastewater treatment in Sweden has mainly been evaluated based on environmental effects and therefore been seen as a “get-rid-of-problem” both related to effluent discharge and sludge disposal. Wastewater as a resource has also been considered to some extent for instance the heat of wastewater (source for central heating systems and in a minor degree for cooling purpose), recovery of sand, sludge for nutrient supply and soil conditioning, and biogas utilization for instance as fuel for busses. Although the profit for different products is much less compared with treatment costs for wastewater treatment a steadily increasing interest is directed towards products recovery at wastewater treatment works.

## **TYPICAL DESIGN OF SWEDISH WASTEWATER TREATMENT PLANTS**

Wastewater treatment plants in Sweden has been gradually built-up starting with general application of mechanical treatment during the 1930's, followed by biological treatment for removal of organic materials during the 1950's and chemical precipitation for phosphorus removal during the 1970's. Removal of nitrogen was implemented at many plants during the 1990's. The treatment efficiency has, therefore, successively been improved and due to the building periods different steps in a treatment plant may have quite different age of operation. The period between 1930 to 1990 was in general characterised by adding a step to the older steps to meet treatment requirements. Nitrogen removal was normally preformed as pre-denitrification (although many post-denitrification also were built) and involved normally an increase of the volume of the aeration basin of an activated sludge plant to secure nitrification and also denitrification.

A typical large wastewater treatment plant in Sweden consists normally of pre-treatment by screens, aerated grit chambers, and pre-sedimentation to which precipitation agents are added (often ferrous sulfate), followed by pre-denitrification and a polishing step with addition of a precipitation agent before a post-sedimentation basin or deep-bed filter. Two-stage precipitation is common practice for phosphorus removal and biological phosphorus removal is only applied at around twenty plants.

The applied technology has in general been successful. Obtained effluent values are often below 0.2 mg Tot-P/l, 10 mg BOD7/l and 10 mg Tot-N/l at larger treatment plants. Due to the many plants a lot of experience has been gathered concerning design and operation. Sludge handling is a growing problem and typical Swedish design at large plants is thickening, followed by anaerobic treatment and mechanical dewatering before final sludge disposal. Some resistance exists from farmers and food industry to apply the dewatered sludge as fertilizer in agriculture and disposal on landfill is not longer allowed. Other disposal methods as use at golf courses, restoring of land etc. have been practiced. The nitrogen-rich supernatant is treated separately at around twenty plans mainly as nitrification/denitrification by SBR-technology (Nicolic & Sundin, 2006) and in one case by use of deammonification (single-stage with moving bed materials) (Ling, 2009, Trela et al., 2009). However, new demands have arisen which means that new challenges for treatment must be addressed:

- Improvement of nitrogen removal
- Concern of green house gases and energy savings
- Recycling of phosphorus to productive land

- Improved removal of pharmaceuticals and household products
- Improved removal of antibiotic resistant bacteria
- System technology
- Design and operational considerations

These challenges will be discussed related to traditional wastewater treatment technology in Sweden. It is argued that replacement by magnesium compounds (partly or totally) of precipitation agents based on iron or aluminum salts could offer an interesting way to meet the new challenges. Magnesium compounds can be obtained from seawater as from concentrated brines from desalting plants or from minerals as dolomite. From these raw materials different ways exist to produce suitable magnesium containing compounds. Some waste streams are rich in magnesium as from softening of water or if magnesium compounds are used (instead of aluminum sulfate) in water treatment.

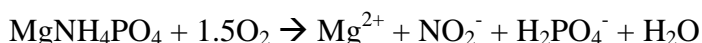
### **IMPROVEMENT OF NITROGEN REMOVAL**

The removal efficiency of ammonium in a pre-denitrification plant is either restricted by the quotient of COD/N or (in excess of COD) of the recirculation ratio of nitrate rich streams (Trela, 2000). The effluent nitrogen concentration is, therefore, much dependent on the influent nitrogen concentration. Thus, removal of nitrogen before the pre-denitrification step is beneficial. Separate treatment of ammonium-rich supernatant from dewatering of digested sludge is one possibility instead to recycle back to the influent. Another possibility may be precipitation of influent wastewater (after some pre-treatment) to form magnesium ammonium phosphate. Two requirements should then be fulfilled:

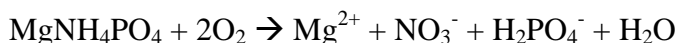
- The solubility of magnesium ammonium phosphate must be exceeded
- The stoichiometry for the precipitation must be considered. For a molar ratio of magnesium, ammonium and phosphate of 1:1:1 ammonium is in large excess of phosphate in the influent wastewater.

