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COMBINED REMOVAL OF PHOSPHORUS AND NITROGEN
FROM WASTEWATER

Degree Programme in Chemical Engineering
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YHDISTETTY FOSFORIN JA TYPEN POISTO JÄTEVEDESTÄ

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Opinnäytetyön aiheena oli fosforin ja typen poisto perunoita käsittelevän tehtaan jätevesistä. Tutkimus tehtiin käyttäen ureolyyttistä fosfaattien saostamista ja yhdistettyä Sharon/Anammox prosessia typen poistamiseen. Tavoitteeksi fosforin poistolle asetettiin muutos pitoisuudesta 50 mg/l alueelle 8-10 mg/l. Prosessilta vaadittiin myös struviitin saostuminen. Typen poiston tavoitteeksi asetettiin 90% alkuperäisestä typen määrästä.

Tutkimuksissa käytettiin yhtä reaktoria fosforin poistolle, yhtä Sharon prosessille ja yhtä Anammox prosessille. Anammox prosessille käynnistettiin toinen reaktori opinnäytetyön kokeellisen osuuden aikana.

Ionikonsentraatio, pH, epäorgaaninen hiili ja virtausnopeus analysoitiin keskimäärin kolme kertaa viikossa. Anammox reaktorista mitattiin myös johtokyky ja fosforin poistoreaktorista mitattiin ureolyyttinen aktiivisuus. Analyysien suorittamiseen käytettiin pääasiassa ionikromatografiaa.

Fosforin poistolle saatiin hyvä poistotehokkuus. Tuloksista huomattiin, että prosessi on erittäin riippuvainen käsitellyn jäteveden pH:sta.

Sharon reaktorin tuloksista pääteltiin, että prosessin parametreja kuten ilmastusta, oli muutettava kun prosessissa käytetty liete vaihdettiin. Anammox toimivuuden huomattiin riippuvan vahvasti Sharon reaktorin toiminnasta. Toisen Anammox reaktorin käynnistämisestä huomattiin, että käynnistysaika on erittäin pitkä.

Yhdistetyllä Sharon/Anammox prosessilla saavutettiin keskimääräinen 76 % poistotehokkuus. Tavoitearvo 90 % saavutettiin usein, mutta ei jatkuvasti. Toimiva prosessi saavutettiin hyvillä poistotehokkuuksilla, mutta lisätutkimuksen tarve todettiin, jotta saavutettaisiin vakaa prosessi.

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The purpose of this study was to remove phosphorus and nitrogen from the wastewater of a potato processing company. The methods used in the research were ureolytic phosphate precipitation and the combined Sharon/Anammox process for the removal of nitrogen. The goal for the removal of phosphorus was set to a reduction in concentration of phosphorus from 50 mg/l to 8-10 mg/l. Formation of struvite crystals was also required. The goal for the removal of nitrogen was set at 90% of the total nitrogen.

Research was done with one reactor for phosphorus removal, one for the Sharon process and one reactor for the Anammox process. A second reactor for the Anammox process was started during the experimental part of this thesis.

Ion concentration, pH, inorganic carbon and flow rate were analysed from all of the reactors on an average of three times a week. Conductivity was also measured from the Anammox reactor and ureolytic activity from the phosphorus removal reactor. Ion chromatograph was mainly used for the analyses.

Good removal efficiency for the phosphorus reactor was gained during the experiments. The results indicated that the process is very dependent on the pH of the wastewater treated.

The results of the Sharon reactor implied that the process parameters, such as aeration, needed to be changed when the sludge that was used was changed. The performance of the Anammox reactor was seen to be dependent on the performance of the Sharon reactor. The start-up of the second Anammox reactor showed that it takes a long period of time.

An average removal efficiency of 76 % was gained by the combined Sharon/Anammox process. The goal of 90 % was reached several times, but not constantly. A functioning process was gained with good removal efficiencies, but further research was seen to be necessary to gain a stable process.

TABLE OF CONTENTS

1	INTRODUCTION.....	6
2	PHOSPHORUS.....	6
2.1	Struvite.....	7
2.2	Recovery from wastewater by struvite crystallization.....	8
2.2.1	Selective ion exchange.....	9
2.2.2	Stirred reactors.....	9
2.2.3	Fluidized bed reactors and air-agitated reactors.....	10
2.3	Ureolytic phosphate precipitation.....	10
3	NITROGEN.....	11
3.1	Nitrification.....	12
3.1.1	Effect of parameters to nitrification.....	13
3.2	Denitrification.....	13
4	SHARON PROCESS.....	14
4.1	Principle.....	14
4.2	Influencing factors.....	15
4.2.1	Temperature.....	15
4.2.2	pH.....	15
5	ANAMMOX PROCESS.....	16
5.1	History.....	16
5.2	Principle.....	17
5.3	Influencing factors.....	18
5.3.1	Temperature and pH.....	18
5.3.2	Organic carbon.....	18
6	COMBINED SHARON/ANAMMOX PROCESS.....	18
6.1	Advantages and disadvantages.....	18
6.2	Principle.....	20
7	ANALYSIS.....	21
7.1	Analytical equipment.....	21
7.1.1	Ion chromatograph.....	21
7.2	Ion chromatography.....	22
7.2.1	Calculations.....	23
7.3	Nessler's method.....	25
7.4	Inorganic carbon.....	25
7.4.1	Basis for measurements.....	25
7.5	VSS/TSS.....	26
7.6	Specific ureolytic activity.....	28

8	EXPERIMENT PROCESS PERFORMANCE.....	29
8.1	Phosphorus removal reactor.....	29
8.2	Sharon reactor.....	30
8.3	Vegetable Anammox reactor.....	32
8.4	Pig manure Anammox reactor start-up.....	32
8.4.1	Wastewater.....	34
9	RESULTS.....	35
9.1	Phosphorus removal.....	35
9.2	Sharon.....	36
9.3	Anammox.....	38
9.3.1	Vegetable.....	38
9.3.2	Pig manure.....	40
9.4	Combined Sharon/Anammox process.....	41
10	CONCLUSIONS.....	42
10.1	Phosphorus.....	42
10.2	Sharon.....	43
10.3	Anammox.....	43
10.3.1	Vegetable Anammox reactor.....	43
10.3.2	Pig manure Anammox reactor.....	44
10.4	Combined Sharon/Anammox process.....	44
	REFERENCES.....	46
	APPENDICES	

1 INTRODUCTION

Release of phosphorus and nitrogen to natural water bodies is one of the main causes of eutrophication and therefore it is recommendable that water treatment facilities remove phosphorus and nitrogen from the wastewater before returning it to natural water bodies.

Conventional techniques for the removal of phosphorus create huge amounts of sludge which has to be disposed off at continuous increasing costs. A new microbiological method is being studied for the removal of phosphates from wastewaters. The method is called ureolytic precipitation of struvite (ammonium magnesium phosphate). In ureolytic precipitation, urea and magnesium salt (MgCl_2) are added to ureolytic sludge to recover phosphate as struvite. Increase in pH, which is a prerequisite for struvite precipitation, and supply of extra ammonium occurs in enzymatic hydrolysis of urea.

To remove nitrogen from the wastewater, autotrophic nitrogen removal (ANR) is used. ANR is a combination of Sharon and Anammox processes. This technique uses less aeration and doesn't require an external carbon source in comparison to classical techniques of nitrogen removal.

The aim of this research is to integrate both techniques for the removal of phosphorus and nitrogen from wastewater.

2 PHOSPHORUS

Phosphorus is essential to all living organisms including bacteria, plants and animals because its availability in most cases controls biological productivity. It is also widely used as a fertilizer in agriculture. In excess amounts phosphorus is the cause of eutrophication in natural water bodies and therefore it is important to remove it from wastewaters before returning it to the environment. /4./

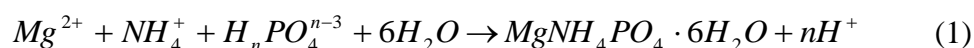
Phosphate resources are limited and by the end of this century a shortage will occur if no attention is paid towards the management of phosphates. Phosphorus demand is projected to increase. The expected global peak in phosphorus production is predicted to occur around 2030 and at the same time the quality of the remaining phosphate rock is decreasing and the production costs increasing. Because phosphorus is a non-renewable resource, it is important to perform research on the possibilities of recycling it. /9./

2.1 Struvite

Struvite is an orthophosphate and its general formula is $AMPO_4 \cdot 6H_2O$, where A corresponds to potassium or ammonia and M to magnesium, cobalt or nickel. It is a white and glowing crystal. Struvite has been found in rotting organic matter such as cow manure and guano. In these, struvite is produced in the bacterial metabolism with magnesium and phosphorus already present. Due to its composition, struvite could be used as a fertilizer in agriculture. /4./

Struvite scale deposits are a problem in wastewater treatment plants. They cause decrease to efficiency and maintenance problems e.g. in pipes. /4./

Struvite precipitates following a general equation ($n=0, 1, 2$):



Struvite develops in two stages, the first stage is nucleation when the crystals are born. The second stage is crystal growth when the crystals develop until equilibrium is reached. Controlling the development of the crystals is difficult. Factors such as the crystal state of initial compounds, thermodynamic of liquid-solid equilibrium, matter transfer between solid and liquid phases, reaction kinetics and many physicochemical parameters (e.g. pH, temperature, mixing energy) have to be taken in consideration when controlling the development of struvite crystals. /4./

