Norwegian University
of Life Sciences

Master's Thesis 2017 30 ECTS
Norwegian University of Life Sciences
Faculty of Environmental Science and Technology
Department of Environmental Science (IMV)

Phosphorus recovery through struvite precipitation: testing of parameters which enhance phosphorus recovery

Anastasiia Buchynska
Specialization in MINA- Sustainable Water Sanitation, Health and Development

Phosphorus recovery through struvite precipitation: testing of parameters which enhance phosphorus recovery

A Thesis submitted in partial satisfaction of the requirements for the degree
Master of Science
in
Environment and Natural Resources - Specialization Sustainable Water and Sanitation, Health and Development.
By

Anastasiia Buchynska

Faculty of Environmental Science and Technology
Department of Environmental sciences (IMV)
Norwegian University of Life Sciences (NMBU)
Ås, Norway
August 2017

Acknowledgment

Primarily, I am grateful to study at the Norwegian University of Life Science, which has provided me with all the necessary facilities and helped me to make this research possible.

I would first like to thank my thesis supervisor, professor Tore Krogstad of the Faculty of Environmental Sciences and Natural Resource Management at NMBU. Prof. Krogstad has always been available for discussions and to provide help, whenever I experienced challenges with the implementation of experiments or writing. I admire by his fidelity to work and I wish to express my sincere appreciation for his advising and aid with this thesis work even during his vacation. He always helped me think critically and has steered me in the right direction whenever he thought it necessary.

I wish to express my sincere thanks to my co-supervisor, professor Petter D. Jenssen, who inspired and encouraged me to work on this topic and to develop my skills in the branch of water treatment engineering.

I am also grateful to Sondre Eikås, Project manager in wastewater treatment and management at HIAS WWTP. Sondre provided professional help during the sampling of wastewater from the HIAS. He was always positive when it came to help and discussion.

I would also like to thank the experts who were involved in the management of laboratory analysis at the Faculty of Environmental Sciences and Natural Resource Management at NMBU; Head Engineer Irene E. Eriksen Dahl, Head Engineer Oddny Gimmingsrud and Senior Engineer Valentina Zivanovic. Without their passionate participation and valuable input, the analysis could not have been successfully conducted.

I also want to especially mention my colleague and friend, MSc Amir Shokouhi, for his positive attitude, sense of humor, and support while working with my thesis. Joint discussions, trips to the HIAS, and work in the laboratory was carried out very quickly, efficiently, and fruitfully.

Finally, I must express my very profound gratitude to my parents, relatives, and friends for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

Thank you.

Anastasiia Buchynska

Summary

Phosphorus is an essential nutrient for growth in all living organisms and is used as fertilizer to maintain food production. Today's recovery of mineral phosphate will lead to a lack of phosphorus as mineral fertilizer since phosphorus will become more expensive over the time. Increased awareness that the mineral phosphate is not a renewable resource means that recycling of phosphorus is an important environmental and food safety issue.

In the given thesis, the recovery of phosphorus was carried out by the precipitation of the ammonium-magnesium-phosphate (struvite) complex. The overriding purpose was to determine the optimal parameters for phosphates removal through the struvite precipitation from the reject- and sludge- wastewater after the biological treatment from the HIAS sewage plant in Hamar, Norway. Furthermore, the goal was to achieve a struvite with the high nutrients content and use it as a potential fertilizer. To accomplish that goal it was formed hypotheses, made the experiments, analysis, and results.

Based on the theory, three hypotheses were formed, which are focused on varying the parameters time, pH and molar ratio of Mg^{2+}: NH_4^+. Firstly, an increase in pH from 8 to 8.3 should increase phosphorus removal through struvite precipitation. Secondly, the reaction time plays role in phosphorus recovery. Thus, the reaction time in the interval 20 to 60 min should be optimal for struvite formation with the high P-recovery. Thirdly, the molar ratio of Mg^{2+}: NH_4^+ at 1.2: 10 and 1.5: 10: should cause about 95% of P removal. Finally, the concentration of toxic elements, such as heavy metals, was expected to meet the legislations requirements after the experiments.

To carry out the experiments, two sources of wastewater have been taken from the HIAS, mixed and added the salt of magnesium. The solution has been mixed and centrifuged. Both the liquid part and the sediment (struvite) have been analyzed. The struvite was weighted and analyzed on the content of elements. The liquid part was analyzed on phosphorus and ammonium recovery, turbidity, conductivity and the content of elements.

The results showed the highest phosphorus recovery of 97% was achieved by the Mg^{2+}: NH_4^+ molar ratio of 1.5:10 and the pH 8.3, which looks like the optimum combination for PO_4^{3-} recovery. All the experiments showed the same ammonium recovery, at about 68.5%. 20 min reaction time showed better struvite removal than at 60 min. It was found that, although, the amount of struvite sedimentation was small, the quality of precipitated struvite was high. The struvite contains a very low number of toxic elements, which are less than in the legislations requirements.

The results showed that the Mg^{2+}: NH_4^+ molar ratio and the pH plays key role in enhancing of phosphorus recovery through struvite precipitation. Moreover, the changing in time also can affect the quality of struvite as a future fertilizer.

Contents

Vocabulary List

Al: Aluminum

As: Arsenic

Ca: Calcium

$Ca_3(PO_4)_2$: tri-calcium phosphate complex

Cd: Cadmium

EC: Electrical conductivity

Fe: Iron

FIA: Flow injection analysis

HCl: Hydrogen chloride

Hg: Mercury

HNO_3: Nitric acid

ICP: Inductively coupled plasma mass spectrometry

K: Potassium

$KMgPO_4 *6H_2O$: Struvite-(K)

Mg: Magnesium (Mg^{2+})

$MgCl_2*6H_20$: Magnesium hexahydrate

$MgCl_2*6H_2O$: Magnesium chloride

$MgCO_3$: Magnesium carbonate

$MgNH_4PO_4(H2O)_6$: Struvite

MgO: magnesium oxide

N: Nitrogen

NaOH: Sodium hydrate

NH_4: Ammonium

NOM: Natural organic material

OM: Organic meter

P: Phosphorus

Pb: Lead

SS: Suspended solids

TP: Total phosphate (PO_4-P)

TSS: Total suspended solids

WWTP: Wastewater treatment plant

1. Introduction

Water with waste from daily life (toilets, shower, dishwasher machines) and industries is called sewage or wastewater [1]. Wastewater contain many bacteria, viruses and pathogens, which are harmful for human health. Also the nutrients which wastewater contains affects the environment [2]. A nutrient as phosphorus can cause eutrophication of water sources, and as a result death of water organisms [3]. At the same time, the mineral phosphorus (P) is an essential fertilizer. The great consumption and no alternative sources of mineral phosphorus, makes phosphorus source limited [4]. To provide more sustainable phosphorus usage and protect environment, it is important to recover P from wastewater.

Conventional water treatment techniques show acceptable P removal, but have a row of disadvantages. That, for example, chemical treatment causes pollution of environment by metals as Fe, Al, Zn. In addition, phosphorus after treatment with Al- and Fe-salts is not fully available for plants [5]. Which forces farmers to use more mineral phosphorus [6].

To decrease using of mineral P, protect environment, and make wastewater treatment more sustainable, wastewater treatment plant in Hamar is developing P-removal through struvite precipitation. Struvite is a mineral containing both phosphorus and nitrogen from nutrients wastewater. It is a good slow release fertilizer safe for environment and people, and provides high phosphorus recovery.

This thesis is focused on struvite precipitation with focus on conditions the maximizing the phosphorus recovery.

1.1 Phosphorus

Phosphorus (P) is essential for all living organism, especially for plants grows [7]. Mineral state of phosphorus contains in rocks, and uses as mineral fertilizer. Since, mineral P is a finite, nonsubstitutable, non-renewable, and geographically restricted resource, there is a concern that exploration by mine production to meet current demand is not sustainable [8]. In addition, P resources are being depleted and additional P fertilizer is needed to ensure food security [9]. In table 1 is shown the world total reserve of mineral P. Thus, distinction between resources which uses and deposits which currently exists showed, that deposits which could be used varies between 240 to less than 60 years [10].

Table 1- World mine production of mineral phosphorus for the 2014 and 2015 and its reserves[1].

	Mine production, ton		**Reserve, ton**
	2014	2015	
United states	25,300	27,600	1,100,00
Algeria	1,500	1,200	2,200.000
Australia	2,600	2,600	1,000,000
Brazil	6,040	6,700	320,000
China	100,000	100,000	3,700,000
Egypt	5,500	5,500	1,200,000
India	1,110	1,100	65,000
Iraq	200	200	430,000
Israel	3,360	3,300	130,000
Jordan	7,140	7,500	1,300,000
Kazakhstan	1,600	1,600	260,000
Mexico	1,700	1,700	30,000
Morocco	30,000	30,000	50,000,000
Peru	3,800	4,000	820,000
Russia	11,000	12,500	1,300,000
Saudi Arabia	3,000	3,300	960,000
Senegal	900	1,000	50,000
South Africa	2,160	2,200	1,500,000
SYRIA	1,230	750	1,800,000
Togo	1,200	1,000	30,000
Tunisia	3,780	4,000	100,000
Vietnam	2,700	2,700	30,000
Other countries	2,370	2,600	380,000
World total	218,000	223,000	69,000,000

Despite that fact, that the World sources of phosphate rock are more than 300 million tons, there is about 90% of P is using for farming industry[11]. Also, the world consumption of P contained in fertilizers and industrial uses increase gradually from 43.7 million tons in 2015 to

---

[1] https://minerals.usgs.gov/minerals/pubs/mcs/2016/mcs2016.pdf

48.2 million tons in 2019. For that reason, there is need to find alternative resource or to extend the life expectancy of phosphorus.

It is necessary to extend the life expectancy P, by increasing availability of P for plants uptake [7], and recycling P by recovery from municipal and waste materials, like wastewater [1] .

1.2 Wastewater and phosphorus.

Wastewater contains high concentration of mineral substances, included phosphorus. There are two forms of phosphates in wastewater, namely inorganic (orthophosphate) and organic (polyphosphate) P [7].

Organic phosphate consists of a phosphate molecule associated with a carbon-based molecule, as in plant or animal tissue. Inorganic phosphorus is the form required by plants. Both organic and inorganic phosphorus can either be dissolved or suspended in the water [12].

Wastewater with high concentration of phosphates and orthophosphates causes several problems to environment. Firstly, high concentration of P causes accumulation of alga (eutrophication) or acidification in water source [13]. As a result, it would lead to a death of aquatic organisms. Other problem is that phosphorus wastewater leads to serious deterioration of surface water bodies, as increase of water salinity. [14]. To avoid the environmental problems the municipalities and industries should work in a cooperation.

From the one hand, to avoid the emission of P, municipalities should decrease the release of P in nature. From the other hand, P should be recycled and recovered during the wastewater treatment.

1.3 Wastewater and chemical treatment

Chemical treatment is a primary treatment, which includes such processes as coagulation which is follows by fluctuation. Coagulation is a process of destabilization of colloidal parts or precipitation of soluble matter in a metal-hydroxide complex (Fig. 1). Following, flocculation is a gentle mixing stage, increases the particle size to visible suspended particles. In addition there could be added flocculants (polymers) to agglomerate of destabilized particles by bridging (Fig. 2) [15].

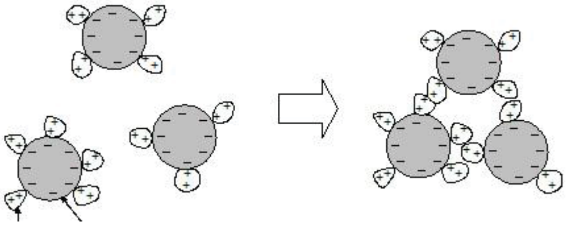


Figure 1 – Coagulation[2]

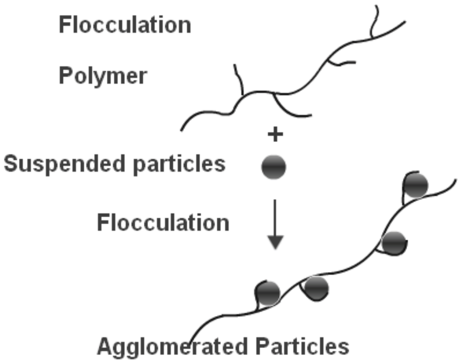


Figure 2 - Flocculation[3]

There are two commonly used types of metal coagulants: the aluminum based coagulants (aluminum sulfate, aluminum chloride and sodium aluminate) and, the iron based coagulants (ferric sulfate, ferrous sulfate, ferric chloride, and ferric chloride sulfate) [16].