A way to solve these requirements is to remove ammonium in precipitated magnesium ammonium phosphate and then recycle magnesium and phosphate ions. Recycling can be based on chemical dissolution and ammonia removal and thermal methods to evaporate ammonium. At KTH introductory studies have been performed to dissolve magnesium ammonium phosphate by bacteria. The idea is similar to bacterial leaching of sulfide containing ores. In this case sulfide is the energy source for bacteria and the hydrogen ions produced facilitates the dissolution. Reactions based on nitritation, nitrification, anammox, and deammonification can be written (Hassanzadeh, 2005, Hultman & Levlin, 2008, Liang, 2009):

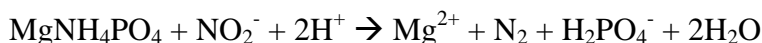
*Nitritation:*



*Nitrification:*



*Anammox:*



*Deammonification:*



Introductory studies based on nitrification and anammox reaction have shown that it is possible to dissolve by bacteria magnesium ammonium phosphate and, thus, give the possibility to recycle magnesium and phosphate ions to influent wastewater. The precipitation/recycling system is a way to biologically remove ammonium and oxidize ammonium to nitrite, nitrate or nitrogen gas. The combination of precipitation of influent wastewater to form magnesium ammonium phosphate followed by bacterial dissolution of the precipitate and recycling of magnesium and phosphate ions to the influent seems to be an interesting possibility in wastewater treatment.

As an illustration example it is assumed that influent wastewater contains 3 mmole of ammonium/l, 0.2 mmole of phosphate/l, and 1 mmole of magnesium/l. The solubility product,  $K$ , for struvite precipitation has at 9.5 a value of about  $10^{-13}$  and can be written (Regy et al., 2002):

$$K = (\text{Mg}^{2+})(\text{NH}_4^+)(\text{PO}_4^{3-})$$

The value of the solubility product ( $10^{-13}$  based on mole) corresponds to a solution of  $\text{Mg}^{2+}$  of 0.1 mmole/l (2.4 mg Mg/l),  $\text{NH}_4^+$  of 0.1 mmole/l (1.4 mg N/l) and  $10^{-2}$  mmole phosphate/l (0.31 mg P/l). Based on the solubility product high removal efficiency could be expected of influent magnesium, ammonium and phosphate ions if the stoichiometrical conditions were met.

Two principle ways can be used to fulfill stoichiometrical requirements. The first method is addition of magnesium and phosphate compounds to reach stoichiometrical requirements and suitable pH-value. However, the costs for the additions are high and the technology does not fulfill conditions to use influent wastewater as main chemical supplier. The second approach is to treat the obtained struvite precipitate to remove ammonium and dissolve the rest product to recycle magnesium and phosphate ions. Two approaches are thermal removal of ammonium followed by chemical dissolution by acids or chemical dissolution by acids followed by ammonia recovery (Buwal, 1993, He et al., 2007, Huang et al., 2009). However, the biological methods to dissolve struvite should also be considered and perhaps used in combination with chemical or thermal methods.

As magnesium compounds are relatively cheap main concern must be directed towards recycling of phosphate to reach stoichiometry. To obtain a concentration of 3 mmole phosphate/l (91 mg P/l) from influent phosphate and recycled phosphate a recycling ratio of 15 must be reached if all precipitated struvite is dissolved. If the flow of the precipitated struvite is 3% of the influent flow the recycle flow is 45% of the influent flow. The need for substantial recycling may be a critical factor for the process.