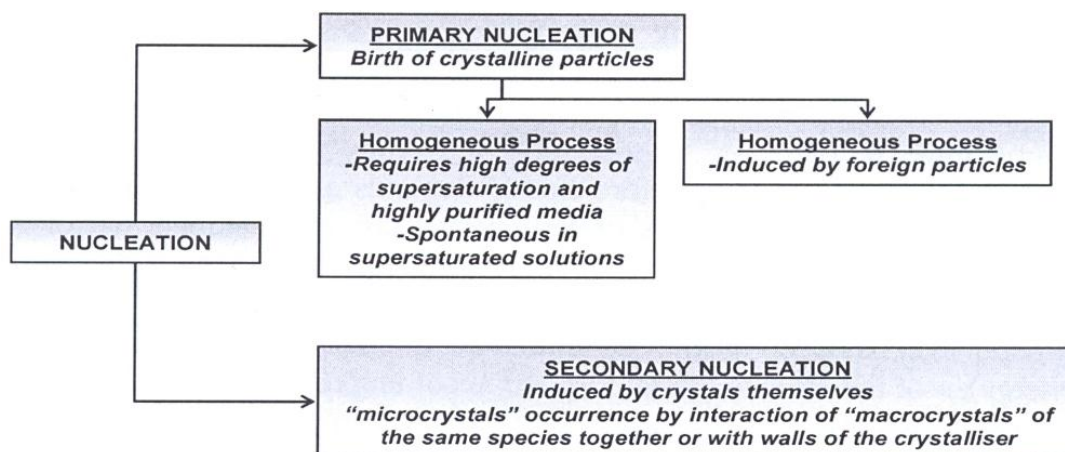


Figure 1. The nucleation process. /4./

2.2 Recovery from wastewater by struvite crystallization

Phosphorus has to be removed from wastewaters in a solid form. Traditionally this is done by a chemical or a biological process fixing the phosphorus in the sludge. Chemically it is done by precipitation of soluble phosphorus with aluminium or iron salts into insoluble phosphate compounds. Biologically it is done with the ability of certain micro-organisms to accumulate phosphates as polyphosphates for their own metabolism. These methods are efficient and are known to reduce the concentration of phosphorus to less than 1 mg/l. /4./

The previous processes have disadvantages such as accumulation of phosphorus in the resulting sludge, increase in sludge volume and spontaneous accumulation of struvite in e.g. pipelines. The biggest disadvantage is that phosphorus precipitates generated are not directly recyclable.

A new technology for removing phosphorus from wastewaters is the crystallization of reusable compounds, e.g. calcium phosphate and struvite. Both of these products can be used as fertilizers and therefore this method has a high potential compared to the conventional methods. The recovery of these products is still mainly experimental due to problems with the product formed, economics of the process and technical difficulties. /4./

Phosphorus recovery methods can be categorized in three main categories:

1. selective ion exchange
2. precipitation in a stirred reactor
3. precipitation in a fluidized bed reactor or air-agitated reactor

2.2.1 Selective ion exchange

Selective ion exchange consists of three-stage combined ion exchange and precipitation system. Effluent from an activated sludge tank is directed to a combined resin columns system consisting of two cationic and two anionic columns. Cationic resins remove ammonium ions and anionic resins remove phosphates. The enriched phosphate and ammonium effluents from the columns are mixed in a reactor to precipitate struvite. The reaction requires addition of NaOH, MgCl₂ and H₃PO₄ to gain the molar ratio Mg:P:N 1:1:1. /4./

With selective ion exchange, efficiencies in removal of phosphorus as high as 90 % have been gained. The process uses chemicals to precipitate struvite, but no additional sludge is formed.

2.2.2 Stirred reactors

In stirred reactors MgCl is usually added to the reactor to gain a molar ratio of Mg:P of 1:1. With addition of NaOH, the pH required to start the nucleation is adjusted. The reactor is continuously stirred and a settling zone is integrated to allow accumulation of particles. The crystallization takes place in the lower part of the reactor while the upper part works as a settling zone. /4./

With stirred reactor, the main advantage is the simplicity of it.

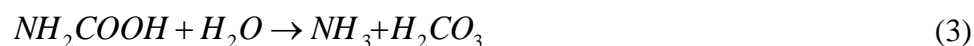
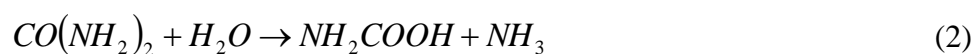
2.2.3 Fluidized bed reactors and air-agitated reactors

Fluidized bed reactors and air-agitated reactors are most commonly used to precipitate struvite. It is possible for struvite to precipitate spontaneously supernatants. Addition of chemicals is required for molar ratio Mg:P:N of 1:1:1. When nucleation has started, it takes place with either interaction between small struvite particles or by contact on seed materials. NaOH is added to gain proper pH for the process. In these reactors, the effluent is fed from the bottom which allows the upward airflows to prevent the forming struvite particles from settling to the bottom of the reactor. /4./

Efficiency of these processes varies from 60 % to 94 %, depending on the type of effluent and nature of crystallization process.

2.3 Ureolytic phosphate precipitation

For the recovery of phosphates an increase in pH is required. Compared to traditional methods, in ureolytic struvite precipitation the increase is produced by bacterial urease activity. Decomposing urea to ammonium increases the pH and also leads to formation of struvite when phosphate (PO_4^{3-}) and magnesium (Mg^{2+}) ions are present. During microbial urease activity, 1 mol of urea is hydrolysed intracellularly to 1 mol of ammonia and carbamate, which then hydrolyses spontaneously to an additional mole of ammonia and carbonic acid. /8./



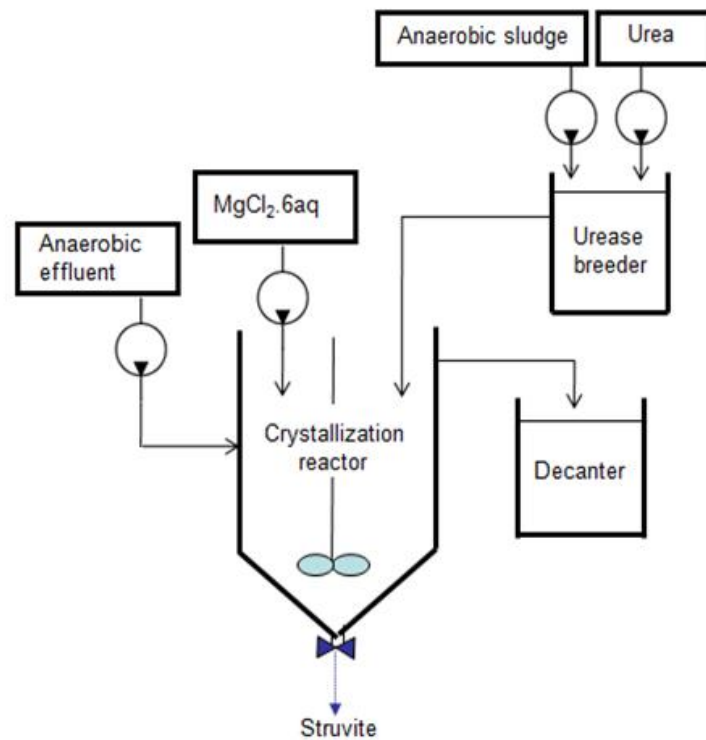


Figure 2. Principle of ureolytic phosphate precipitation process.

3 NITROGEN

Nitrogen is an important fertilizer, but excess release of it to natural waters can lead to eutrophication and oxygen depletion. Ammonium and organic nitrogen are the most common forms of nitrogen in wastewater treatment plants. Ammonium is usually removed by biological nitrification/denitrification. In this combined process, ammonium is first converted to nitrate and further on converted to nitrogen gas. The process has a high potential removal efficiency, stability and reliability. It is generally used to treat relatively low concentrations of nitrogen in wastewaters. For high concentrations the nitrification-denitrification process over nitrite is more suitable.

/5./

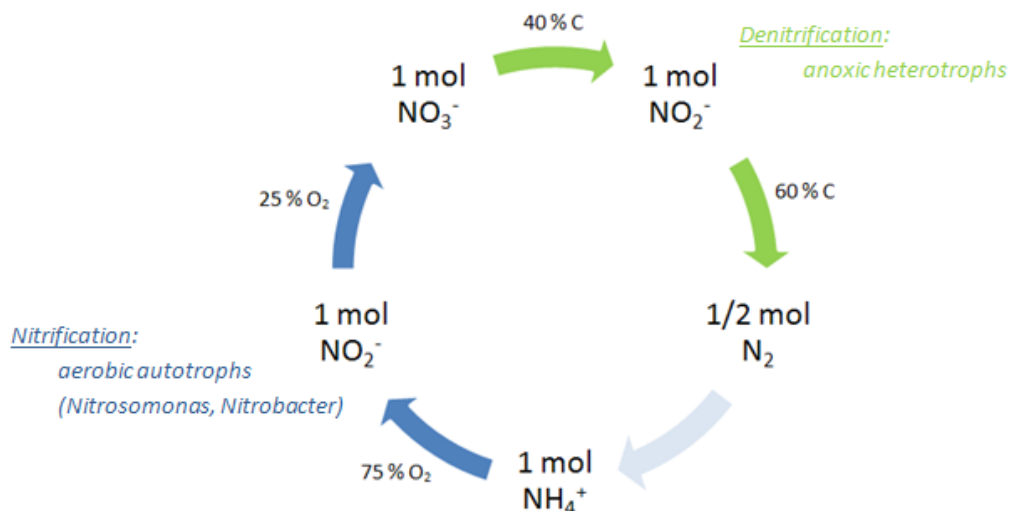


Figure 3. Nitrogen cycle in wastewater treatment.