Then metal coagulants are added to water the metal ions (Al^{3+} and Fe^{3+}) hydrolyze rapidly, forming a series of metal hydrolysis species. The parameters which affecting formation of metal hydrolysis species are the efficiency of rapid mixing, the pH, and the coagulant dosage. Though coagulation-flocculation is widespread treatment process, there are some disadvantages during and after the treatment process, namely removal of natural organic matter (NOM) and turbidity, technical issues and, P bioavailability. Firstly, itself the coagulation-flocculation process removes only about 60%-70% of NOM. Thus, there is need for other processes like oxidation,

---

[2] http://chemistry.tutorvista.com/physical-chemistry/flocculation.html,

[3] http://www.apec-vc.or.jp/e/modules/tinyd00/index.php?id=57&kh_open_cid_00=43

filtration and sedimentation for complete wastewater treatment [15]. In addition, Al-based coagulants increases turbidity, reduces disinfection efficiency, and losses in hydraulic capacity [17]. Secondly, at treatment plant performance, high concentrations of residual dissolved Al indicate incorrect coagulant dosing, inefficient use of the coagulant, or problems in the chemistry of treatment process [17]. Finally, the range of metal coagulants, namely metal ammonium phosphate, are not soluble enough to achieve significant P removal. Moreover, in that form P is not available for plants by biological based slow release mechanism [18].

To decrease P leaching, make it available for plants, and simplify wastewater treatment technology vital to investigate alternative ways of P-recovery. One of those methods is to recovery P through struvite precipitation from wastewater.

1.4 Wastewater and Struvite.

As was mentioned before, wastewater contain many nutrients. The crucial nutrients for struvite precipitation are magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphorus ($P0_4^{3-}$). If these three components react in ratio 1:1:1, forms white powder, struvite [19]. Because a final product contains high amount of P, struvite could be used as an alternative fertilizer instead of mineral P.

Although, struvite contains useful nutrients, if to improperly treat wastewater or not to extract struvite during wastewater treatment process, it could case technical problems. Struvite will pollute treatment equipment and clog municipal pipelines (Fig. 3) [20]. Moreover, to clean or remove pipelines could cause extra economical expenses, which are time-consuming and expensive processes.

Figure 3 - Struvite deposit in pipeline[4]

To minimize wastewater treatment expenses and maximize P recovery, wastewater treatment plant in Hamar (HIAS), investigates, develops and, includes the stage of struvite precipitation in a water treatment process.

1.5 Wastewater treatment plant in Hamar (HIAS - Hedmark Interkommunale Avløps-samband).

The focus of HIAS is to deplete pollution of Mjøsa. Thus, the company clean the wastewater from the owner municipalities: Hamar, Løten and Ringsaker [21]. In a row with pollution of Mjøsa, HIAS chasing a goal of recovery maximum quantity of P to achieve sustainable water treatment and food production.

Nowadays, the treatment process contains three conventional steps: mechanical, biological and chemical treatment. These stages insure purification from mechanical particles, biological materials, and nutrients as phosphorus. In addition, HIAS applies the stage of sludge treatment, while biomass goes for agriculture.

---

[4] *http://www.freshawl.com/struvite_removal.html*

1.5.1 Mechanism of treatment, stages of water purification.

1.5.2 Mechanical

Mechanical treatment (primary) withhold coarse bodies and suspension of wastewater. In a primary stage suspended solids (SS) separates from organic matter (OM) [22]. The total suspended solids of the incoming waste water are reduced by at least 50 %. The stages of the mechanical treatment at HIAS is shown in a Figure 4.

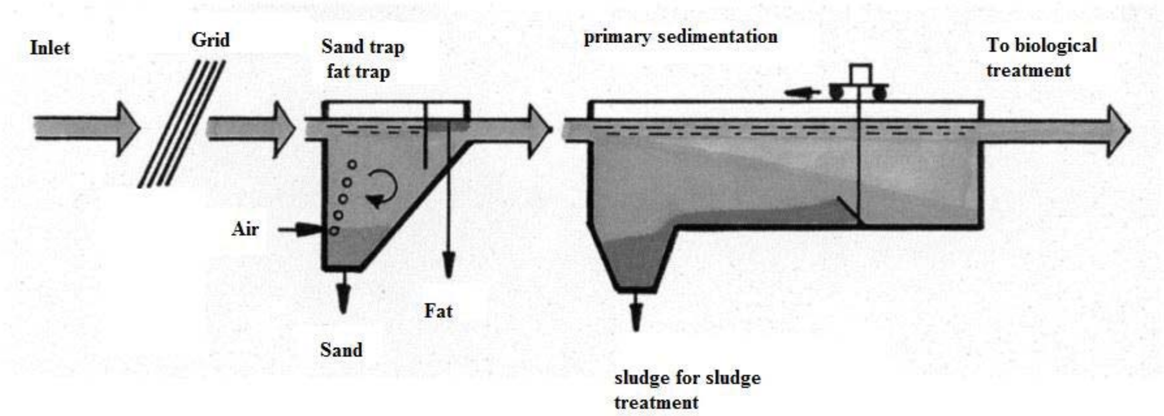


Figure 4 - Mechanical treatment at HIAS[5]

After the mechanical treatment followed by the biological treatment.

1.5.3 Biological

Biological treatment is an important part of any wastewater treatment plant. It treats wastewater from both municipality and industry. During biological treatment, natural microorganisms clean the wastewater for loose organic matter. The process could handle under aerobic and anaerobic conditions [22].

At HIAS purification takes place in a two-step process: air pools and sedimentation ponds [23]. The biological treatment is shown in Figure 5.

---

[5] http://www.hias.no/vann-avlop/avlop/avlopsrensing/mekanisk/

In the air pool the air blow into the water, which supply oxygen and food for the microorganisms to thrive them and grow bigger and heavier. After the wastewater is transferred to the sediment pool, microorganisms fall to the bottom of ta tank in a form of the sludge. From this, some of the sludge is pumped back to the aeration pool to maintain the culture of microorganisms. The rest is pumped out to the sludge process.

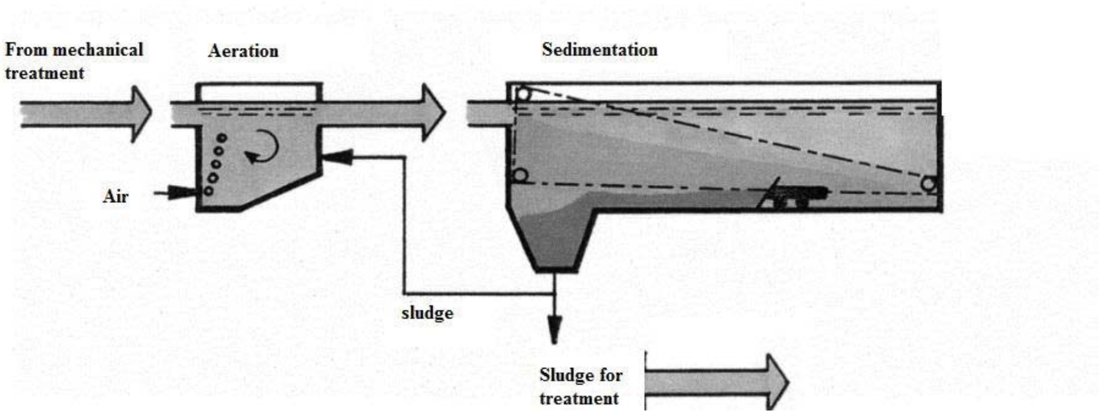


Figure 5 - Biological treatment at HIAS[6]

The chemical treatment takes place after biological treatment.

1.5.4 Recovery of P within chemical treatment

Chemical treatment focuses on recovery of nutrients, such as phosphorus.

Nowadays, at HIAS, uses precipitant, namely aluminum sulfate.

$$Al^{3+} + PO4^{3-} = Al(PO_4) \tag{1}$$

The process proceeds in two steps: fluctuation and precipitation (Fig. 6). During the flocculation process the phosphorus binds to the aluminum sulfate and forms larger particles. Wastewater is led to sedimentation pools, where the phosphorous particles fall to the bottom of the sedimentation pool, and pumped on to sludge treatment. The purified water in the pools is returned to Mjøsa through an outlet.

---

[6] http://www.hias.no/vann-avlop/avlop/avlopsrensing/biologisk/

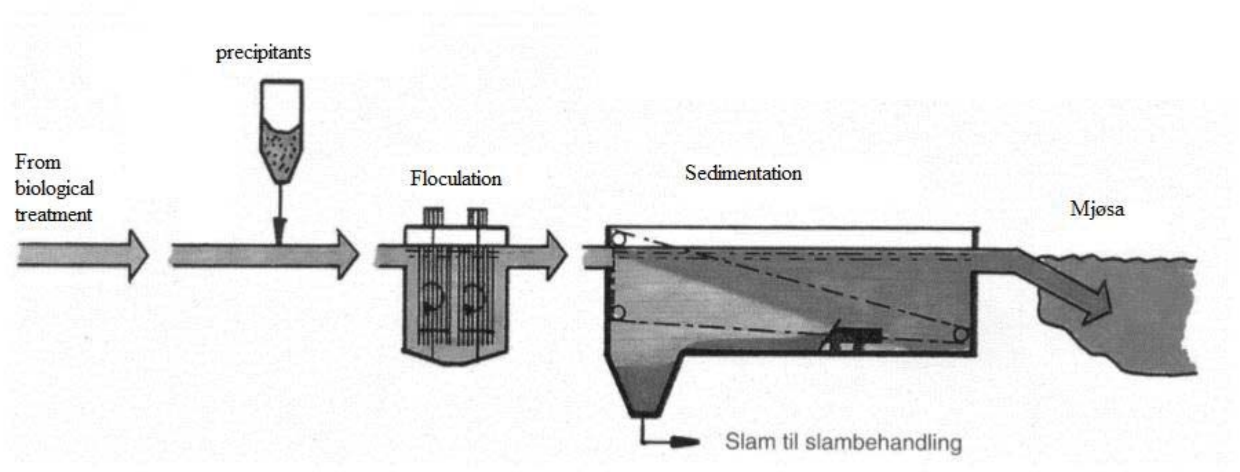


Figure 6 - Chemical treatment at HIAS[7]

After, the chemical treatment followed by the sludge treatment.

1.5.5 Sludge treatment

Sludge has both disadvantages and advantages. The downside of sludge is a presence of moisture, specific smell and bacteria, which could be dangerous for human health [22]. Contrary, it is a source of energy [24], and could be useful and safe for environmental.

At HIAS Sludge from the three purification stages (mechanical, biological and chemical) is pumped to the sludge treatment (Fig. 7). The mud from the three purification stages falls to the bottom and thickens from 1% dry matter to approximately 2.5%.

Most water is removed through the thicker. The target is about 15% solids content. After the sludge is stored in silo prior to thermal hydrolysis. In a thermic hydrolysis, the sludge is treated by stem. It becomes sterile. The thermal hydrolysis makes the sludge content of organic matter more easily degraded by microorganisms in the subsequent rotary tank. In a rotary tank, the microorganisms convert organic matter into biogas. After follows the step of dewatering the sludge with filter press. The rest water is returned to the drainage treatment [25].