## **CONCERN OF GREEN HOUSE GASES AND ENERGY SAVINGS**

Energy savings and energy production in wastewater treatment plants become increasingly important due to increasing energy costs and concern related to emission of green house gases. As a large fraction of consumed water consists of hot water, heating pumps are commonly used for supply to central heating systems and to less degree for cooling purposes. In this way savings in use of fossil fuels can be obtained reducing emissions of carbon dioxide. Better equipment and methods for ventilation/heating of buildings, and improved process technology are other ways to reduce carbon dioxide emissions. In addition, it is important to consider the energy used for building materials, production of chemicals, and transport to and away from the plant.

The two energy rich components in influent wastewater are mainly organic materials and ammonium. Removal of them by aeration (degradation of main part of organic material into carbon dioxide and nitrification) means significant energy consumption (normally as electricity). Significant energy savings and possibilities for energy production exist if removal of organic material and ammonium is performed at anaerobic conditions:

- Organic material is degraded to methane (fats), methane and carbon dioxide (carbohydrates), and methane, carbon dioxide, ammonium and hydrogen carbonate (protein) as end products. Methane can be used for energy production (as electricity and fuel for busses). As methane has a larger potential as green house gas than carbon dioxide, it is important to avoid losses of methane during the energy production process (as losses during sludge storage or due to the water solubility of methane).
- Much energy can be saved if ammonium is oxidized to nitrogen gas through the deammonification process. This process involves partial nitrification (oxidation by oxygen about half of the ammonium to nitrite) followed by the anammox reaction with reaction of formed nitrite with remaining ammonium to nitrogen gas. A special problem is the possibilities of forming nitrous gas (laughing gas) during the partial nitrification process. Some special issues are:
  - Nitrous gas is a very potent green house gas
  - Nitrous gas is formed at stress conditions for nitrification or denitrification bacteria for instance at low oxygen and pH-values. Low oxygen conditions are normally used in partial nitrification to avoid nitrate formation.
  - Stress conditions with formation of nitrous or nitric oxide may give rise to growth of filamentous bacteria and may be a reason for formation of stable foams.

Addition of magnesium compounds to influent wastewater may have an important role in energy savings and energy production. The reason is that magnesium compounds are very efficient to remove organic materials due to precipitation and adsorption (up to 90% has been reported) and has the possibility to precipitate organic nitrogen and ammonium. In this way, main part of influent organic material and ammonium can be transferred to a small stream as a precipitate for further treatment at anaerobic conditions.

## RECYCLING OF PHOSPHORUS TO PRODUCTIVE LAND

Phosphorus is a limiting factor in the future for food production if available apatite resources are considered. Therefore, a goal has been set up in Sweden that 60% of influent phosphorus should be used at productive land before 2015. At central wastewater treatment plants mainly two approaches have been used:

- Strong emphasis on up-stream activities to secure that the obtained sludge has a quality that will not cause health or environmental problems. A large fraction of produced sludge from wastewater treatment plants fulfill requirements from authorities but there is not a consensus from farmers, food industry, researchers etc. that it is safe enough to use sludge as fertilizer and soil conditioner in agriculture.
- Special treatment of sludge to separate toxic substances from the sludge and produce a phosphorus product and also recover precipitation agents. The technology involves thermal treatment (thermal conditioning under pressure or incineration) followed by separation technologies based on wet chemistry (precipitation or ion exchange). Developed systems have so far not come into practice.

It is possible that magnesium compounds may have a significant role for recovery of phosphorus as a product. Two recently developed processes will be used as illustration:

- *Ostara*. This process developed at University of Columbia, Canada, and later driven commercially is installed or under construction in full-scale at a few plants in Canada and USA. The process technology is based on biological phosphorus removal in the main stream followed by digestion of sludge. During the digestion process “excess” phosphorus is released together with magnesium and potassium ions. Ammonium is also released due to degradation of proteins. By use of crystallization technique struvite is obtained and marketed for instance as slow release fertilizer for parks, golf courses etc. (Benisch et al., 2009).
- *SUSAN*. In an EU-project a process is developed with addition of magnesium and potassium chloride and sludge is treated thermally. The chloride addition gives formation of volatile metal chlorides and means a substantial transfer of metals in the sludge to the air phase that must be treated. The sludge contains magnesium and potassium phosphates that can be used as fertilizer (Adam et al., 2008, SUSAN, 2008).