3.1 Nitrification

Nitrification, or aerobic oxidation of ammonium to nitrate, takes place in aerobic conditions. First step is the conversion of ammonium to nitrite and the second step is the conversion of nitrite to nitrate. The stoichiometric equation for the conversion of ammonium into nitrite is /6./:



The stoichiometric equation for conversion of nitrite to nitrate is /6./:



These reactions are produced by two different groups of autotrophic bacteria, *Nitrosomonas* and *Nitrobacter*. These particular types of bacteria use ammonium and nitrate as a source of energy for growth. No single bacteria have been found to be able to convert ammonium to nitrate in a single step. /5.,6./

Main parameters that have an effect on nitrification are free ammonia and free nitrous acid, pH, temperature and dissolved oxygen. /5./

3.1.1 Effect of parameters to nitrification

Free ammonia, NH_3 , and free nitrous acid, HNO_2 , work as substrate/inhibitor in the nitrification process. Increase in pH causes an increase in the amount of ammonia while the amount of nitrous acid decreases. These events promote ammonium oxidizers but suppress nitrite oxidizers. Ammonia is the main inhibitor of nitrification at high pH (>8) and nitrous acid at low pH (<7.5). /5./

Optimal pH for nitrification is at the range of 7 and 8. The effect of pH can be seen at the $\text{NH}_4^+/\text{NH}_3^-$ and HNO_2/NO_2 ratios. NH_3 is used as substrate at slightly alkaline conditions while at certain pH values NH_3 and HNO_2 can act as inhibitors as mentioned previously. /5./

The bacteria are very sensitive to the temperature of the liquid where they live. Nitrification has been shown to occur in temperature range of 4 to 45 °C, with the optimum growth ratio at 35 to 42 °C. Long-term exposing to temperatures over 40°C is very likely to cause deactivation. /5.,6./

Dissolved oxygen is very important for ammonium and nitrite oxidizers because nitrifiers are only able to work in aerobic conditions. General knowledge is that nitrification is not inhibited with dissolved oxygen concentrations of higher than 2,0 mg/l. /5.,6./

3.2 Denitrification

Denitrification occurs under anaerobic conditions in the presence of organic carbon (process is done by heterotrophic bacteria). In most wastewater treatment plants, the ratio of nitrogen over carbon is too high. In this case, an external carbon source (e.g. methanol) is added, which results in a higher cost for the treatment plant. Following equation describes the denitrification of nitrate into nitrogen gas /6./:



4 SHARON PROCESS

4.1 Principle

The Sharon process (Single reactor system for High activity Ammonium Removal Over Nitrite) is a biological technique to remove nitrogen from nitrogen rich wastewaters. Sharon process takes place in an intermittently aerated, completely stirred continuous flow reactor without sludge retention. The process converts ammonium to nitrite under aerobic conditions using ammonium-oxidizing bacteria. This process is also called nitrification. The stoichiometry is given in equation 4. When converting ammonia to nitrite by Sharon process instead of further conversion to nitrate, 25 % less energy for aeration is needed. /1./

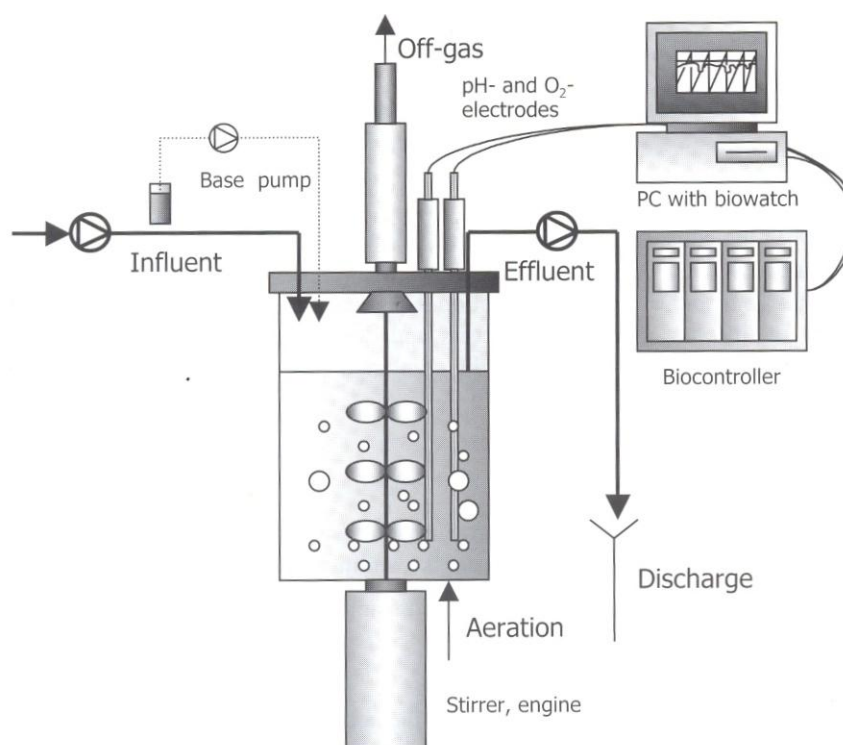


Figure 4. Schematic presentation of the Sharon reactor. /1./

For the combined Sharon/Anammox process, Sharon reactor is used only for partial nitrification, but it is also possible to use it for denitrification. In such case, there will also be denitrifying bacteria in the reactor.

4.2 Influencing factors

There are two important parameters for the operation of a Sharon reactor, temperature and pH, which will be explained in the following sections. Also because the Sharon reactor converts ammonia only to nitrite, nitrite oxidizing bacteria need to be washed out from the reactor.

4.2.1 Temperature

Conditions in Sharon reactor are more suitable for ammonium-oxidizing bacteria than for nitrite-oxidizing bacteria. Figure 5 shows that shorter minimum sludge age at higher temperatures is more beneficial for ammonium-oxidizing bacteria. Combination of high operational temperature (35 °C) and short hydraulic retention time (1 day) causes the nitrite oxidizers to be selectively washed out. /1./

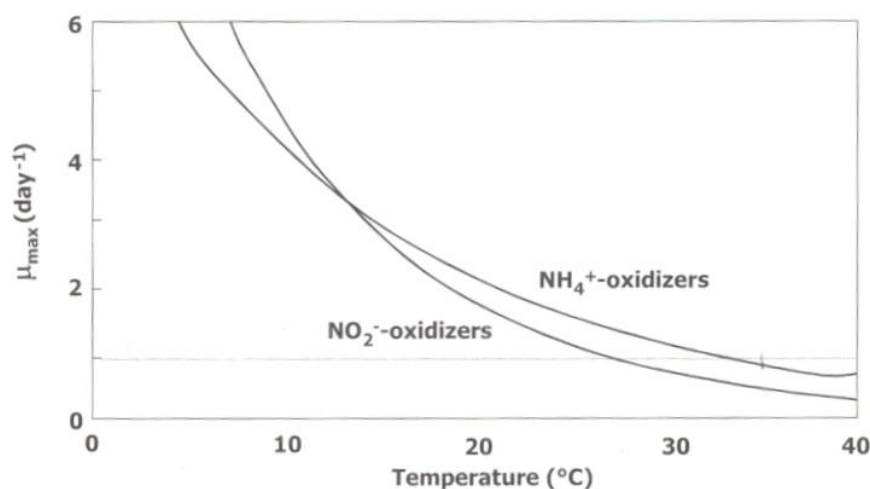


Figure 5. The effect of temperature on the maximal growth rate of ammonium and nitrite oxidizers /1./

4.2.2 pH

By controlling the pH of the reactor it is possible to make the conditions of the reactor more suitable for ammonium-oxidizing bacteria and less suitable for the nitrite oxidizing bacteria.

The oxidation of ammonium to nitrite is an acidifying reaction, which however is partially neutralized by the bicarbonate present in the wastewater. This effect is described with the following equation:



5 ANAMMOX PROCESS

5.1 History

In 1995 Mulder and his group discovered a process of ammonium removal in an anoxic fluidized bed reactor with the simultaneous conversion of nitrate to nitrogen gas. A year later it was proved to be a biological process with inactivation by heating, gamma radiation or antibiotics. Later research showed that it was nitrite instead of nitrate that was being used as a substrate.

The bacteria were identified in 1999. The process was patented under the name Anammox by the University of Delft in the Netherlands. /2./

5.2 Principle

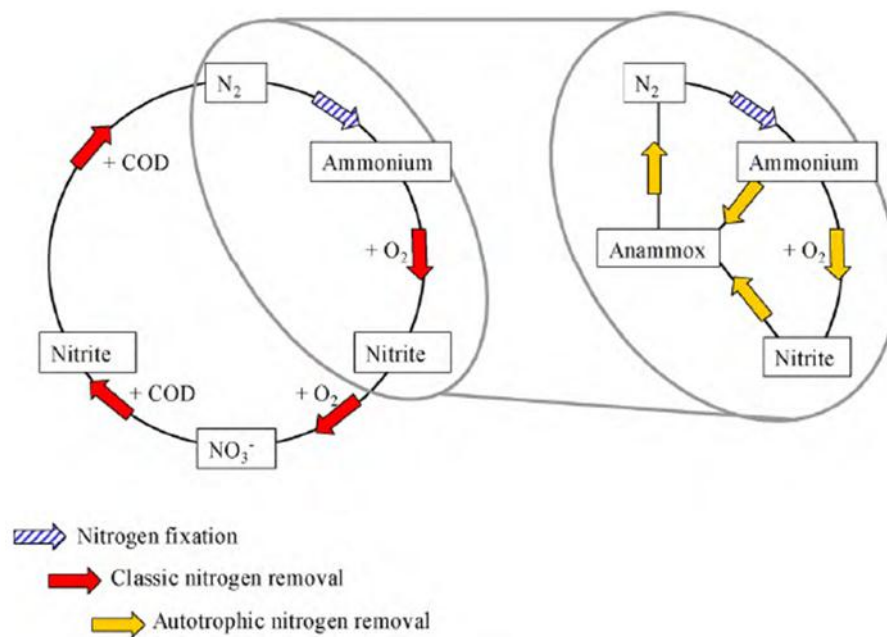
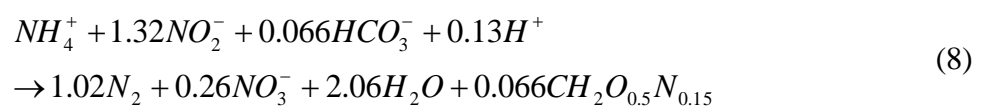


Figure 6. Nitrogen cycle with autotrophic nitrogen removal. /5./

The Anammox process (Anaerobic AMMonium Oxidation) is a biological process used to remove ammonium from wastewater. Anaerobic conditions are required for the conversion of ammonium to nitrogen gas with nitrite as electron acceptor. This conversion can take place completely without any addition of BOD because the Anammox process is autotrophic. Ammonium is utilized by the bacteria as an electron donor to convert nitrite to nitrogen gas. /1./

The stoichiometry of Anammox reaction is described in the following reaction, which has been confirmed by a full-scale reactor in Rotterdam, The Netherlands. /2./



Anammox bacteria grow slowly, which is an advantage and disadvantage at the same time. It is an advantage because forming of bacterial sludge is minimal, but the disadvantage is that the process requires a long start-up period. /1./

The Anammox process should always be combined with a partial nitrification process. /5./

5.3 Influencing factors

5.3.1 Temperature and pH

Optimal temperature range for Anammox bacteria is 30-40 °C with an irreversible decrease of Anammox activity at 45 °C.