---

[7] http://www.hias.no/vann-avlop/avlop/avlopsrensing/kjemisk/

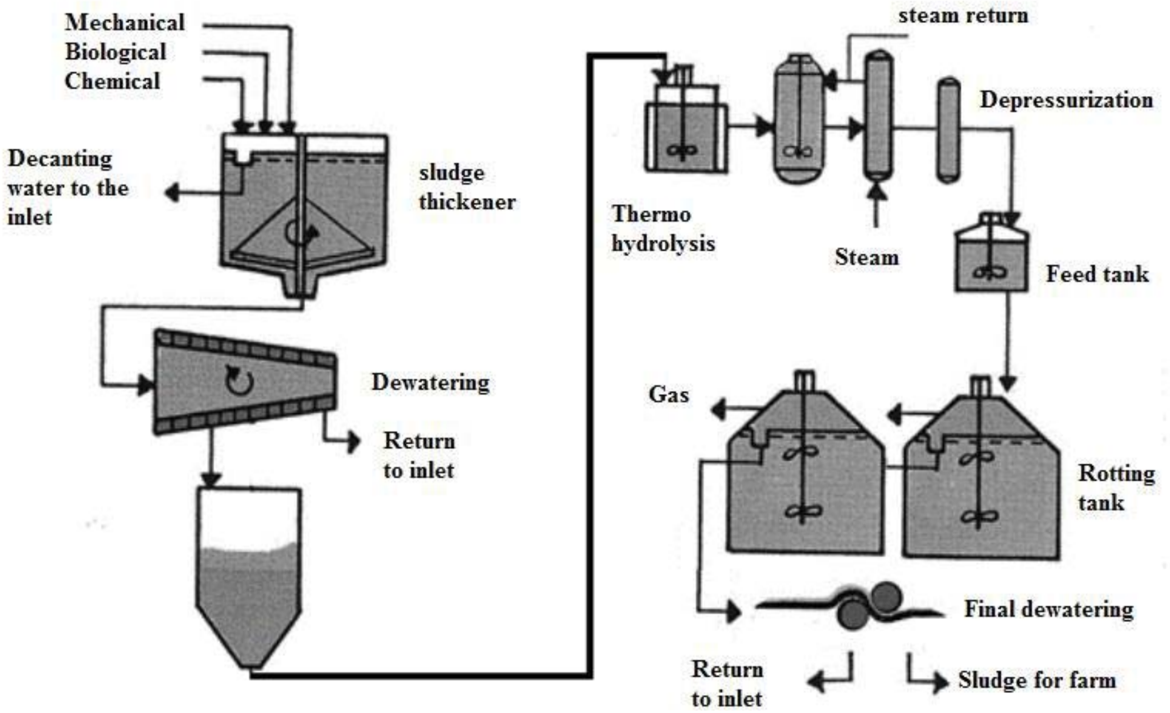


Figure 7 - Sludge treatment at HIAS[8]

1.5.6 Nowadays situation at HIAS.

In present, there are plans for removing the chemical treatment and building full-scale struvite reactor. The scheme of the new treatment stages, including struvite reactor is shown in Figure 8.

Thus, water from mechanical and biological treatments will go to sludge treatment. Part of sludge will go to agriculture industry. While the rest of sludge will follow to struvite reactor, where will occur the stage of nutrients recovery, such as N and P.

---

[8] http://www.hias.no/vann-avlop/avlop/slambehandling/

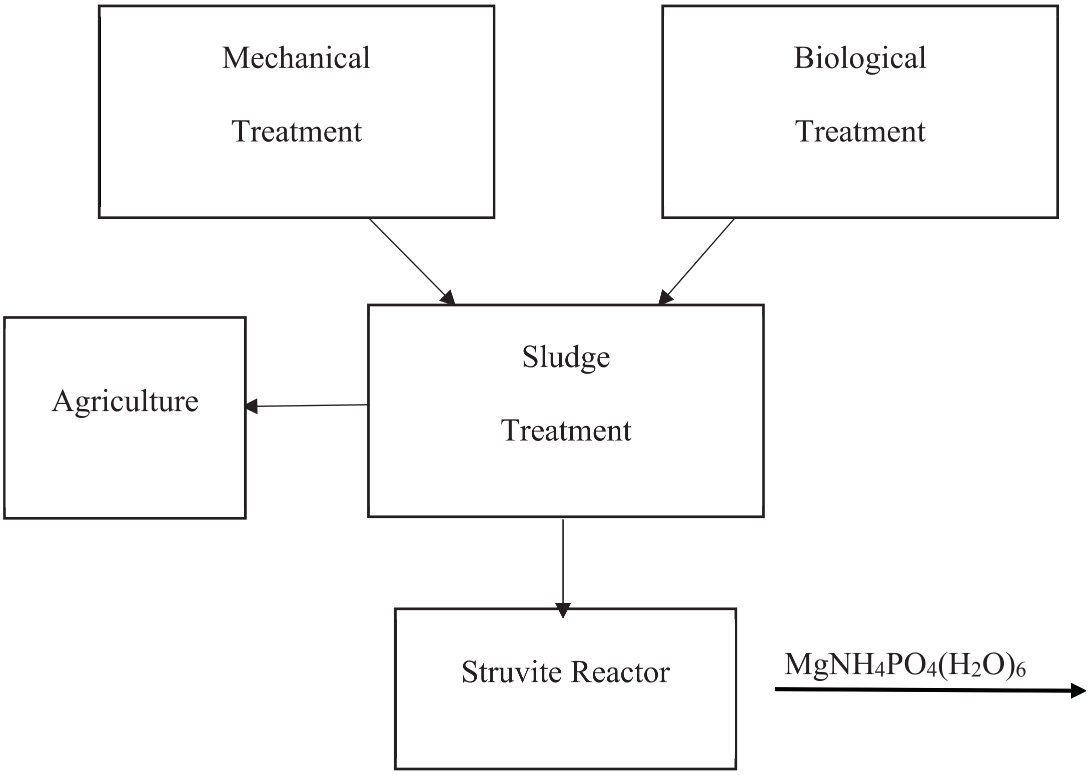


Figure 8 - Struvite reactor at HIAS

1.6 Purposes.

Prior study on HIAS has been focused on the innovative design with a goal of wastewater treatment without chemical treatment stage. Thus, there is only mechanical and biological treatment with the sludge treatment would located at the end. That leads to the consequences as decreasing of phosphorus removal because smaller amount of P will be metal bonded. Moreover, greater degree of P in the sludge will be dissolved or organically bound. Thus, to shift chemical treatment process and to avoid the P-lose, next study was focused for installing of struvite reactor [26].

Nowadays goal of HIAS is to achieve maximum P-recovery through Struvite precipitation. That solves several issues: operational cost, environmental and agricultural. Firstly, the operational cost would be reduced by reducing the dependence on chemicals, sludge disposal and time for cleaning struvite formation that occurs in the recycled ways rich in phosphorus [27]. In addition, the removing of chemical treatment would decrease the size of treatment plant. Secondly, struvite production will help to maintain the food industry by the producing easy soluble P-contained fertilizer. Moreover, P-recovery though the struvite precipitation is an alternative source of the mineral phosphorus.

The recovery of phosphorus has the potential to reduce operating costs by reducing reliance on chemicals, sludge disposal and downtime for cleaning struvite formation that occurs in the recycled streams rich in phosphorus.

2. Theory

2.1 Struvite characteristics

Struvite, usually, forms after anaerobic digester, where releases high concentration of ammonium and phosphate. Struvite forms orthorhombic (straight prisms with a rectangular base) crystals in ratio 1: 1: 1 between magnesium, ammonium, and phosphate (Eq. 2).

$$Mg^{2+} + NH_4^{+} + H_nPO_4^{3-n} + 6H_2O = MgNH_4PO_4 * 6H_2O + nH^{+} \quad (2)$$

The main chemical and physical characteristics of struvite are shown in Table 2.

Table 2 – Chemical-physical properties of struvite

Nature	Mineral salt
Chemical name	Magnesium ammonium phosphate hydroxide
Formula	$MgNH_4PO_4$
Molecular mass	245,41 g.mol^{-1}
Color	Colorless, white (dehydrated), yellow or brownish, light gray
Density	1,1711g/cm
Solubility	Low in water: 0.018 g.100 ml^{-1} at 25 ° C, High in acid: 0.33 g.100 ml^{-1} at 25 ° C in 0.001 N HCL; 0.178 g.100ml -1 at 25 ° C in 0.01 N HCL [28]

The concentration of the constituent ions depends on the amount of treatment the source water received and the characteristics of the influent. At secondary treatment plants, magnesium is usually the limiting ion in the formation of struvite in the system. Thus, it requires edition of magnesium sources, such as bio-product from magnesium oxide production, the pyrolysate of magnesite, magnesite mineral, bittern and seawater [29]. Although all of them could be used in a wastewater treatment, most of them are expensive and require additional treatment. One example is $MgCO_3$, which is mined from magnesium rocks. It must be further heated to be converted into MgO to become dissolve in urea. At the same time bittern (magnesium chloride and magnesium sulfate) is extracted from seawater [30]. It is easy to access, because main source locates at coastal areas. Thus, in comparison with $MgCO_3$, $MgCl_2*6H_2O$ and $MgSO_4*7H_2O$ are relatively cheap, wide-spread and easy in a use.

Other component, as ammonia comes from the urea from wastewater. In a contrast with magnesium, the concentration of ammonium is usually much higher than both magnesium and phosphate, but its percentage increase in the return line is low [31].

Phosphate drives from different branches of life, and could be found in wastewater, waste from food industries, detergents and other [11]. Since, phosphate and ammonium enrich the struvite, it could be used in the agronomical industry.

The use in the agronomic industry goes both economically and ethically well. Because the struvite as a white powder, is easy to transport and apply on fields. It contains vital nutrients, which are necessary for the plants. Also, struvite does not burn the roots due to its slow releasing characteristics, which is common with traditional ammonium–phosphate fertilizers [19]. It is slightly soluble in water which helps to avoid rainfalls and would not be flashed away from the soil for a long time. The biological nitrification mechanism is enhanced, that makes it bioavailable for plants [32].

Although struvite tends to precipitate in wastewater, there is challenges which can affect struvite grows, precipitation and quality. The reason for that, is a content of many ionic species, as Ca^{2+}, K^{+}, CO_3^{2-} in wastewater. This species can influence the formation of struvite by reacting with its component ions, namely Mg^{2+}, PO_4^{3-} and NH_4^{+}. That's why it is vital to investigate and maintain parameters which affecting struvite formation, namely pH, molar ratio and retention time.

2.1.1 pH

The pH at which struvite may precipitate is one of the main factors influencing the crystallization process. pH can affect solubility of struvite, quantity of struvite precipitation, transformation of NH_4^{+}, crystal growth and its characteristics.

According to the equation (2), the reaction between magnesium, ammonium and phosphate ions causes the release of hydrogen ions (H^{+}) in solution, which leads to drop of pH. It causes spontaneous precipitation of struvite [28]. In addition, the rate of pH decreases the speed at which struvite particles are forming. That can influence the quality of the crystals formed.

Changing of pH is highly affecting activities of NH_4^+. Thus, for example, as pH increases from 7 to 9, the present of total ammoniacal nitrogen (NH_4^+) decreases from 99% to 64% [33]. Solution pH also affects struvite crystal growth rate. An increase in pH caused an increase of supersaturation and a resultant increase in the growth rate. In addition, an increase of pH from 8 to 11 could decrease 5 times the mean crystal size of struvite formed in solutions. Some of the research about the optimal pH of struvite formation is shown in Table 3.

Table 3 - Review of the optimal pH for Struvite precipitation

Source	**pH**
A. W. Taylor, A. W. Frazier, 1963	>5.5
X.-D. Hao, C.-C. Wang, 2005	7.5 - 9.0
Bouropoulos and Koutsoukos, 2000	8.5 - 9.5.
L. Pastor, D. Mangin, R. Barat 2008	8.2-9.5 [34]
Hao, X.D., Wang, C.C., 2008	8 -11

pH for struvite formation depends on conditions of plants and goals of manufacturers. In this way, if need to maximize struvite purity while slower precipitation, the pH should be near 8.7. J.Wang (2005) claims that pH up to 8.7 create regular crystal shape, and the precipitates represent struvite with high-purity. Higher pH then 10 leads to the formation of amorphous precipitate and decreases the struvite purity in the deposits [35].

To have more clear understanding of the behavior of struvite precipitation under the different pH, the dependence of concentration of nitrogen, phosphorus and magnesium versus pH is shown in Figure 9.