At KTH it has been suggested to combine ammonium-rich supernatant with side-stream technology for biological phosphorus removal (as PhoStrip). Precipitation or crystallization of struvite can be obtained by adjusting the pH-value (Levlin & Hultman, 2003).

## IMPROVED REMOVAL OF PHARMACEUTICALS AND HOUSEHOLD PRODUCTS

Pharmaceuticals and some household products are a potential threat to health and environment. Rest products from pharmaceuticals must be released from the human body in a water soluble form (often as conjugates). Many of the pharmaceuticals are only biodegradable to a small extent and due to their water solubility only removed to a minor extent by chemical precipitation. Some household products have similar properties as pharmaceuticals. If pharmaceuticals should be

removed efficiently at Swedish wastewater treatment plants some complementary treatment seems to be necessary:

- Oxidizing agents as ozone, hydrogen peroxide, UV sometimes in combination to split larger molecules into smaller units that are not harmful to environment and often biodegradable. An interesting chemical may be permanganate as it selectively splits phenol groups that often are important components in endocrinal disturbing substances.
- Adsorption materials of which activated carbon is the mainly used material
- Membrane technology by use of membrane technology to hinder penetration of the substances (nanofiltration, reverse osmosis)

Effects of magnesium compounds to remove pharmaceuticals may not have been studied. The efficient removal of organic materials in addition of magnesium compounds to the influent may cause a lower concentration of non-biodegradable organic substances and may be on advantage in removal of pharmaceuticals (chemical need of oxidizing agents, need of adsorption material, clogging of membrane etc.).

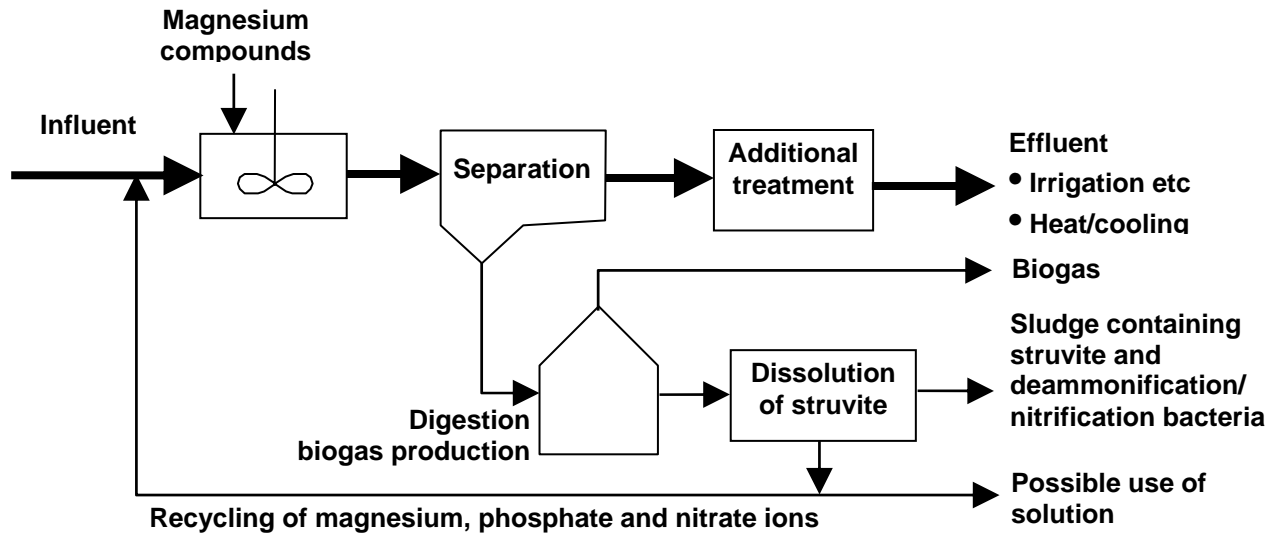
### **IMPROVED REMOVAL OF ANTIBIOTIC RESISTANT BACTERIA**

Swedish wastewater treatment plants do not normally have disinfection of the effluent. The increased use of antibiotics in society may motivate improved removal of antibiotic resistant bacteria. Technology is similar to that of removal of pharmaceuticals and the combined effects of treatment for removal of pharmaceuticals and antibiotic resistant bacteria should be considered. Possible positive effects of use of magnesium compounds may include a more efficient transfer of the bacteria to the sludge phase and use of elevated pH-value (as 9.5-10.5).