Optimal pH range for Anammox process is 6,7 – 8,3 with 8,0 being the optimal value.

5.3.2 Organic carbon

Undigested animal streams contain high nitrogen concentrations and high organic carbon levels. Fast biodegradable organic content can be converted to biogas during anaerobic digestion. In the partial nitrification step before Anammox process, most of the fast degradable organic content is oxidized. This makes the content of organic carbon of the stream low enough for Anammox process. If the content is too high, the denitrifiers might have a negative impact on the Anammox bacteria. /5./

6 COMBINED SHARON/ANAMMOX PROCESS

6.1 Advantages and disadvantages

The combination of Sharon and Anammox processes is a new way to replace the conventional nitrification/denitrification process. In comparison to the conventional method, combined Sharon/Anammox process produces less sludge and doesn't require any organic carbon. /3./

The conventional nitrification/denitrification process requires a lot of energy for aeration. The combined Sharon/Anammox process requires 60% less oxygen and thus less energy. There is no external need for an organic carbon source (e.g. methanol) in the combined Sharon/Anammox process which lowers the treatment costs and the need for additional resources. This is the main reasons why the combined Sharon/Anammox process is a sustainable method in treating nitrogen rich streams with low content of organic carbon. /1./

Disadvantage in process is the nitrate by-product that comes from the metabolic process of the bacteria. As shown in figure 7, the amount of nitrate in the effluent is approximately 10 % of the total nitrogen.

The Anammox bacteria are very slow in their growth and it is estimated to take at least three months for the start-up. Duration of the start-up is being researched by using different wastewaters and different Anammox bacteria. /1./

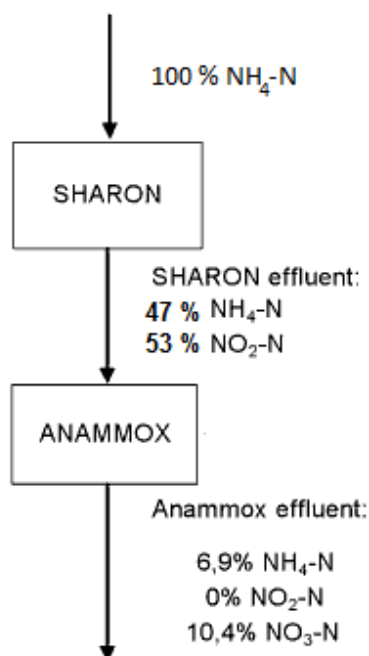


Figure 7. Basic principle of combined Sharon/Anammox process /2./.

6.2 Principle

The Sharon reactor is fed with the wastewater in order to convert the incoming ammonium partially to nitrite. The goal is to get an ammonium-nitrite ratio of 1:1,3 for the effluent of the Sharon reactor. The effluent of the Sharon reactor is then used as the influent of the Anammox reactor. In the Anammox reactor, the goal is to convert all of the nitrite and most of the ammonium to nitrogen gas. /1./

The combined Sharon/Anammox process can be described with the following simplified equation (complete conversion of ammonium) /3./:



In practical applications there is always nitrate in the effluent.

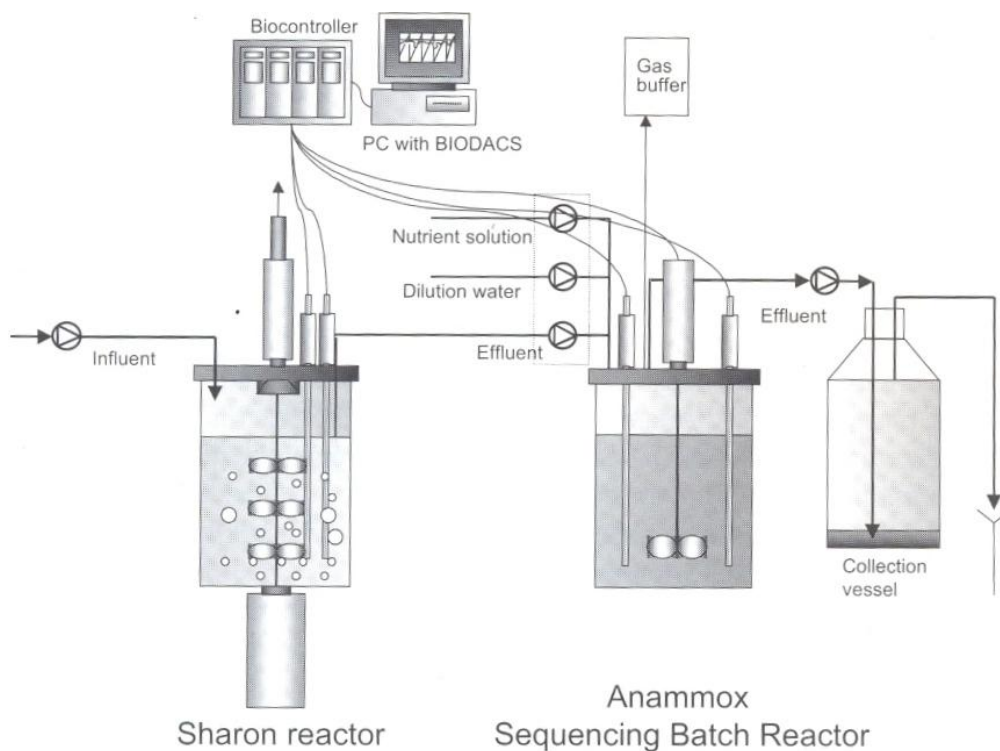


Figure 8. Schematic representation of the enrichment set-up where the Anammox was enriched using effluent from the Sharon reactor as feedstuff. /1./

7 ANALYSIS

7.1 Analytical equipment

7.1.1 Ion chromatograph

Ion chromatography is a form of chromatography that separates ionic molecules (usually in water-based solutions) and identifies them based on their electrical conductivity. /7./

Main components of the ion chromatograph are column, suppressor and detector. The column consists of a hollow cylinder packed under high pressure with a chemical resin and its function is to separate components in an injected sample. The column is a sensitive part of the equipment and therefore a guard column precedes the column to prevent e.g. large particles of going in to the column.

Suppressors are used to enhance the detection of ions by lowering background conductivity (mainly of the eluent). Detector is used to measure the quantity of components after they have been separated in the column. /7./

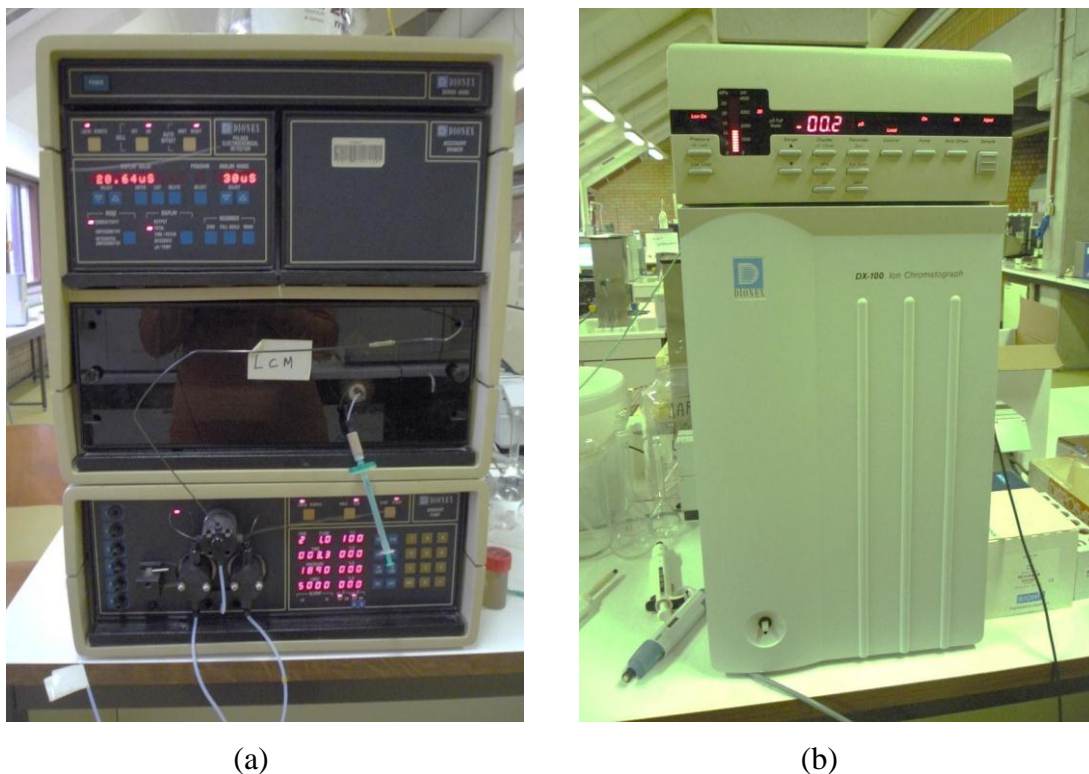


Figure 9. a) Dionex 4500i ion chromatograph used in the measurements of anions. b) Dionex DX-100 ion chromatograph used in the measurements of cations.

7.2 Ion chromatography

Ion chromatography was used to determine the concentrations of certain ions in the effluents and influents of the reactor. Calibration lines were done for anions and cations once a month (Appendix 1) with known ion concentrations of 2, 5, 10, 15 and 20 ppm for the ions the columns are able to detect.