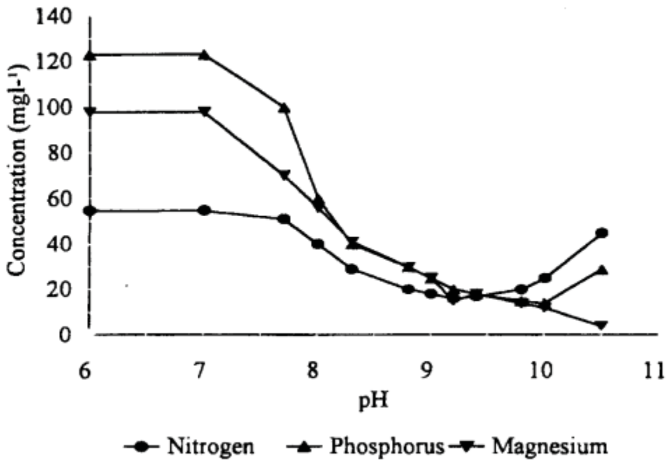


Figure 9 - Concentrations of nitrogen, phosphorus, and magnesium versus pH at 25C [36]

At the pH 6 to 7 elements as nitrogen, phosphorus and magnesium are not reacting with each other. After the pH increases from 7 to 8, the crystals are in the growth stage and the struvite slowly starts to precipitate. It means that crystal lattices is formed by absorbing NH_4^+ , PO_4^{3-} and Mg^{2+} in the solution on the crystal lattices own surface and polymerizing with other crystals to form larger crystals [37]. Moreover, the speed of struvite precipitation is gradually increases. At the pH between 9.0-9.4, the rapid struvite precipitation is occurred. When the pH is more than 10 the struvite crystals starts to ruin.

In a line with the pH, the molar ratio plays vital role in struvite precipitation and phosphorus recovery.

2.1.2 Molar ratio

Ratio between magnesium, ammonium, and phosphorus plays crucial role in struvite formation. By using different ratio, there is a chance to increase product yield, nutrient removal and decrease the operational cost.

Unless conventional ratio for the struvite formation is Mg: N: P = 1:1:1 (Tab. 4), the amount of PO_4^{3-} and Mg^{2+} in wastewater are not proportional and inadequate [29]. Thus, to get the high performance of nutrients recovery, the molar ratio should be changed. That could be done by increasing ions amount of Mg^{2+} and NH_4^+.

H. Huang (2011) with collegues noticed that when Mg^{2+}: NH_4^+ molar ratio increased from 1.5 to 2.5 the PO_4-P removal ratio rapidly increased. While, further increase in Mg^{2+}: NH_4^+ molar ratio 2.5-3.5 caused a slow increase in the removal ratio of PO_4-P. On the other hand, B. Etter et al. (2011) claims that a minimum molar ratio of 1.2 mol Mg $molP^{-1}$ is enough to remove about 95% of phosphate [38]. L.Pastor, D. Mangin, R. Barat (2008) confirm the theory that increasing in Mg and N molar ratio increases the efficiencies of nutrients recovery throgh struvite precipitation [34].

Table 4 - Molar ratio for struvite formation

Source	Ratio Mg: N: P
Conventional	1:1:1
L. Pastor, D. Mangin, R. Barat, 2008	0.8-2:1.8-2.4:1
B. Etter, E. Tilley, R. Khadka, 2011	>1.2-1.8:1:1
H. Huang, C. Xu, and W. Zhang, 2011	1.5-3.5:1:1
A. Miles, T.G. Ellis, 2001	1.25:1:1

2.1.3 Retention time HRT/ Reacting time

Hydraulic retention time (HPT) is a measure of the average length of the time that a compound remains in a storage unit [39]. In a case with struvite, it is the time that wastewater with additional magnesium salt proceeds in struvite reactor. In a laboratory conditions, it is equally to equate terms hydraulic retention time and reaction time.

Reaction time influence recovery of nutrients by struvite crystallization. There is no precise retention time for struvite precipitation. In a literature given several examples of variation the retention time. Thus, according to Li-yuan Chai (2017), the optimal reaction time for struvite precipitation with high nutrients recovery is 30 min [40]. Other research were conducted during 60 min and 2 hours of precipitation [41]. H. Huang, (2016) carried experiment from 0 to 180 min, and claim that reaction time is the key factor which affect the recovery of phosphorus [42]. To maximize P-removal, is vital to verify conditions of struvite formation. Thus, next hypothesizes are based on three main variations which affects P-removal through struvite precipitation.

3. Hypothesis

Based on the theory on how a range of factors influence the precipitation of the struvite the following hypothesis is defined to try to optimize the struvite precipitation at HIAS sewage plant.

Hypothesis 1:

An increase in pH from 8 to 8.3 will increase phosphorus removal through struvite precipitation.

Hypothesis 2:

Retention time in the interval 20 to 60 min is optimal for struvite formation with high P-recovery.

Hypothesis 3:

Ratio of Mg^{2+}: NH_4^+ 1.2: 10 and 1.5: 10 causes about 95% of P removal.

Hypothesis 4:

The concentration of toxic elements (heavy metals), in the struvite, would feet the legislations requirements under the ratio of Mg^{2+}: NH_4^+ 1.2: 10 and 1.5: 10, pH 8.0, 8.3.

4. Materials and methods.

During the laboratory experiment several reagents and solutions were used. The waste water containing NH_4 and PO_4-P was taken from WWTP in Hamar. For struvite precipitation was added magnesium chloride hexahydrate ($MgCl_2$*$6H_20$, Merck) to a mixture of the wastewater.

To adjust pH was used sodium hydroxide (2M NaOH) and hydrogen chloride (1M HCl). To measure phosphates was used 1 mg/L phosphate stock solution, 1 M ascorbic acid and, 1M ammonium molybdate. To define metals and non-metal elements was used ultra-pure nitric acid (HNO_3) and ultra-pure hydrogen chloride (HCl).

4.1 Sampling of wastewater from HIAS

Two sources of wastewater from HIAS sewage plant were used for the experiments. One source contained NH_4 and other PO_4-P. Ammonium wastewater sample was taken from the reject water after biological treatment. Phosphorus wastewater sample was taken from a sludge after biological treatment (Fig. 5). It was thickened over a disc-filter, then left for 16 hours for secondary PO_4 release.

Concentrations of wastewater were measured both at HIAS and laboratory at NMBU. The results of measurements showed that the concentrations of rejected water and sludge water were 2262 mg/l of NH_4-N and 189 mg/l of PO_4-P respectively. To compare the concentrations of the total nitrogen and phosphorus in average in normal wastewater (NH_4-N of 8 to 10 mg/L, PO_4-P of 1 to 3 mg/L) [31], the concentrations of the experimental wastewater is very high. The high amount of NH_4 corresponds to a molar ratio Mg^{2+}: NH_4^+ = 1:10. This could be explained by the fact that on a given thesis was used wastewater, taken from the reject- and sludge- parts after the biological treatment. Additional properties of experimental wastewater are shown in Table 5.

Table 5 - Properties of the ammonium and phosphorus wastewater as a water from the reject- and sludge- parts after the biological treatment at the HIAS sewage plant, and an experimental wastewater, which represent a mix of sludge- and reject-water in a ratio of Mg: N 1:10.

Properties	Sludge water	Reject water	Experimental WW Mg^{2+}: NH_4^+= 1:10
Turbidity, NTU	452	144	405
Conductivity, micro s/cm	2013	14	5.76
PO4, mg/l	189	-	189
NH4, mg/l	-	2262	2262
pH	5.1	8.3	7.0-7.6
Na, mg/L	-	-	83
Mg, mg/L	-	-	40
Al, mg/L	-	-	1.6
P, mg/L	-	-	150
K, mg/L	-	-	160
Ca, mg/L	-	-	92
As, ug/L	-	-	9.4
Cd, ug/L	-	-	0.2
Hg, ug/L	-	-	<0.055
Pb, ug/L	-	-	1.3

4.2 Design of experiment

According to the hypothesis and theory, the maximum P-recovery should happen under the conditions which are shown on Table 6. For the better ortho-P removal efficiency, the PO_4 and NH_4 ratio were constant while Mg ratio changed: Mg: NH_4: PO_4 = ***1.2***:10:1 and ***1.5***:10:1. The experiment carried on constant pH 8.0 and 8.3 during 20, 40 and, 60 min. According to the Table 6, the amount of experiments is (2*1*1*12*3) *3 repetition =36.

Table 6 - Conditions for struvite precipitation with variations for all factors

Mg	**NH4**	**PO4**	**pH**	**Time**
1.2			8.0	20
	10	1		40
1.5			8.3	60

All experiments were carried on jar-tests in laboratory conditions, in IMV department at NMBU (Fig. 10).

4.3 Sample treatment at lab

Sample volume for each jar was 550 ml. Since the ratio of NH_4 and PO_4 were constant, it was taken the same volume of reject- and sludge- water for each ratio, namely 150 ml and 400 ml respectively. It was mixed in a jar. To get ratios of Mg 1.2 and 1.5, was added 0.45 and 0.61 g of $MgCl_2*6H_20$ respectively. Magnetic stirrer carried the mixing, firstly, 1 min on 300rpm, and after 20, 40, 60 min on 100rpm (Tab. 7). The pH was measured and maintained during the all experiments. To maintain pH 8.0 and 8.3 was used solution of 1M HCl and 2M NaOH.

Table 7- Design of jar-test experiment

Ratio of Mg: NH_4: PO_4, mole	Sludge water, ml	Reject water, ml	$MgCl_2$, g
1.2:10:1	300	150	0.46
1.5:10:1			0.61

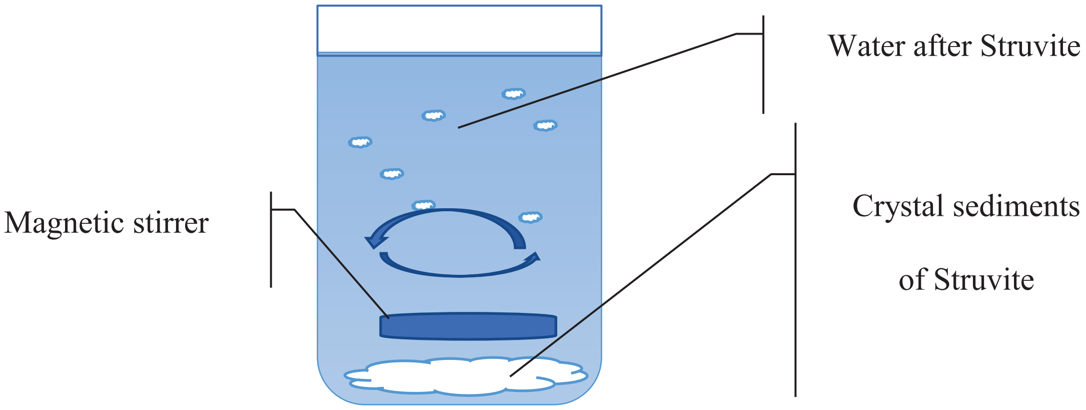


Figure 10 - Jar test with struvite precipitation

After the struvite precipitation, all samples were centrifuged for 10 min at a speed of 3000rmp at temperature 20C. The residual liquid was separated and analyzed for phosphorus, ammonium, turbidity, conductivity, FIA, and ICP. Precipitation as struvite was dried in laboratory own for 2-3 days. To avoid evaporation of ammonium, the temperature was set to 65◦C. After, the dry sediments have been weighted and sent for ICP - analysis.

4.4 Analytical analysis

4.4.1 Phosphates - spectrophotometric analysis

Spectrophotometry is an experimental technique which is used to measure the concentration of solutes in a specific solution [43]. A specific solution absorbs the light on different waves and intensities. Each wave corresponds specific substance. Thus, it is possible to identify different dissolved substances and its concentration depends on a task.

The tool which makes spectrophotometry analyze calls spectrophotometer (Fig. 11). Spectrophotometer should be warmed up and turned on at least 15 min before running any sample. To measure phosphates, spectrophotometer should be adjusted to the wavelength 700 nm.