### **SYSTEM TECHNOLOGY**

A treatment system by use of addition of magnesium compounds to the influent is illustrated in Figure 1. Important parts for the system function are:

- Use of influent concentrations of magnesium, ammonium and phosphate, addition of magnesium compounds (for pH-adjustment with MgO and to increase the magnesium ion concentration) and recycling of magnesium and phosphate ions. As discussed earlier two requirements should be fulfilled (a) enough concentration of magnesium, ammonium, and phosphate ions to accomplish precipitation and (b) suitable stoichiometrical balance between magnesium, ammonium, and phosphate.
- Transfer of precipitated sludge to the digester for biogas production and removal of biodegradable organic substance
- Bacterial oxidation of ammonium to nitrite, nitrate or nitrogen gas and recirculation of dissolved ions (magnesium, phosphate, nitrite and nitrate) to the influent

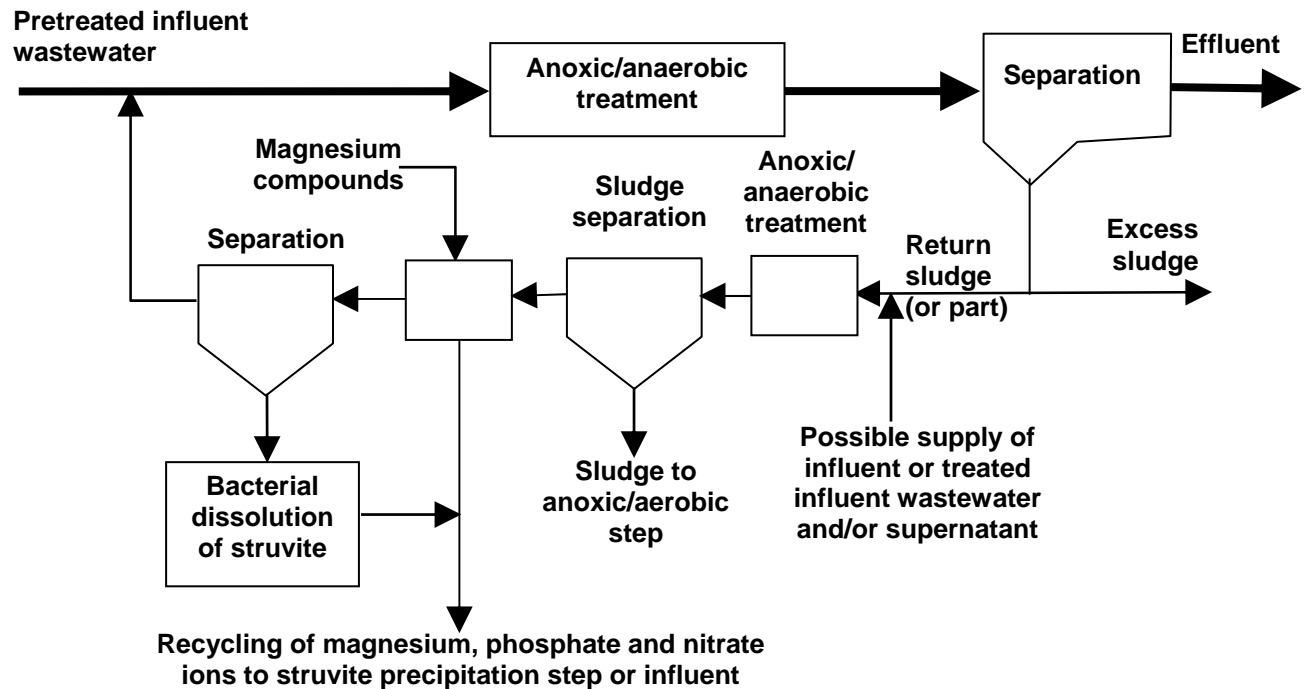


**Figure 1.** General process scheme of struvite precipitation, biogas production, dissolution of struvite and recirculation of magnesium and phosphate ions.