For the phosphorus removal reactor, ammonium (NH_4^+), magnesium (Mg^{2+}) and phosphate (PO_4^{3-}) were measured from the influent and effluent.

For the Sharon and Anammox reactors, ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) were measured from the influent and the effluent.

Each sample was diluted to have a concentration between 2-20 ppm for the ions mentioned previously. From the areas of the ions the concentration was determined with the help of the calibration lines (Appendix 3-6). These measurements were done

to observe the removal efficiency of the reactors and how well the reactors are working.

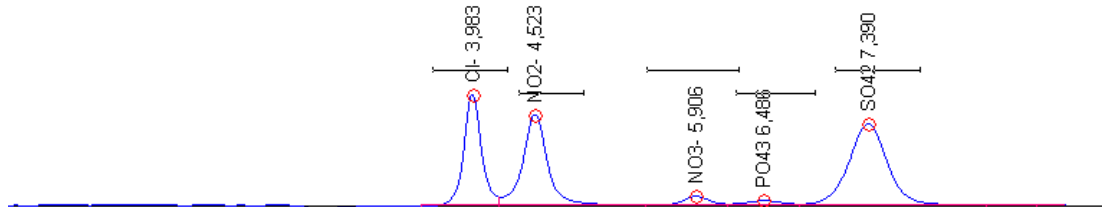


Figure 10. Example of an anion measurement with the ion chromatograph. Sample measured was the effluent stream of the pig manure Anammox reactor.

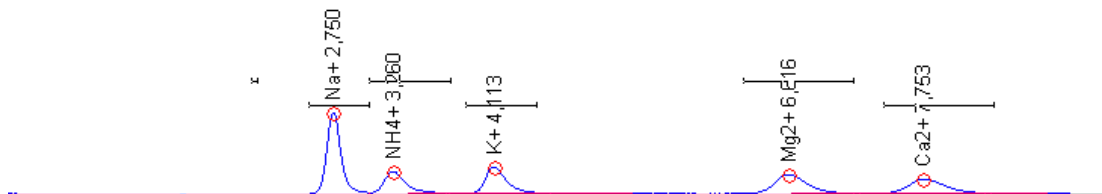


Figure 11. Example of a cation measurement with the ion chromatograph. Sample measured was the effluent stream of the pig manure Anammox reactor.

7.2.1 Calculations

Based on the calibration lines (Appendix 1) the concentrations of the ions were calculated with equation 11 as presented in the example.

$$c = \frac{A - b}{k} * \frac{V_s}{V_{tot}} \quad (10)$$

- where
- c = concentration
 - A = area measured by ion chromatograph
 - b = trace of the calibration line
 - k = slope of the calibration line (l/mg)

V_s = volume of the sample

V_{tot} = total diluted volume

Example 1. Calculation of the concentration of ammonia in the Sharon effluent stream.

$$c = \frac{A - b}{k} * \frac{V_s}{V_{tot}}$$

$$c = \frac{8,4216 - 5,1139}{2,2518 \frac{l}{mg}} * \frac{2,5ml}{50ml} = 29,38 \frac{mg}{l}$$

At small areas (< area of 2 ppm calibration) interpolation is performed by the following equation:

$$c = \frac{c_1 - c_0}{A_1 - A_0} * A_i * \frac{V_s}{V_{tot}} \quad (11)$$

where c_1 = concentration of chosen point of calibration line

c_0 = zero concentration

A_1 = area of the chosen point of calibration line

A_0 = zero area

A_i = area measured for the sample with ion chromatograph

V_s = volume of the sample

V_{tot} = total diluted volume

Example 2. Calculation of low concentration of nitrite in the Sharon influent stream.

$$c = \frac{c_1 - c_0}{A_1 - A_0} * A_i * \frac{V_s}{V_{tot}}$$

$$c = \frac{(2-0) \frac{mg}{l}}{787,1211 - 0} * 181,1332 * \frac{2,5ml}{50ml} = 9,20 \frac{mg}{l}$$

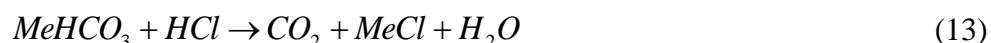
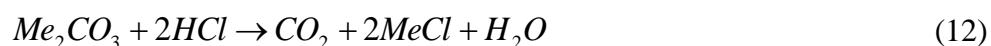
7.3 Nessler's method

Nessler's method was used to measure the concentration of ammonia during the period when the ion chromatograph was not functioning. Nessler's reagent, $\text{HgI}_2 + \text{NaOH}$, is added to a vial with the sample measured. Reaction with ammonium produces a yellow colour. Concentration is then measured photometrically with a tungsten lamp with narrow band interference filter at the wavelength of 420 nm. Measurement range was from 0 to 100 mg/l ($\text{NH}_3\text{-N}$).

7.4 Inorganic carbon

Total inorganic carbon (C_T or TIC) is the sum of inorganic carbon species in a solution, such as carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate anion (HCO_3^-) and carbonate anion (CO_3^{2-}).

Total inorganic carbon is measured by acidifying the sample to convert inorganic carbons towards an undissociated CO_2 .



After this, a chemically inert gas is bubbled through the liquid to separate the gas from the solution. The gas is then trapped and measured with infrared spectroscopy to determine the TIC.

7.4.1 Basis for measurements

In the phosphorus removal reactor during microbial urease activity, 1 mol of urea is hydrolysed intracellularly to 1 mol of ammonia and carbamate, which then hydrolyses spontaneously to an additional mole of ammonia and carbonic acid (equations 2

and 3). If the reaction occurs, there will be an increase in the amount of inorganic carbon in the effluent stream compared to the influent stream.

Sharon process is an acidifying reaction which is neutralized by the bicarbonate present in the sludge water (equation 7). If oxidation of ammonium to nitrite is active in the reactor and it is neutralized by the bicarbonate in the water it can be seen as a decrease of inorganic carbon in the effluent compared to the influent.

Anammox bacteria use HCO_3^- as the carbon source (equation 8). Therefore if the Anammox bacteria are working, it can be seen as a decrease of inorganic carbon in the effluent stream compared to the influent stream.



Figure 12. Shimadzu TOC-VCPN Total organic carbon analyser used in the measurements of inorganic carbon.

7.5 VSS/TSS

Volatile suspended solids, VSS, and total suspended solid, TSS, are measured from the sludge samples of the reactors. First step is to dry the sludge in an oven of $100\text{ }^\circ\text{C}$ overnight and measure the mass of it. Next it is placed in an oven of $600\text{ }^\circ\text{C}$ for at least 2 hours. After that the mass is measured again.

TSS gives the organic and inorganic composition of the sample. The values are calculated with the following equations:

$$TSS = \frac{(b-a)}{V} \quad (14)$$

where a = mass of the container (g)
 b = mass after 100 °C oven (g)
 V = volume of the sample (ml)

Example 3. Calculation of TSS of the phosphorus removal reactor.

$$TSS = \frac{(b-a)}{V}$$

$$TSS = \frac{(53,0265g * 1000 \frac{mg}{g} - 52,8521g * 1000 \frac{mg}{g})}{20ml} * 1000 \frac{ml}{l} = 8720mg / l$$

VSS is the organic fractions of the sample, it is calculated with the following equation:

$$VSS = TSS - \frac{(c-a)}{V} \quad (15)$$

where a = mass of the container (g)
 c = mass after 600 °C oven (g)
 V = volume of the sample (ml)

Example 4. Calculation of VSS of the phosphorus removal reactor.

$$VSS = 8720 \frac{mg}{l} - \frac{(52,9867 g * 1000 \frac{mg}{g} - 52,8521 g * 1000 \frac{mg}{g})}{20 ml} * 1000 \frac{ml}{l}$$

$$= 1990 \frac{mg}{l}$$

7.6 Specific ureolytic activity

Ureolytic activity is measured with the sludge used in the phosphorus removal reactor. A sample is washed and centrifuged to separate the sludge from the solution. It is then mixed in to a salt solution (0,5 g of $KHCO_3$ and NaCl in 1 litre of water) until the total mass is 95 g. After this step, pH is adjusted to 7,5-7,7 and 5 ml of a urea stock solution (2000 mg/l urea-N) is added. From this point (0 min) samples are taken at 10, 20, 30, 60, 90 and if necessary 120 minutes from the start until all of urea is converted to ammonia (100 mg/l NH_4^+ -N) by the ureolytic bacteria.

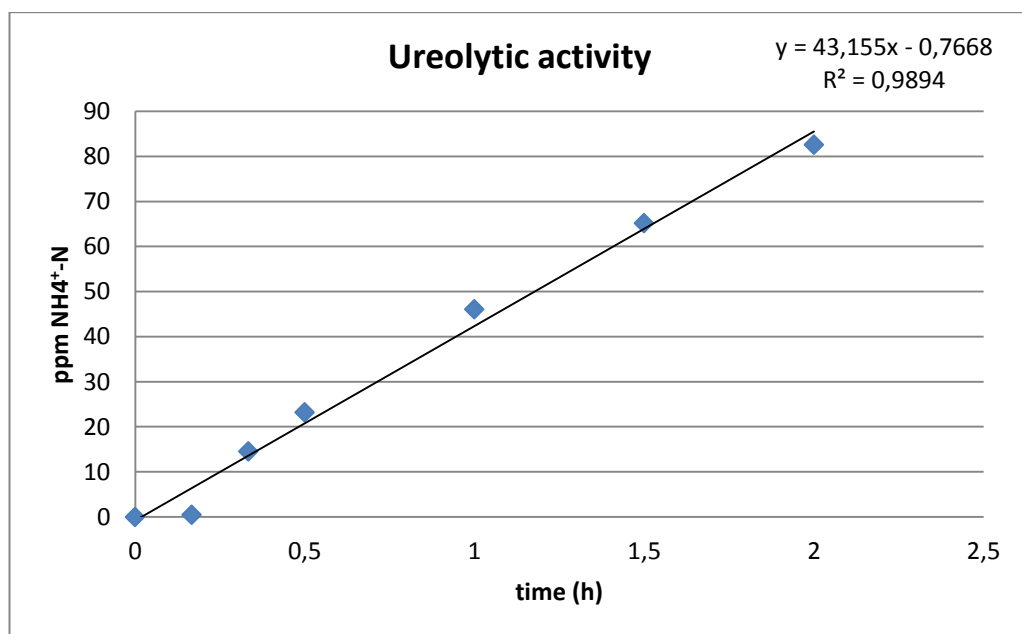


Figure 13. Line from measurement results of ureolytic activity of the sludge from phosphorus removal reactor.