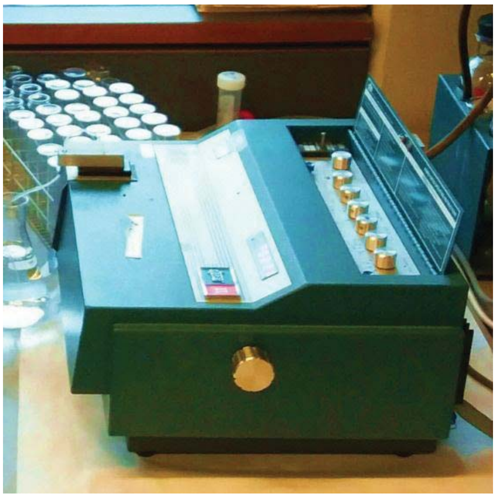


Figure 11 - Spectrophotometer at NMBU, IMV laboratory

Sample preparation for phosphorus measurement.

According to the Norwegian standards [44], should be prepared three main solutions, namely blanked, standard and, a solution of the sample. The blank solution contains 10ml of distilled water and the standard solution contains 10 ml of 1 mg/l phosphate stock solution. Later, to the 10 ml of standard solution, blanked solution and, diluted sample was added 0.4ml ascorbic acid and after 30 sec 0.4 ml 1M ammonium molybdate. After 20min the samples was measured. To calculate the concentration of phosphates was used the equation 3.

$$\frac{ABS\ sample}{ABS\ STD} * dilution\ rate = [ppm,\ \ \frac{mg}{L}] \tag{3}$$

Where,

ABS – absorbance,

STD – standard solution

4.4.2 Ammonium – Flow injection analysis (FIA)

To measure the concentration of ammonium was used the flow injection analysis. FIA is an automated method of chemical analysis (Fig. 12). The sample is injected into a flowing carrier solution and mixes with reagents before reaching a detector.

Figure 12 - Flow injection analysis tool[9]

After the centrifuge, the liquid samples were taken. Since experimental wastewater contained a high concentration of ammonium, each sample was diluted 1000 times and sent for flow injection analysis. Laboratory stuff carried the flow injection analysis.

---

[9] https://www.hach.com/flow-injection-analysis/lachat-quikchem-flow-injection-analysis-system/family?productCategoryId=35547627752

4.4.3 Turbidity, water clarity

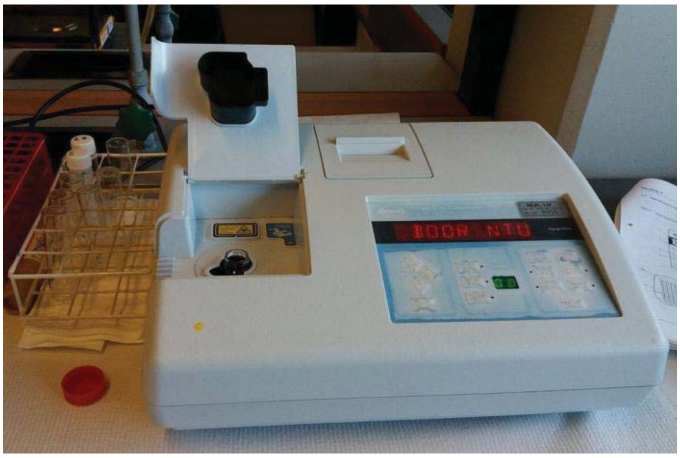


Figure 13 - Turbidity meter at NMBU, IMV laboratory

Turbidity defines the purity of water. Turbidity in a water is caused by the presence of TSS (total suspended solids), which absorbs the light rays. Turbidity can cause operational problems, as reducing disinfection treatment [22].

Turbidity measures with the help of turbidity meter. Photoelectric cell measures scattered light on a digital scale (Fig. 13). The instrument is calibrated with the standard solutions of the colloidal substances. The rate of measurement is from 0 to1000 NTU (nephelometric turbidity units).

4.4.4 Electrical conductivity analysis

Electrical conductivity (EC) is an ability of water to conduct electricity. EC uses to measure the salinity of the water. EC depends on salts ions and its balances. Moreover, electrical conductivity depends on temperature. Thus, while temperature increases, conductivity increases too. EC is measured in terms of conductivity per unit length. In given thesis, EC is shown in µS/cm (micro-Siemens/ cm) [43]. Electro-conductivity is measured by the conductivity meter (Fig. 14).


Figure 14 - Conductivity meter at NMBU, IMV laboratory

4.4.5 ICP-MS - Inductively coupled plasma mass spectrometry

A significant part of the anthropogenic emission of heavy metals ends up in wastewater. Different industries processes with such elements as Pb, Mn, Zn, Hg, Fe, which are discharged in a waste. Even after the treatment process, there is a very low concentration of elements in a solution. To define those metals and several non-metals elements in a solution is applied inductively coupled plasma mass spectrometry analysis (ICP-MS).

The ICP-MS analysis at NMBU was carried with the help of laboratory staff at IMV department. Since focus of thesis is to maximize P-recovery, was important to define elements which can inhibit P-removal and decrease its efficiency. Thus, during the ICP-MS analysis were determined next elements: Na, Mg, Al, P, K, Ca. Also, to avoid getting an excess of the heavy metals into the water was studied a presence of Cd, Hg, Pb and As in experimental wastewater.

Sample preparation for ICP-MS

After centrifuging of struvite solution, 2ml of water sample was taken to the 10ml tube. It was diluted with 6 ml of distilled water and added 1ml ultra-pure HNO_3. Then was added 0.1ml ultra-pure HCl and, finished with distilled water to 10ml. The solution has been sent to ICP-MS analysis. To make a mass spectrometry measurement, was used reference material.

5. Results and discussion

5.1 Phosphorus recovery

The results after the experiments showed that, the average recovery of phosphates is quite high (Fig. 15). However, the ranking of treatments shows a significant difference in a phosphorus reduction. Thus, the lowest amount of Mg 1.2 with the lowest pH 8 gives the lowest recovery of phosphates, namely 89,5%. In a contrast, the highest pH 8.3 with the highest ratio of Mg 1.5 gives the higher phosphates recovery, at almost 97%. It seems like the lower pH shows negative effect for phosphorus recovery.

Although, the high pH reflects the high results of P recovery, the drop of P-recovery at 60 min with Mg 1.2 (Figure 15b), can be explained by the presence of calcium ions in a water phase. H. Yan and K. Shih (2016) confirm that struvite formation under the high pH of initial water can be negatively affected by the interference from calcium ions [45]. As shown in a table 5, the content of calcium in the initial water is 92 mg/L while after 68 mg/L (Tab.10), which can negatively affect the formation of magnesium phosphate complex. The other study (Warmadewanthi and J. C. Liu, 2009), states that with the increasing of pH, dominant precipitants is brucite ($Mg(OH)_2$), and the phosphorus removal efficiency will be decreased. It happens because of competition between hydroxyl and PO_4^{3-} ions, and because brucite is the dominant Mg species in a high pH [46].

Although, if to compare the phosphorus removal rate at the pH 8.3, ratio Mg: PO_4 =1.2:1 and 1.5:1 it is seen that the recovery rate is high for both ratio, and they follow the similar behavior. Moreover, the removal efficiency of PO_4^{3-} can increase significantly with increased molar ratio, and removal efficiency reached 92.1% as molar ratio increased to 3:1. Although, given thesis was focused on variation of ratio between Mg: N, can be assumed that high Mg concentration in solution cause maximum PO_4^{3-} recovery and compensate the negative effect of pH [46].

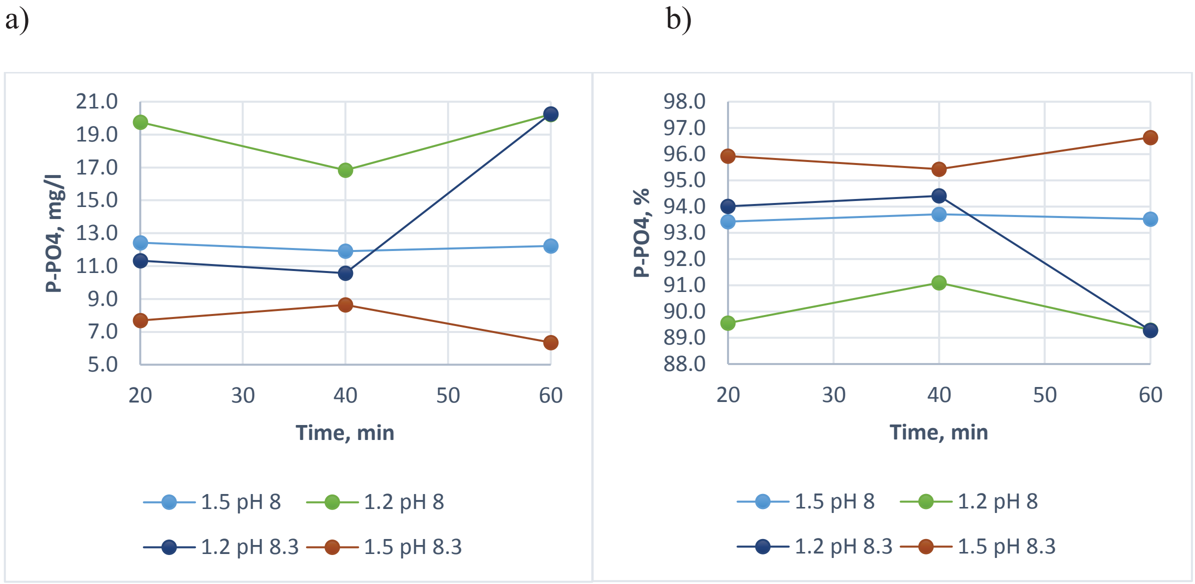
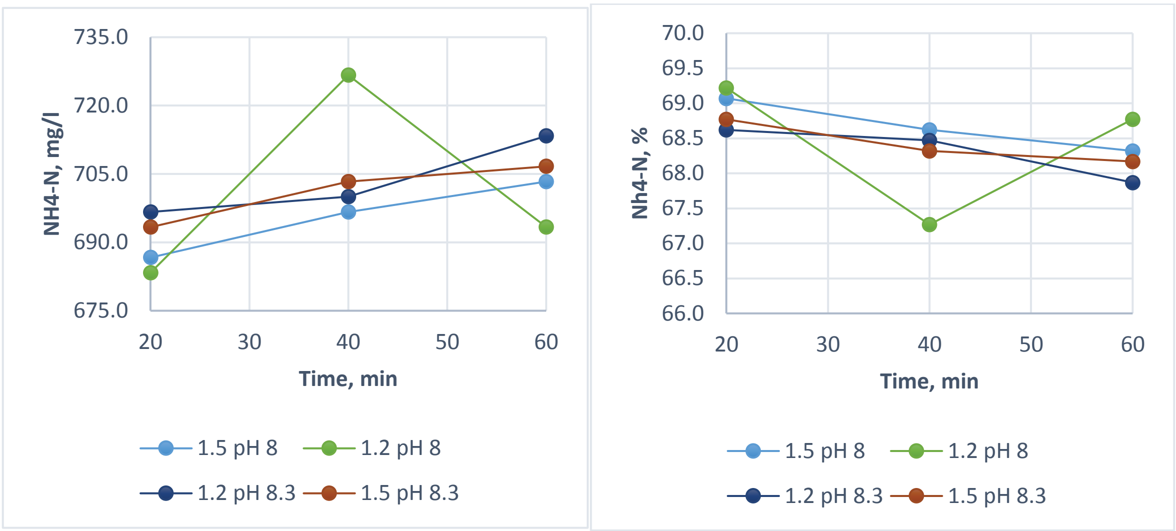


Figure 15 - a) concentration of phosphorus in an experimental wastewater after struvite precipitation; b) phosphorus recovery from experimental wastewater after struvite precipitation under the pH 8; 8,3; reaction time: 20, 40, 60 min; ratio Mg: N=1.2:10; 1.5:10; temperature 25C

5.2 Ammonium recovery

In a contrast with the phosphorus reduction, the ammonium recovery shows a different pattern. The same conditions (Mg=1.5, pH 8.3) for the highest concentration of phosphorus recovery (96%) shows the lowest concentration of ammonia (68.5%). That can be a consequence of the experimental pH 8 and 8.3.