Additional treatment may be necessary to reach different requirements:

- If irrigation is wanted the degree of nutrient removal is not important if irrigation is used the year around. A higher pH-value in the precipitation step will improve disinfection efficiency. A special problem is the salt concentration and reverse osmosis or ion exchange may be important if reuse for drinking water purpose is considered. This is of special importance in water scarce regions and the water content in wastewater may be regarded as the main resource (Suleaman, 2009).
- For Swedish treatment plants additional treatment may involve consideration of recycled nitrate and remaining COD after precipitation to mainly remove the organic material by denitrification. To remove pharmaceuticals and antibiotic resistant bacteria a new or complementary treatment step may be necessary. Additional products to heat in wastewater and biogas are phosphate and nitrogen as magnesium ammonium phosphate in sludge and/or magnesium, phosphate and nitrate ions in a concentrated solution.
- A possibility for Swedish and other plants is illustrated in Figure 2. The general concept of Figure 1 is applied as side-stream process. In this case the need for high recirculation of dissolved struvite is diminished although the role of bacterial dissolution gets a smaller role as less ammonium is handled. A combination of system according to Figure 1 and 2 may be advantageous also due to diminishing risks of clogging by struvite.





**Figure 2.** Possible additional treatment based on similar concepts as in figure 1.

## DESIGN AND OPERATIONAL CONSIDERATIONS

Struvite can cause severe clogging problems. An important aspect is therefore to use strategies to avoid precipitation on pumps, pipes etc. for instance by pH-control or making one of the components (magnesium, ammonium, phosphate) a limiting factor for precipitation. Different factors can improve the precipitation of magnesium ammonium phosphate as use of seeding material.

Implementation of a magnesium compound based wastewater treatment at existing Swedish wastewater treatment plant with pre-precipitation and digestion may involve the following steps:

- Successive replacement of existing precipitation agent with magnesium compounds. It is then expected an increased transfer of organic material to the sludge phase and also of ammonium and organic nitrogen.
- The increased separation of organic material gives possibilities of increased biogas production and, therefore, increased use of digester capacity, both the digestion process and also equipment for handling of the produced biogas. Many possibilities exist to improve digester capacity as increase of sludge concentration before the digester, pre-treatment of sludge before digestion and use of thermophilic digestion.
- Due to the increased transfer of organic material and ammonium to the sludge phase less volume is needed for biological wastewater treatment in the main stream. It seems, therefore, reasonable that certain volumes can be used for bacterial dissolution of magnesium ammonium phosphate.

- Internal recirculation of the remaining sludge after dissolution has several potential benefits as reduction of sludge mass from the plant (especially if thermophilic digestion is used), seeding of nitrification or deammonification bacteria (Plaza et al., 2001, Leu & Stenstrom, 2009) and use of the sludge as weighting and support material for bacterial growth.

As the proposed treatment system with addition of magnesium compounds is based on new ideas and therefore not tested it is advisable that laboratory tests should be performed followed by pilot-plant studies. The system function can be tested at Hammarby Sjöstadswerk there the different treatment parts can be installed in a rather simple way.

## **CONCLUSIONS**

- Wastewater treatment has in Sweden in general fulfilled environmental requirements based on considerations from authorities. Main concern has been directed towards BOD, total phosphorus and total nitrogen for the main stream and quality aspects of the formed sludge.
- More stringent or new requirements may be put forwards and new challenges include improved nitrogen removal, concern of green house gases and energy savings, recycling of phosphorus, and improved removal of pharmaceuticals and antibiotic resistant bacteria
- Existing treatment plants in Sweden can only partly fulfill these possible new requirements without new investments and change of operational modes
- Use of magnesium compounds seems to be a promising and cost-effective way to partly meet new challenges

## **ACKNOWLEDGEMENT**

Thanks are given to discussions and help from staff at Dep. of Land and Water Resources, KTH, by Reza Hassanzadeh, Erik Levlin, Monica Löwén and Jozef Trela and many master thesis students. In addition, fruitful discussions have been given from staff at Swedish Institute of Environment (IVL) in relation to work at Hammarby Sjöstadswerk and SWECO AB.

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