The samples are analysed with ion chromatograph to get the concentration of ammonium in the solution. The remaining solution is used to determine VSS and TSS to calculate the specific ureolytic activity.

The ureolytic activity gives an idea of the activity of the sludge. Dividing the ureolytic activity with the VSS of the sludge makes it possible to compare with other measurements.

$$\text{specific ureolytic activity} = \frac{k}{\text{VSS}} \quad (16)$$

where k = slope of the result line (mg of NH_4^+ per hour)

VSS=volatile suspended solids measured from sludge sample (g)

Example 5. Calculation of specific ureolytic activity of the phosphorus removal reactor.

$$\begin{aligned} \text{specific ureolytic activity} &= \frac{k}{\text{VSS}} \\ &= \frac{43,155 \frac{\text{mg}}{\text{h}} * 24 \frac{\text{h}}{\text{d}}}{1000 \frac{\text{mg}}{\text{g}} * 1,990 \text{g}} = 0,521 \frac{\text{gNH}_4\text{-N}}{\text{gVSS} \cdot \text{d}} \end{aligned}$$

8 EXPERIMENT PROCESS PERFORMANCE

8.1 Phosphorus removal reactor

The reactor used had the volume of 4 litres. It was fed with anaerobic effluent from a potato processing factory, sludge, urea and magnesium ($\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$) with the average flow rates of:

wastewater	0,66 l/h
urea	0,01 l/h

magnesium 0,034 l/h

Although the wastewater already contains magnesium, addition of it is required to get larger amounts of phosphates to precipitate. The process also requires an increase in pH which is done by means of bacterial urease activity.

Struvite crystals formed in the reactor are removed from the bottom of the reactor.



Figure 14. Phosphorus removal reactor. 1) Influent stream 2) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ stream 3) Urease breeder 4) Crystallization reactor, volume 4 litres 5) Effluent stream.

8.2 Sharon reactor

The Sharon reactor was fed with the effluent of the phosphorus removal reactor. Volume of the reactor was 23 litres and it was continuously stirred and aerated between certain time intervals that were changed during the experiment. The feed stream is directed to the top of the reactor.



Figure 15. 23l Sharon reactor 30.11.2010. 1) Influent stream 2) reactor 3) Effluent stream.



Figure 16. Phosphorus removal and Sharon process. 1) Phosphorus removal influent 2) Crystallization reactor 3) Phosphorus removal effluent / Sharon influent 4) Sharon reactor 5) Sharon effluent.

8.3 Vegetable Anammox reactor

The Anammox reactor was fed with the effluent of the Sharon reactor. The volume of the reactor was 3,7 litres and it was continuously stirred with the feed stream directed to the bottom of the reactor to make the treated water flow through the layer of bacteria. This reactor is called Vegetable Anammox reactor.

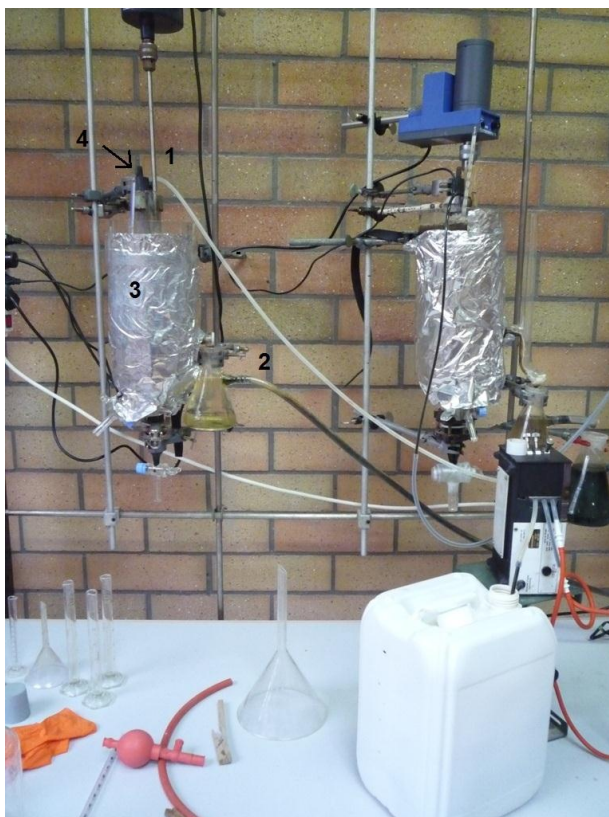


Figure 17. Anammox reactor 30.11.2010 (left). 1) Influent stream 2) Effluent stream 3) Reactor, volume 3,7 litres 4) Thermometer / heater.

8.4 Pig manure Anammox reactor start-up

The reactor that was started up had a volume of 21 litres. Approximately two thirds of the top of the reactor was filled with poly-urethane sponge, leaving the bottom part empty. Purpose of this was to have a surface for the bacteria to attach to. The influent stream of the reactor was directed to the bottom of the reactor. This hole was also used to place a mixer to the bottom of the reactor. The effluent stream was di-

rected to exit from the top of the reactor. This was done to make the fluid travel through the sponge where the bacteria are settled.

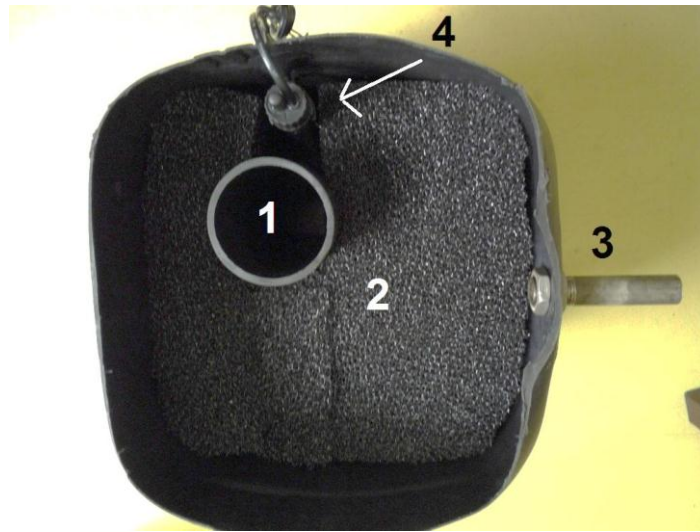


Figure 18. Empty Anammox reactor. 1) Tube to direct influent to the bottom 2) Carrier material (poly-urethane sponge) 3) Effluent point 4) Heater.

First step was to fill the reactor with nitrifying and denitrifying sludge taken from a piggery manure processing plant (DANIS NV, Belgium) in order to get the bacteria to the reactor. The sludge was heated until 35 °C. After heating, wastewater was fed to the reactor at an approximate HRT (hydraulic retention time) of 2 days. This reactor is called pig manure Anammox reactor.



Figure 19. Full setup of pig manure reactor.

8.4.1 Wastewater

Wastewater treated was made from diluted wastewater from a factory that treats pig manure. It was added to 60 litres of de-mineralized water. Because the pig manure already contains ammonia and bicarbonate, so there was no need for addition of these components. Following substances were also added to make the conditions proper for Anammox bacteria:

30 g NaNO_2

102 g NaNO_3

24 g $\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$

3 g KH_2PO_4

During start-up, it is important that the wastewater contains sufficient nitrate to prevent sulphate reduction. During sulphate reduction, sulphide is released which is toxic to Anammox bacteria.

After these steps 60 litres of tap water was added. Tap water also has nutrients needed by the bacteria and therefore only half of the wastewater was made with demineralized water.

9 RESULTS

9.1 Phosphorus removal

Phosphorus removal was studied for a period of one month. During this period only one type of wastewater (anaerobic effluent) was treated and one type of sludge (denitrifying) used. Both of these were from a potato processing factory.

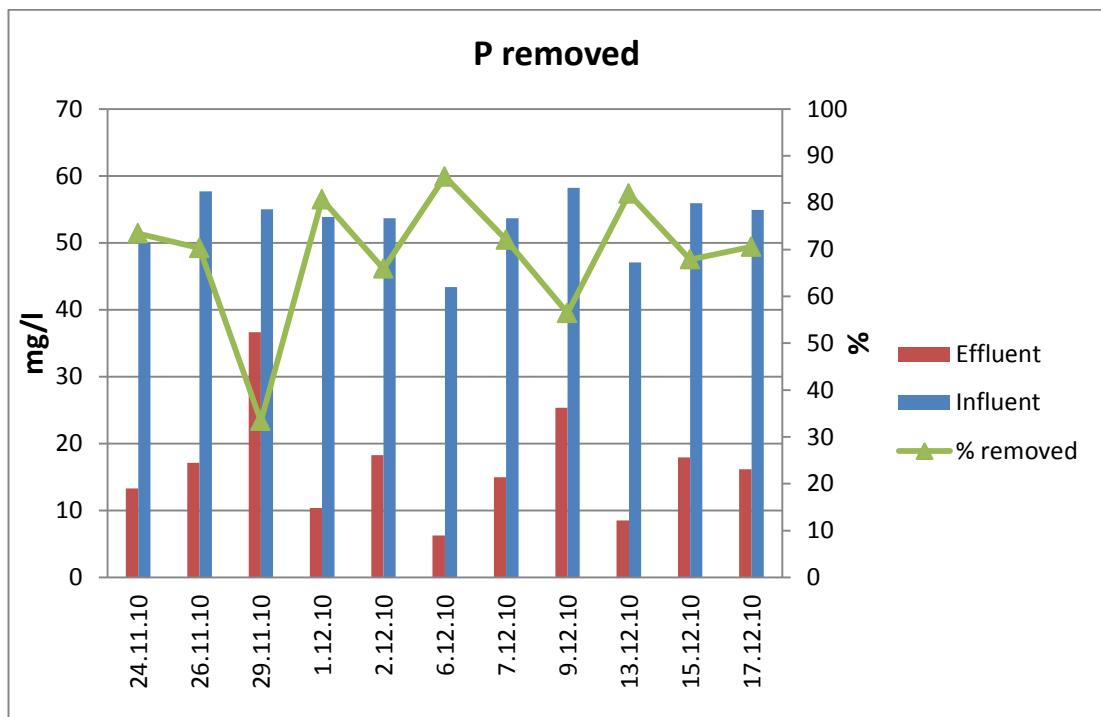
Table 1 shows that average amount of phosphorus in the influent was 53 mg/l with difference of ± 10 mg/l, this meant that the tests performed were done to a steady stream of phosphorus. Only the amount of magnesium was changed due to there not being enough magnesium in the start for the precipitation of struvite.