The pH range is very important for ammonium recovery, because the bacteria for nitrification and denitrification have their own optimal pH value [47]. For Nitrobacteria, it is 6.5-8.3, and for Nitrosomonas is 8.0-8.5. Thus, the change in pH influences the reduction of nitrogen in general [42]. Theoretically, the experimental pH should give a high ammonium recovery. Although, the ranking between the treatments shows almost the same reduction of ammonium, which is about 68.5-69.5% (Fig. 16, b). Those results, from the other hand, are confirmed by the W. Stumm (2013), who stated that with the increasing of pH>7, the ammonium recovery during the struvite precipitation drops down [33].


a)

b)

Figure 16 - a) concentration of ammonium of an experimental wastewater after struvite precipitation; b) ammonium recovery from experimental wastewater after struvite precipitation under the pH 8; 8,3; reaction time: 20, 40, 60 min; ratio Mg: N=1.2:10; 1.5:10, temperature 25C.

Since ranking of treatments and pattern of ammonium recovery is very similar, the point of Mg=1.2, pH 8 could indicate the mistake in analysis.

5.3 Turbidity

The turbidity removal is one of the main characteristics which illustrates the struvite precipitation. During the given experiment, there are three factors which can affect turbidity removal, namely changing in pH, time and ratio of Mg: N.

According to the figure 15 (a, b) the turbidity recovery was followed by the two patterns. The similar behavior was noticed at Mg ratio 1.2 and 1.5 pH 8.3, namely recovery of turbidity was 85-86%. That effect may alternate, if to reduce pH to 8 and increase Mg concentration. In that way, it can compensate the effect of reduction in the pH. The same could happen if to reduce Mg ratio to compensate for the increasing in pH number. The next variable which can affect the turbidity removal is the time.

According to the figure 17, for the pH 8 and some variables at pH 8.3, the turbidity increases with increasing of time. That indicates that the part of phosphorus still stays in a form of suspended particles, which is too light to be centrifuged. To find out if the changing of the time causes significant changes in turbidity recovery or not, the one-way ANOVA Variations analyses were conducted [48].

From the Figure 17(b) is seen, that the turbidity removal at 20 min shows better numbers, more than 87%, while at 60 min the recovery dropped to 84%. Thus, to get whether any means between the three groups of time (20, 40, 60) are statistically significantly different from each other, was used the Null Hypothesis (Eq. 4):

$$H_O: \mu_1 = \mu_2 = \mu_3 = \cdots = \mu_k \tag{4}$$

Where,

μ = group mean, assume that all means are equal

k = number of groups.

If the one-way ANOVA returns a statistically significant result, the alternative hypothesis (Ha) works. That means that at least one mean is different from the others. After the row of calculations (EXCEL statistics data analysis), was achieved the next numbers (Tab.8).

Table 8 - The one-way ANOVA Variations analyses, calculated within three groups of turbidity recovery: 20, 40 and 60 min. SS- sum of squares, DF- degrees of freedom, M - Mean square, F-statistic = MSB/MSW, P- refers to hypothesis, whether to accept it or not, assume that P-value=0.05. F-critical- the area on F-distribution, which

Variation Source	SS	DF	M	F	P	F-critical
Between groups (SSB)	9.7	2	4.8	5.5	0.0087	3.3
Within groups (SSW)	29.1	33	0.9			
Total (SST)	38.8	35				

As it is showed in the table 8, the P-value is less than theoretical P (0.0087<0.05). It indicates the rejection of Null hypothesis. In addition, the value of F-statistic is more than F-critical (5.5>3.3) and locates on rejection region. Thus, it can be assumed that the drop of turbidity recovery from 87 to 84% during the time is a statistically significantly changes. Thus, the increasing of time can affect struvite precipitation.

Although, the results of increase in time showed increasing in turbidity, at the given thesis, the time less than 20 min was not under the consideration. That decision was based on a literature review and the rate of supersaturation of struvite. Also, according to Huang (2016) the supersaturation for struvite formation was achieved after 30 min of steering [42].

From the other side, was noticed that turbidity recovery at the point with Mg 1.5 and pH 8, shows the same small numbers and poor turbidity removal for the all 3 replications of experiment. According to N. Z. Ning and A. Aris (2016), the pH which is equal or lower than 8 showed the poor performance in removal of turbidity during the struvite precipitation [49]. Since, the peak of turbidity recovery was achieved at pH 8.3, for both Mg ratio 1.2 and 1.5 and, time 40 min (Fig15, b), it can be assumed that the higher pH causes the higher turbidity removal. It is caused by sudden increasing of struvite precipitation, which is confirmed by the amount of sludge precipitation (tab. 11).

However, further increasing of time (60 min) in a line with the same pH 8.3 and Mg ratio 1.2 and 1.5 cased the increase of turbidity in a water phase. One of the assumptions is based on the study (A. Triger, J.-S. Pic, and C. Cabassud, 2012), where increasing of turbidity is explained by the agglomeration of a large numbers of new smaller crystals, which induce turbidity [50]. The similar hypothesis was noticed by A. Uysal, Y. D. Yilmazel, and G. N. Demirer (2010), who explain the increasing of turbidity by high content of TSS in a wastewater [51]. The last one is confirmed by the presence in the experimental wastewater a high amount of inorganic and organic elements (Tab.5), which could bind with each other into small-size complexes, which is difficult to centrifuge.

a) b)

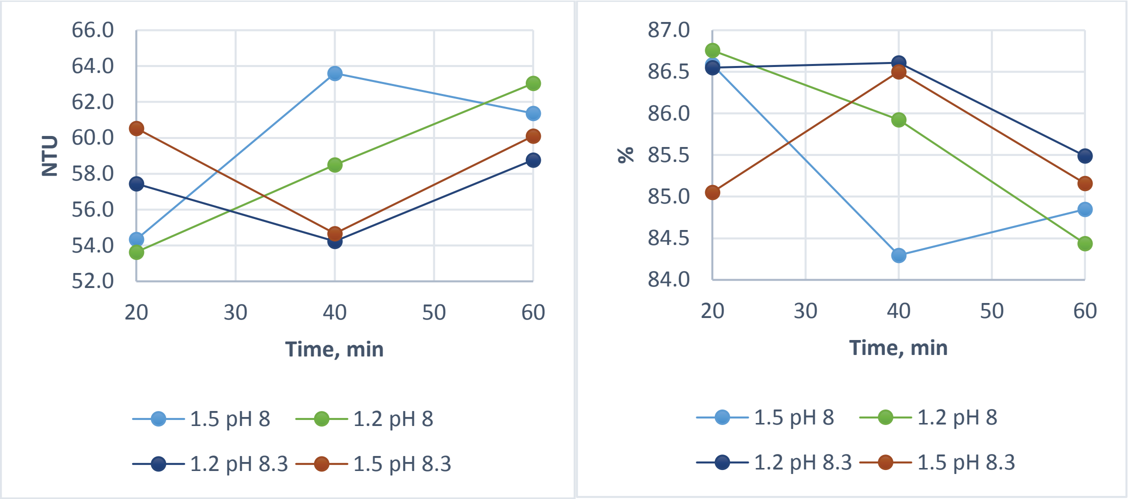


Figure 17 - a) Turbidity efficiency in an experimental wastewater after struvite precipitation; b) Turbidity removal efficiency of experimental wastewater after struvite precipitation at the pH 8; 8,3; reaction time: 20, 40, 60 min; ratio Mg: N=1.2:10; 1.5:10, temperature 25C.

5.4 Electrical conductivity analysis

The results from the EC-analysis showed that the electrical conductivity has dramatically increased after the experiment. Thus, before the experiments the electrical conductivity of the experimental water was about 5.7 µS/cm, after the experiments, the salinity of water has rapidly increased up to 7 µS/cm (Fig. 18).

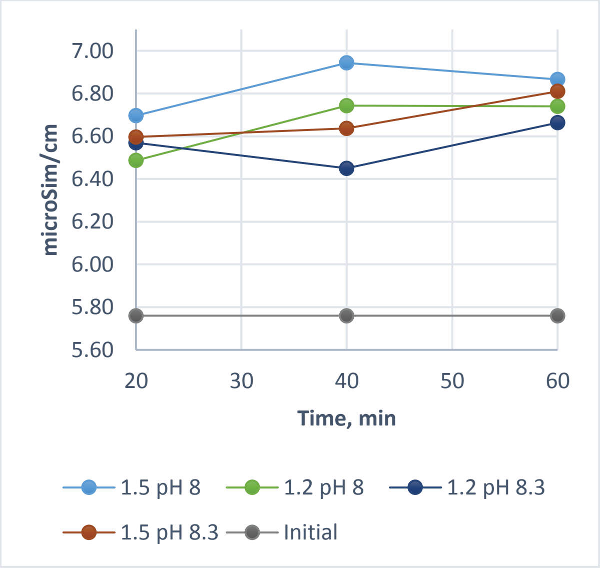


Figure 18 - Conductivity of experimental wastewater after struvite precipitation at the pH 8; 8,3; reaction time: 20, 40, 60 min; ratio Mg: N=1.2:10; 1.5:10; temperature 25C to compare with initial conductivity of experimental wastewater mixture.

The increase in conductivity could be explained by that fact that quite a high amount of 2M NaOH was added during each experiment (Tab 9). It was made to maintain the stable pH.

Table 9 - The consumption of 2M NaOH during the experiments, which was used to maintaining the pH 8 and 8.3

Time, min	pH	N	Mg	NaOH, 2M, ml	Time, min	pH	N	Mg	NaOH, 2M, ml
20	8	10	1.2	3.5	20	8	10	1.5	3.4
40	8	10	1.2	4.3	40	8	10	1.5	3.3
60	8	10	1.2	4.3	60	8	10	1.5	3.8
20	8.3	10	1.2	4.6	20	8.3	10	1.5	4.6
40	8.3	10	1.2	4.5	40	8.3	10	1.5	4.1
60	8.3	10	1.2	4.6	60	8.3	10	1.5	4.5

5.5 Elements other than Phosphorus and Ammonium.

In a row with the phosphorus and ammonium, there are many other elements which play a role on water and struvite quality. To find out the quality of water samples, the ICP-analyses was conducted. The data of elements analyses are shown in Table 10.

All water samples contain a high amount of sodium and magnesium. It is explained by the experimental set. During all experiments, a high amount of both Mg (to maintain ratio) and 2M NaOH (to maintain pH) were added (Tab.9).

The other element which represents relatively high numbers in a water phase is potassium. Usually, potassium in a small amount increases struvite precipitation. However, the high amount of K^+ creates a complex like struvite, namely $KMgPO_4 * 6H_2O$ [52]. But because there is a high concentration of potassium is present in the water phase (Tab.10), it means that it did not react with the phosphorus and struvite was prioritized to precipitate.

In a line with the other elements, recovery of calcium is important. The high concentration of calcium compete with magnesium and form the tri-calcium phosphate complex ($Ca_3(PO_4)_2$), which is usually settled on a plant's equipment [45]. Moreover, calcium phosphate can bind that phosphorus, which can be recovered by the struvite precipitation. The data from the Table

10 shows a high content of Ca^{2+} in a water phase. It means that calcium was not bind with phosphorus. Also, according to H. Q. Yu, J. H. Tay (2001), the high concentration of calcium can inhibit the struvite crystallization [53], which as a result can give a low yield of struvite (Tab. 11).

Moreover, the presence of many different elements reflects to the presence of Total Suspended Solids (TSS) in a water phase. A. Uysal, Y. D. Yilmazel, and G. N. Demirer (2010) confirms that the presence of TSS in large amounts gives way to precipitation of these solids in place of the components of struvite, thus inhibiting the formation of struvite [51]. It is also confirmed by the increasing of turbidity (Fig. 17a)

The next threat for human health is the heavy metals. According to results from ICP (Tab.10), initial concentration of heavy metals, as mercury, cadmium and arsenic almost did not change. Although, the numbers were very small, it means that metals did not precipitate in a form of struvite, but still are present in a liquid phase. On the one hand, that water need an extra treatment and struvite with a law amount of heavy metals could work as a safe fertilizer.