Measurement results were constant with little changes to average, besides two measurements (figure 20) performed on 29.11.2010 and 9.12.2010. These days the removal efficiency was lower than required due to pH being lower than the process requires.

Specific ureolytic activity was measured and calculated (example 5) twice from the sludge with results of 0,99 and 0,52 g $\text{NH}_4\text{-N/d}\cdot\text{gVSS}$. Based on these results, the activity of the sludge varies highly.

Table 1. Parameters measured from the phosphorus removal reactor.

Parameter	Unit	Average	±
NH ₄ -N influent	mg/l	178	39
NH ₄ -N effluent	mg/l	274	56
Mg influent	mg/l	36	9
Mg effluent	mg/l	199	172
PO ₄ -P influent	mg/l	53	10
PO ₄ -P effluent	mg/l	17	20
pH influent		7,9	0,4
pH effluent		8,2	0,3
Inorganic carbon influent	mg/l	287	43
Inorganic carbon effluent	mg/l	318	47
Flow rate	l/h	0,65	0,11
HRT	d	0,19	0,04

Figure 20. Concentration of phosphorus (PO₄³⁻P) in the influent and effluent and the % removed.

9.2 Sharon

Sharon process was studied for the period of three months. Goal was to get an effluent with approximately 1:1,3 ratio of NH₄-N:NO₂-N in order to get the effluent of Sharon reactor to become a suitable influent for the Anammox reactor. Table 2

shows that the averages of all the measurements were not at the goal values and that values varied in a large scale. Figure 21 shows values measured from the effluent in per cents.

The sludge used in the process was changed twice, first 3.11 and then 10.11. Before the change of sludge, the reactor was working reasonably well, but after the change too much of the ammonium was converted to nitrite. Aeration was changed for the reactor to less starting from aeration every 6 minutes from 0 to 0,30 mg of dissolved oxygen to aeration every 15 minutes with the range of dissolved oxygen staying the same. After the second change of sludge the opposite occurred and not enough of the ammonium was converted to nitrite. Aeration was again changed to every 5 minutes from 0 to 0,30 mg of dissolved oxygen.

Table 2. Parameters measured from the Sharon reactor.

Parameter	Unit	Average	±
NH ₄ -N influent	mg/l	156	77
NH ₄ -N effluent	mg/l	89	75
NO ₂ -N influent	mg/l	7	17
NO ₂ -Neffluent	mg/l	103	84
NO ₃ -N influent	mg/l	6	33
NO ₃ -Neffluent	mg/l	6	16
pH influent		8,1	0,3
pH effluent		8	0,4
Inorganic carbon influent	mg/l	264	141
Inorganic carbon effluent	mg/l	166	126
Flow rate	l/h	0,6	0,2
HRT	d	1,7	1

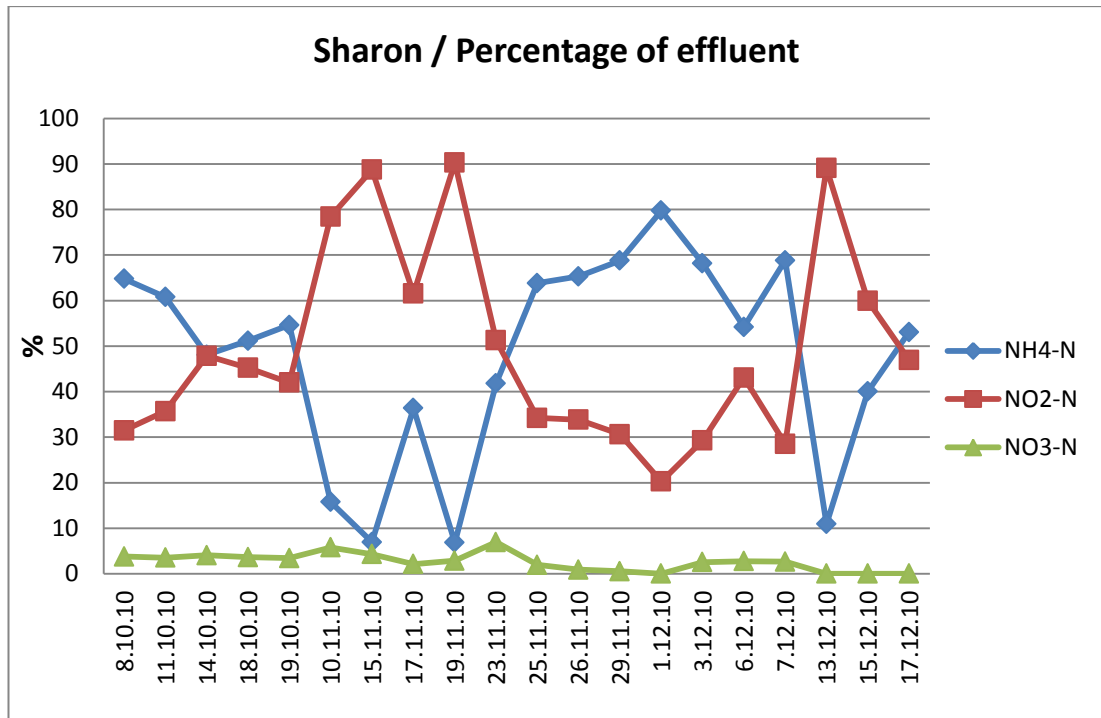


Figure 21. Percentage of nitrite, nitrate and ammonium in the effluent stream of the Sharon reactor.

9.3 Anammox

9.3.1 Vegetable

The effluent of the Sharon reactor was used as the influent for the Anammox reactor. The difference of the $\text{NH}_4\text{-N}:\text{NO}_2\text{-N}$ ratio caused that the influent was not always at the ratio of 1:1,3, which is the optimal ratio for the Anammox bacteria. At the beginning the conversion efficiency was at a good level, but with higher concentrations of nitrite and ammonia in the influent (Sharon effluent, figure 21) the efficiency appeared to decrease (figure 22).

The influent was changed 6.12 by only inserting ammonium to the reactor to test if there is both Sharon and Anammox bacteria in the reactor. This was done because there are bacteria from the Sharon reactor coming to the Anammox reactor in the wastewater. These bacteria might grow in the same spongy filling with the Anammox bacteria, meaning that both of the processes would be in the same reactor.

First none of the ammonium was converted, but by the end of the experiments it was slowly increasing.

Table 3 shows that the values of $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ in the influent and effluent varied in a large scale.

Table 3. Parameters measured from the vegetable Anammox reactor.

Parameter	Unit	Average	\pm
$\text{NH}_4\text{-N}$ influent	mg/l	101	130
$\text{NH}_4\text{-N}$ effluent	mg/l	28	88
$\text{NO}_2\text{-N}$ influent	mg/l	66	105
$\text{NO}_2\text{-N}$ effluent	mg/l	33	49
$\text{NO}_3\text{-N}$ influent	mg/l	14	17
$\text{NO}_3\text{-N}$ effluent	mg/l	30	24
pH influent		7,9	0,5
pH effluent		8,2	0,4
Conductivity influent	mS/cm	5,3	1,81
Conductivity effluent	mS/cm	5,34	1,4
Inorganic carbon influent	mg/l	140	104
Inorganic carbon effluent	mg/l	119	75
Flow rate	l/h	0,106	0,04
HRT	d	0,986	0,26

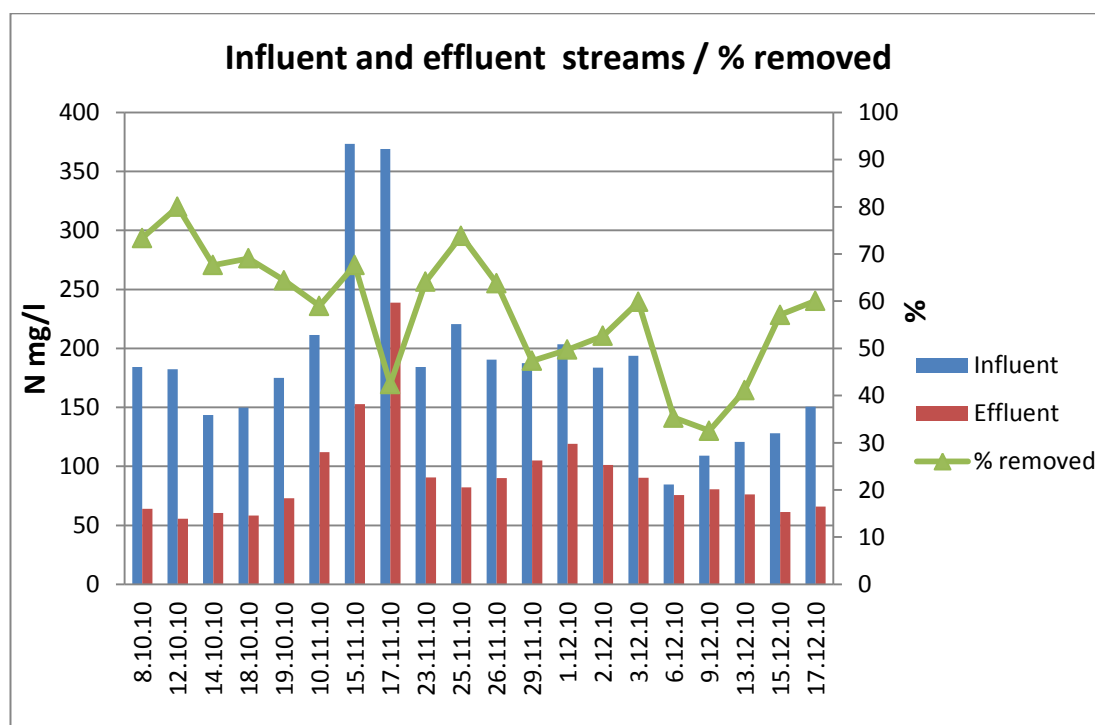


Figure 22. Nitrogen concentrations in the influent and effluent streams of the vegetable Anammox reactor and percentage of nitrogen removed.