In a contrast to the heavy metals, the concentration of phosphorus in a water phase has dramatically decreased, from 250 mg/L to less than 20 ml/L. That positively reflects on struvite quality, because PO_4-P settled in a form of struvite, which in a future would be used as nutrient-reached fertilizer.

.

Table 10 - ICP data of an experimental wastewater before and after struvite precipitation under the pH 8; 8,3; reaction time: 20, 40, 60 min; ratio Mg: N=1.2:10; 1.5:10, temperature 25C .

Time, min	pH	N	Mg	Na, mg/L	Mg, mg/L	Al, mg/L	P, mg/L	K, mg/L	Ca, mg/L	As, ug/L	Cd, ug/L	Hg, ug/L	Pb, ug/L
Experimental WW	-	10	1	83	40	1.6	150	160	92	9.4	0.02	<0,055	1.3
20	8.0	10	1.2	363	49.3	0.35	20.3	156	71.6	9.07	0.03	N/A	1.10
40	8.0	10	1.2	390	82.0	0.38	16.0	170	77.3	9.17	0.03	N/A	1.00
60	8.0	10	1.2	450	44.0	0.33	14.6	163	68.0	9.30	0.05	0.06	1.08
20	8.0	10	1.5	470	71.6	0.36	11.0	156	71.3	9.20	0.07	0.05	0.77
40	8.0	10	1.5	493	50.0	0.40	20.3	163	69.3	9.10	0.03	N/A	0.60
60	8.0	10	1.5	433	76.3	0.40	14.3	153	67.6	8.80	0.02	N/A	1.10
20	8.3	10	1.2	436	45.3	0.35	16.0	160	68.3	9.57	0.02	N/A	0.81
40	8.3	10	1.2	410	74.6	0.38	10.5	153	69.3	8.67	0.03	N/A	0.56
60	8.3	10	1.2	436	49.0	0.39	20.3	163	68.0	8.97	0.02	N/A	1.40
20	8.3	10	1.5	426	78.6	0.37	14.0	163	71.0	8.90	0.01	N/A	0.58
40	8.3	10	1.5	433	49.3	0.32	21.0	160	68.3	8.77	0.02	N/A	0.53
60	8.3	10	1.5	483	74.6	0.38	9.93	160	74.0	8.70	0.02	N/A	1.13

5.6 The struvite precipitation and analysis

After the set of the experiments a very small amount of sludge was achieved (Fig. 19). To be able to make an analysis of the elements content, it was decided to group sludge from each replication and make an average. Such method excludes statistical analyses, but is still useful to make a rough expertise. Thus, after the all experiments were achieved 12 sludge samples (Tab. 11).

Figure 19 – The example of the struvite which was achieved under the different conditions, such as time (20, 40 and 60), pH (8.0; 8.3), ratio of Mg: N (1.2: 10; 1.5: 10)

Table 11 - The amount of struvite precipitated under different conditions: time (20, 40, and 60), pH (8.0; 8.3), and ratio of Mg: N (1.2: 10; 1.5: 10)

Time, min	pH	N	Mg	The mass of sludge, g
20	8.0	10	1.2	0.53
40	8.0	10	1.2	0.49
60	8.0	10	1.2	0.54
20	8.0	10	1.5	0.52
40	8.0	10	1.5	0.55
60	8.0	10	1.5	0.45
20	8.3	10	1.2	0.46
40	8.3	10	1.2	0.79
60	8.3	10	1.2	0.45
20	8.3	10	1.5	0.42
40	8.3	10	1.5	0.42
60	8.3	10	1.5	0.42

It is vital to produce struvite sludge with the high nutrients content and minimum toxic content, which can negatively affect the food produced by use of struvite fertilizer.

The results from the ICP (Tab.12) shows that sludge contains quite low amount of Mg, K, Ca. Originally magnesium, potassium and calcium are present in wastewaters in organic or inorganic forms, and so they can be found in sludge [1]. Thus, given concentrations do not affecting struvite quality. In a contrast to inorganic and organic elements, the concentration of heavy metals should be defined very precisely.

Heavy metals can be absorbed onto the surface of struvite or incorporated into its crystal lattice, and so to reduce the purity of the product [1]. However, as seen from Table 12, the content of heavy metals as As, Cd, Hg and Pb is much lower if to compare with EU requirements of heavy metals in sewage sludge [54]. It makes the struvite safe, ecologically friendly and suitable in using as a fertilizer.

Table 12 - Total content of elements in struvite sludge and a comparison with the European regulation for the heavy metals Cd, Hg and Pb.

Time, min	pH	N	Mg	Na, mg/L	Mg, g/kg	Al, g/kg	K, g/kg	Ca, g/kg	As, mg/kg	Cd, mg/kg	Hg, mg/kg	Pb, mg/kg
EU Regulations, mg/kg	-	-	-	-	-	-	-	-	-	0.2-0.4	0.16-0.25	7.5-12
20	8.0	10	1.2	20.0	87.0	0.6	10.0	13.0	0.68	0.012	0.020	1.3
40	8.0	10	1.2	21.0	86.0	0.6	8.3	18.0	0.64	0.010	0.018	0.94
60	8.0	10	1.2	19.0	84.0	0.9	8.3	19.0	0.73	0.015	0.024	1.3
20	8.0	10	1.5	22.0	88.0	0.6	11.0	15.0	0.71	0.014	0.016	1.2
40	8.0	10	1.5	15.0	99.0	0.6	6.7	16.0	0.68	0.013	0.018	1.1
60	8.0	10	1.5	14.0	93.0	0.9	6.7	16.0	0.77	0.015	0.023	1.1
20	8.3	10	1.2	16.0	87.0	0.5	7.2	15.0	0.51	0.013	0.013	1.9
40	8.3	10	1.2	21.0	83.0	0.9	9.2	18.0	0.70	0.015	0.024	1.3
60	8.3	10	1.2	13.0	89.0	0.6	6.2	16.0	0.75	0.010	0.021	0.97
20	8.3	10	1.5	21.0	84.0	0.5	8.6	13.0	0.61	0.020	0.016	3.3
40	8.3	10	1.5	15.0	84.0	0.6	7.7	13.0	0.59	0.019	0.018	1.2
60	8.3	10	1.5	13.0	110.0	0.9	6.2	16.0	0.87	0.016	0.024	1.9

6. Conclusion

Chemical precipitation through the pH and time elevation, and Mg^{2+}: NH_4^+ molar ratio amendment, can be used to recover a high amount of PO_4^{3-} as a struvite from the reject- and sludge-wastewater after the biological treatment.

- The Mg^{2+}: NH_4^+ molar ratio of 1.5:10 and the pH 8.3 is the optimum combination for PO_4^{3-} recovery, yielding up to 97% in the experiment. This confirms hypothesis 1 and 3 on page 26.
- The Mg concentration plays key role in phosphorus recovery. In a case with low pH, high concentration of Mg can compensate the negative effect of pH on phosphorus recovery.
- The recovery of ammonium with the increasing of pH (8 to 8.3) showed the similar numbers, at about 69%.
- Hypothesis 2 on page 26 is not fully confirmed because struvite precipitation seems to decrease at 60 min compared to 40 min testing. However, the retention time at 20 min increases the struvite precipitation and phosphorus recovery the most efficiently.
- Parameters such as pH and Mg^{2+}: NH_4^+ molar ratio can compensate the negative effect of each other on phosphorus removal from the wastewater. That allows varying pH and molar ratio depending on wastewater treatment plants goals and conditions
- The heavy metals content in the precipitated struvite is very low for all molar ratio, pH and time configurations tested, and meet the limits which can be present in a fertilizer. This confirms hypothesis 4 on page 26.

7. Recommendations for further investigations

Although the results of given thesis showed positive outcome about phosphorus recovery, the additional definition of the optimal parameters for struvite recovery should be done. There are few recommendations:

- Test the reaction time less than 20 min. If the precipitation of struvite for less than 20 min will give satisfactory results for phosphorus recovery, this would be advantageous for the treatment plant. The decrease in the time reduces energy consumption, therefore reduces the cost of running treatment plants and negative impact on the environment.
- Increase the sample volume to recover more struvite and to analyze the precipitate for microbial content. This should be done to confirm the safety of struvite as a fertilizer.
- To make a pilot scale study to produce struvite in amounts needed to test plant availability of especially phosphorus in small greenhouse systems. This should be performed before field application studies.

It is important to continue the development of phosphorus recovery through struvite precipitation, because as have been shown from the research, struvite can play crucial role in the future wastewater treatment and food industry. In the future recycling of phosphorus will become an important environmental and food safety issue. Therefore, the work started by HIAS is a key step to show how to optimize the treatment process by avoiding pollution of treatment equipment and pipelines, and provide environmentally sustainable, renewable nutrient source for the agriculture industry.

8. References

[1] B. C. Punmia, A. K. A. K. Jain, and A. K. A. K. Jain, “Waste Water Engineering,” *Laxmi Publication (P) Ltd*, vol. 192. 2005.

[2] V. M. Monsalvo, *Wastewater and Public Health: Bacterial and Pharmaceutical Exposures*. Apple Academic Press, 2015.

[3] N. A. Sciences, *Eutrophication: Causes, Consequences, Correctives; Proceedings of a Symposium*. National Academy of Sciences, 1969.

[4] E. Schnug and L. J. De Kok, *Phosphorus in Agriculture: 100 % Zero*. Springer Netherlands, 2016.

[5] T. Krogstad, T. A. Sogn, Å. Asdal, and A. Sæbø, “Influence of chemically and biologically stabilized sewage sludge on plant-available phosphorous in soil,” *Ecol. Eng.*, vol. 25, no. 1, pp. 51–60, 2005.

[6] N. P. Cheremisinoff, *Handbook of Water and Wastewater Treatment Technologies*. Butterworth-Heinemann, 2002.

[7] E. Schnug and L. J. De Kok, *Phosphorus in Agriculture: 100 % Zero*. Springer Netherlands, 2016.

[8] E. Valsami-Jones, *Phosphorus in Environmental Technology*. IWA Publishing, 2004.

[9] H. Tiessen, M. V. Ballester, and I. Salcedo, “Phosphorus and Global Change,” in *Phosphorus in Action: Biological Processes in Soil Phosphorus Cycling*, E. Bünemann, A. Oberson, and E. Frossard, Eds. Berlin, Heidelberg: Springer Berlin Heidelberg, 2011, pp. 459–471.

[10] J. Dhillon, G. Torres, E. Driver, B. Figueiredo, and W. R. Raun, “World Phosphorus Use Efficiency in Cereal Crops,” *Agron. J.*, 2017.

[11] J. R. Brummer, J. A. Keely, and T. F. Munday, “Phosphorus,” in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2000.

[12] P. C. F. C. Gardolinski, P. J. Worsfold, and I. D. McKelvie, “Seawater induced release and transformation of organic and inorganic phosphorus from river sediments,” *Water Res.*, vol. 38, no. 3, pp. 688–692, 2004.

[13] N. A. Sciences, *Eutrophication: Causes, Consequences, Correctives; Proceedings of a Symposium*. National Academy of Sciences, 1969.

[14] J. Schmidt, *Soil Erosion: Application of Physically Based Models*. Springer Berlin Heidelberg, 2013.

[15] S. Sharma and R. Sanghi, *Advances in water treatment and pollution prevention*. 2012.

[16] Z. Zhang, C. Wu, Y. Wu, and C. Hu, “Comparison of coagulation performance and floc properties of a novel zirconium-glycine complex coagulant with traditional coagulants.,” *Environ. Sci. Pollut. Res. Int.*, no. 2012, Feb. 2014.

[17] E. L. Sharp, S. A. Parsons, and B. Jefferson, “Seasonal variations in natural organic matter and its impact on coagulation in water treatment.,” *Sci. Total Environ.*, vol. 363, no. 1–3, pp. 183–194, Jun. 2006.

[18] R. W. McDowell and G. F. Koopmans, “Assessing the bioavailability of dissolved organic phosphorus in pasture and cultivated soils treated with different rates of nitrogen fertiliser,” *Soil Biol. Biochem.*, vol. 38, no. 1, pp. 61–70, Jan. 2006.

[19] J. D. Doyle and S. A. Parsons, “Struvite formation, control and recovery,” *Water Res.*, vol. 36, no. 16, pp. 3925–3940, Sep. 2002.

[20] I. S. Turovskiy and P. K. Mathai, *Wastewater Sludge Processing*. Wiley, 2006.

[21] I. About HIAS, “Hamar vannbehandlingsanlegg,” 2017. [Online]. Available: http://www.hias.no/vann-avlop/vannforsyning/vannbehandling/hamar/.

[22] N. P. Cheremisinoff, *Handbook of Water and Wastewater Treatment Technologies*. Butterworth-Heinemann, 2002.

[23] Hias renseanlegg, “Biologisk rensetrinn.” [Online]. Available: http://www.hias.no/vann-

avlop/avlop/avlopsrensing/biologisk/.

[24] T. I. Onyeche, “Sludge as source of energy and revenue,” *Water Sci. Technol.*, vol. 50, no. 9, p. 197 LP-204, Nov. 2004.

[25] Nettansvarlig Hias IKS, “Slambehandling.” [Online]. Available: http://www.hias.no/vann-avlop/avlop/slambehandling/.

[26] Hans Emil Glestad, “Phosphorus recovery by struvite on Hias wastewater treatment plant,” NMBU, 2014.

[27] L. Shu, P. Schneider, V. Jegatheesan, and J. Johnson, “An economic evaluation of phosphorus recovery as struvite from digester supernatant,” *Bioresour. Technol.*, vol. 97, no. 17, pp. 2211–2216, 2006.

[28] K. S. Le Corre, E. Valsami-Jones, P. Hobbs, and S. A. Parsons, “Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review,” *Crit. Rev. Environ. Sci. Technol.*, vol. 39, no. 6, pp. 433–477, 2009.

[29] H. Huang, C. Xu, and W. Zhang, “Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology,” *Bioresour. Technol.*, vol. 102, no. 3, pp. 2523–2528, 2011.

[30] C. S. M. C. R. Institute, *Salt Research and Industry*, no. v. 15. 1979.

[31] B. Halling-Sørensen and S. E. Jorgensen, *The Removal of Nitrogen Compounds from Wastewater*. Elsevier Science, 1993.

[32] N. A. Booker, A. J. Priestley, and I. H. Fraser, “Struvite Formation in Wastewater Treatment Plants: Opportunities for Nutrient Recovery,” *Environ. Technol.*, vol. 20, no. 7, pp. 777–782, 1999.

[33] W. Stumm and J. J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. Wiley, 2013.

[34] L. Pastor, D. Mangin, R. Barat, and A. Seco, “A pilot-scale study of struvite precipitation

in a stirred tank reactor: Conditions influencing the process," *Bioresour. Technol.*, vol. 99, no. 14, pp. 6285–6291, 2008.

[35] J. Wang, J. G. Burken, X. (Jackie) Zhang, and R. Surampalli, "Engineered Struvite Precipitation: Impacts of Component-Ion Molar Ratios and pH," *J. Environ. Eng.*, vol. 131, no. 10, pp. 1433–1440, Oct. 2005.

[36] H. S. Shin and S. M. Lee, "Removal of Nutrients in Wastewater by using Magnesium Salts," *Environ. Technol.*, vol. 19, no. 3, pp. 283–290, Mar. 1998.

[37] C. Fang, T. Zhang, R. Jiang, and H. Ohtake, "Phosphate enhance recovery from wastewater by mechanism analysis and optimization of struvite settleability in fluidized bed reactor," *Sci. Rep.*, vol. 6, p. 32215, 2016.

[38] B. Etter, E. Tilley, R. Khadka, and K. M. Udert, "Low-cost struvite production using source-separated urine in Nepal," *Water Res.*, vol. 45, no. 2, pp. 852–862, 2011.

[39] A. K. Banerjee, *The Effect of Hydraulic Retention Time (HRT) and Temperature on the Acid-phase Anaerobic Digestion of Primary Sludge and Industrial Wastewater*. University of Manitoba, 1997.

[40] L. CHAI *et al.*, "Two-sectional struvite formation process for enhanced treatment of copper–ammonia complex wastewater," *Trans. Nonferrous Met. Soc. China*, vol. 27, no. 2, pp. 457–466, Feb. 2017.

[41] M. T. Munir, B. Li, I. Boiarkina, S. Baroutian, W. Yu, and B. R. Young, "Phosphate recovery from hydrothermally treated sewage sludge using struvite precipitation," *Bioresour. Technol.*, vol. 239, pp. 171–179, Sep. 2017.

[42] H. Huang, P. Zhang, Z. Zhang, J. Liu, J. Xiao, and F. Gao, "Simultaneous removal of ammonia nitrogen and recovery of phosphate from swine wastewater by struvite electrochemical precipitation and recycling technology," *J. Clean. Prod.*, vol. 127, pp. 302–310, 2016.

[43] H. Ali, *Fundamentals of Irrigation and On-farm Water Management:*, no. v. 1. Springer New York, 2010.

[44] Standard Norge, *Vannundersøkelse - Bestemmelse av fosfor - Spektrometrisk metode med ammoniummolybdat (ISO 6878:2004)*. 2004, p. 28.

[45] H. Yan and K. Shih, “Effects of calcium and ferric ions on struvite precipitation: A new assessment based on quantitative X-ray diffraction analysis,” *Water Res.*, vol. 95, pp. 310–318, 2016.

[46] Warmadewanthi and J. C. Liu, “Recovery of phosphate and ammonium as struvite from semiconductor wastewater,” *Sep. Purif. Technol.*, vol. 64, no. 3, pp. 368–373, 2009.

[47] S. Villaverde, P. A. García-Encina, and F. Fdz-Polanco, “Influence of pH over nitrifying biofilm activity in submerged biofilters,” *Water Res.*, vol. 31, no. 5, pp. 1180–1186, 1997.

[48] M. Harmon, *Practical and Clear Graduate Statistics in Excel - The Excel Statistical Master*. Excel Master Series, 2011.

[49] N. Z. Ning and A. Aris, “Enhancement of Struvite Precipitation from Leachate by Coagulation.”

[50] A. Triger, J.-S. Pic, and C. Cabassud, “Determination of struvite crystallization mechanisms in urine using turbidity measurement,” *Water Res.*, vol. 46, no. 18, pp. 6084–6094, 2012.

[51] A. Uysal, Y. D. Yilmazel, and G. N. Demirer, “The determination of fertilizer quality of the formed struvite from effluent of a sewage sludge anaerobic digester,” *J. Hazard. Mater.*, vol. 181, no. 1, pp. 248–254, 2010.

[52] J. a. Wilsenach, C. a H. Schuurbiers, and M. C. M. van Loosdrecht, “Phosphate and potassium recovery from source separated urine through struvite precipitation,” *Water Res.*, vol. 41, no. 2, pp. 458–466, 2007.

[53] H. Q. Yu, J. H. Tay, and H. H. P. Fang, “The roles of calcium in sludge granulation during uasb reactor start-up,” *Water Res.*, vol. 35, no. 4, pp. 1052–1060, 2001.

[54] V. J. Inglezakis, A. A. Zorpas, A. Karagiannidis, P. Samaras, I. Voukkali, and S. Sklari, “European Union legislation on sewage sludge management,” *Fresenius Environ. Bull.*, vol. 23, pp. 635–639, 2014.

Attachment 1: Phosphorus recovery

Processing option: All elements analyzed (Normalized)

Time, min	pH	N	Mg	PO_4-P mg/l	Time, min	pH	N	Mg	PO_4-P mg/l
20	8	10	1.2	19.75	20	8	10	1.5	12.43
40	8	10	1.2	16.83	40	8	10	1.5	11.90
60	8	10	1.2	20.23	60	8	10	1.5	12.23

Time, min	pH	N	Mg	PO_4-P mg/l	Time, min	pH	N	Mg	PO_4-P mg/l
20	8.3	10	1.2	11.33	20	8.3	10	1.5	7.69
40	8.3	10	1.2	10.57	40	8.3	10	1.5	8.64
60	8.3	10	1.2	20.27	60	8.3	10	1.5	6.35

Time, min	pH	N	Mg	PO_4-P, %	Time, min	pH	N	Mg	PO_4-P, %
20	8	10	1.2	89.56	20	8	10	1.5	93.43
40	8	10	1.2	91.10	40	8	10	1.5	93.71
60	8	10	1.2	89.30	60	8	10	1.5	93.53

Time, min	pH	N	Mg	PO_4-P, %	Time, min	pH	N	Mg	PO_4-P, %
20	8.3	10	1.2	94.01	20	8.3	10	1.5	95.93
40	8.3	10	1.2	94.41	40	8.3	10	1.5	95.43
60	8.3	10	1.2	89.28	60	8.3	10	1.5	96.64

Attachment 2: Ammonium recovery

Processing option: All elements analyzed (Normalized)

Time, min	pH	N	Mg	NH_4-N, mg/l	Time, min	pH	N	Mg	NH_4-N, mg/l
20	8	10	1.2	683	20	8	10	1.5	686
40	8	10	1.2	726	40	8	10	1.5	696
60	8	10	1.2	693	60	8	10	1.5	703

Time, min	pH	N	Mg	NH_4-N, mg/l	Time, min	pH	N	Mg	NH_4-N, mg/l
20	8.3	10	1.2	696	20	8.3	10	1.5	693
40	8.3	10	1.2	700	40	8.3	10	1.5	703
60	8.3	10	1.2	713	60	8.3	10	1.5	706

Time, min	pH	N	Mg	NH_4-N, %	Time, min	pH	N	Mg	NH_4-N, %
20	8	10	1.2	69	20	8	10	1.5	69.07
40	8	10	1.2	67	40	8	10	1.5	68.62
60	8	10	1.2	68	60	8	10	1.5	68.32

Time, min	pH	N	Mg	NH_4-N, %	Time, min	pH	N	Mg	NH_4-N, %
20	8.3	10	1.2	68	20	8.3	10	1.5	68.77
40	8.3	10	1.2	68	40	8.3	10	1.5	68.32
60	8.3	10	1.2	67	60	8.3	10	1.5	68.17

Attachment 3: Turbidity

Processing option: All elements analyzed (Normalized)

Time, min	pH	N	Mg	NTU	Time, min	pH	N	Mg	NTU
20	8	10	1.2	53.6	20	8	10	1.5	54.3
40	8	10	1.2	58.5	40	8	10	1.5	63.6
60	8	10	1.2	63.0	60	8	10	1.5	61.3

Time, min	pH	N	Mg		Time, min	pH	N	Mg	
20	8.3	10	1.2	57.4	20	8.3	10	1.5	60.5
40	8.3	10	1.2	54.2	40	8.3	10	1.5	54.6
60	8.3	10	1.2	58.7	60	8.3	10	1.5	60.1

Time, min	pH	N	Mg	%	Time, min	pH	N	Mg	%
20	8	10	1.2	86.7	20	8	10	1.5	86.5
40	8	10	1.2	85.9	40	8	10	1.5	84.3
60	8	10	1.2	84.4	60	8	10	1.5	84.8

Time, min	pH	N	Mg	%	Time, min	pH	N	Mg	%
20	8.3	10	1.2	86.5	20	8.3	10	1.5	85.0
40	8.3	10	1.2	86.6	40	8.3	10	1.5	86.5
60	8.3	10	1.2	85.4	60	8.3	10	1.5	85.1

Attachment 4: Conductivity

Processing option: All elements analyzed (Normalized)

Time, min	pH	N	Mg	µS/cm	Time, min	pH	N	Mg	µS/cm
20	8	10	1.2	6.49	20	8	10	1.5	6.70
40	8	10	1.2	6.74	40	8	10	1.5	6.94
60	8	10	1.2	6.74	60	8	10	1.5	6.87

Time, min	pH	N	Mg	µS/cm	Time, min	pH	N	Mg	µS/cm
20	8.3	10	1.2	6.57	20	8.3	10	1.5	6.60
40	8.3	10	1.2	6.45	40	8.3	10	1.5	6.64
60	8.3	10	1.2	6.66	60	8.3	10	1.5	6.81

Norges miljø- og biovitenskapelig universitet
Noregs miljø- og biovitskapelege universitet
Norwegian University of Life Sciences

Postboks 5003
NO-1432 Ås
Norway