9.3.2 Pig manure

The reactor, processing wastewater from a factory that treats pig manure, was started at a larger scale as the reactor processing wastewater from a potato processing plant. Volume of the reactor was 21 litres. By the end of the measurements it had been running constantly for 1,5 months.

An Anammox reactor should convert both ammonium and nitrite and produce a small amount of nitrate (equation 9). During the 1,5 months after the start-up, only nitrite and nitrate were converted instead of ammonium and nitrite converted and nitrate formed. Figure 23 shows that hardly any change in the conversions of ammonium and nitrite occurred during the 1,5 months.

Table 4 shows that instead of decrease in inorganic carbon there is an increase in the amount of inorganic carbon.

Table 4. Parameters measured from pig manure Anammox reactor.

Parameter	Unit	Average	±
NH ₄ -N influent	mg/l	89	22
NH ₄ -N effluent	mg/l	86	81
NO ₂ -N influent	mg/l	151	76
NO ₂ -Neffluent	mg/l	17	40
NO ₃ -N influent	mg/l	53	137
NO ₃ -Neffluent	mg/l	12	35
pH influent		8,1	0,6
pH effluent		8,4	0,2
Conductivity influent	mS/cm	1,8	0,2
Conductivity effluent	mS/cm	1,7	0,3
Inorganic carbon influent	mg/l	86	23
Inorganic carbon effluent	mg/l	112	21
Flow rate	l/h	0,4	0,2
HRT	d	2,1	1,3

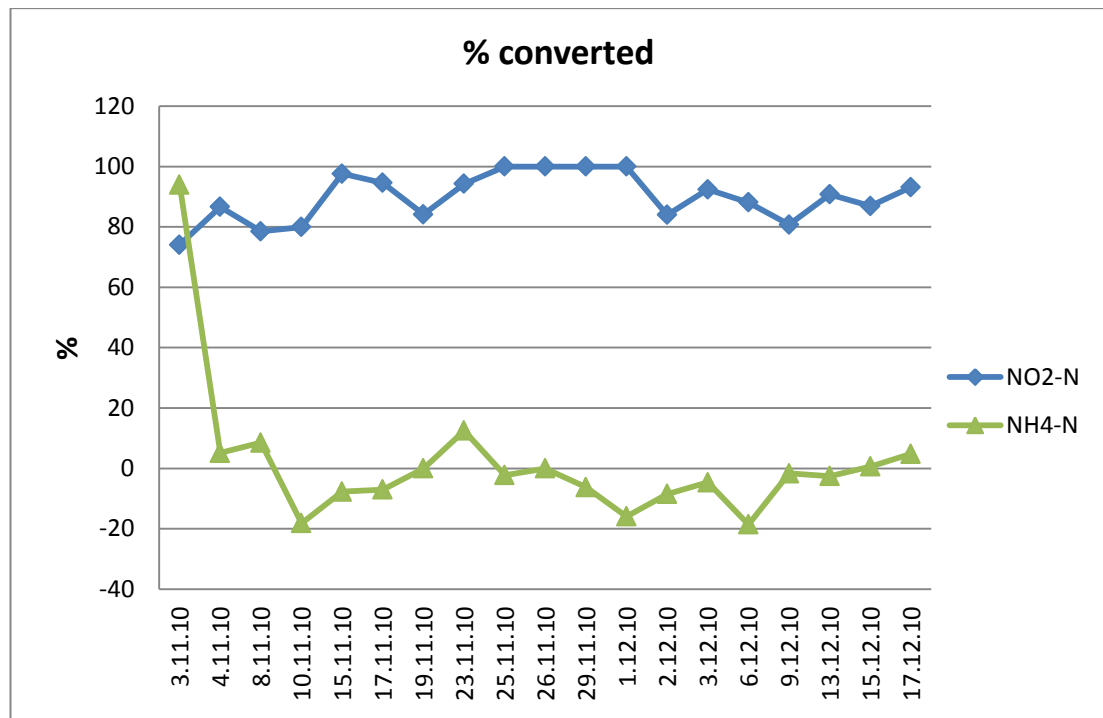


Figure 23. Percentage of nitrite and ammonia converted in the pig manure Anammox reactor.

9.4 Combined Sharon/Anammox process

Figure 24 shows the removal of nitrogen in the combined Sharon/Anammox process. There are three measurement points when the removal efficiency was lower than 40 %, but many results give a removal efficiency higher than 80%.

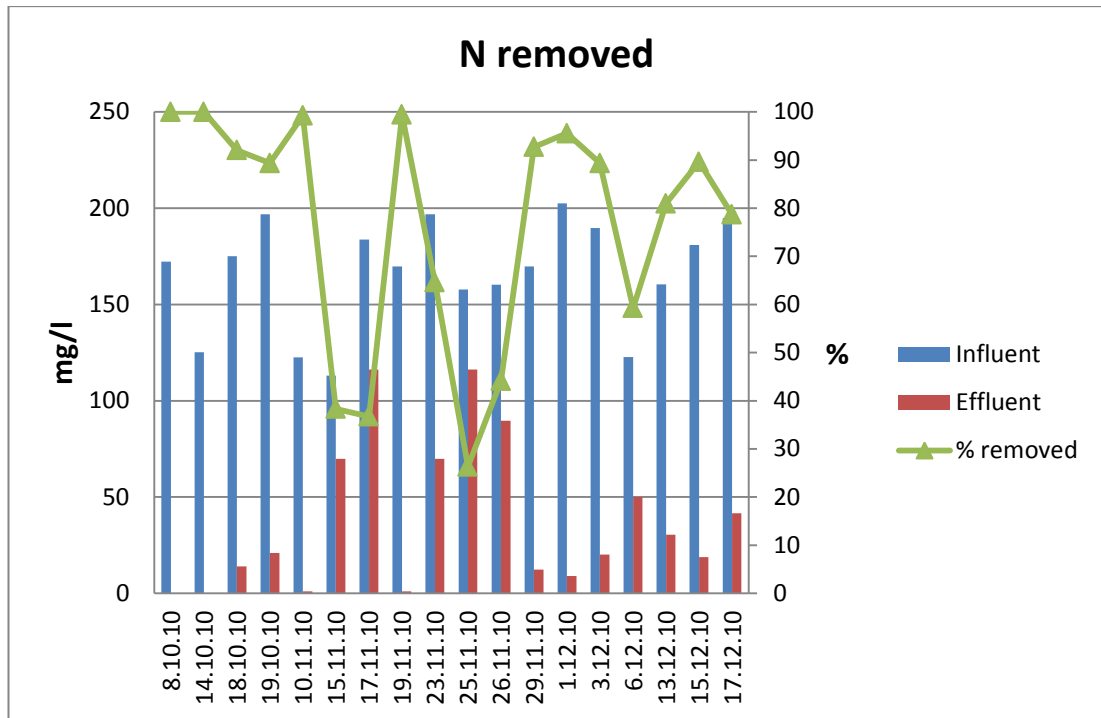


Figure 24. Amount of nitrogen in the influent and the effluent of the combined process and percentage removed.

10 CONCLUSIONS

10.1 Phosphorus

Average removal efficiency of 71% was gained for the removal of phosphorus starting from the phosphorus removal reactor to the effluent of the Anammox reactor. The goal for the efficiency was at approximately 80% (from 50 mg/l $\text{PO}_4\text{-P}$ to 8-10 mg/l $\text{PO}_4\text{-P}$). The removal was at required values, but the process wasn't stable enough to leave out of control samples for a longer period of time.

The shape of struvite gained was a round ball-like as wanted.

10.2 Sharon

Results varied highly for the Sharon reactor and a stable process was not gained. The first change of sludge caused too much conversion of ammonium to nitrite that was attempted to control by changing the aeration of the reactor to less and thus making the bacteria less active. This proved not to be at any effect to the conversion. After the second change of sludge there was not enough ammonium converted to nitrite. Aeration of the reactor was increased to get the bacteria convert more ammonium, but by the end of the experiments it had not proved to move the process to the required values and a more stable form.

The results showed that the control parameters, such as aeration, need to be changed with different types of sludge used and water treated. Yet more research needs to be performed to gain a stable process and a proper influent for the Anammox process.

10.3 Anammox

10.3.1 Vegetable Anammox reactor

The results varied a lot and the $\text{NO}_2\text{-N}:\text{NH}_4\text{-N}$ ratio was lower than required for the process. The conversion occurred in the reactor, but the efficiency was never at the required level of 90% (figure 22). Nitrogen was removed in the form of nitrogen gas. The main cause for the low removal efficiency was the ratio of $\text{NO}_2\text{-N}:\text{NH}_4\text{-N}$, which has to be at the range of 1-1,32 for the bacteria to work properly and to gain a removal efficiency high enough. During most of the experiment this ratio was lower than 1.

The test performed to see whether or not the both processes, Sharon and Anammox, occur in the same reactor was not finished by the end of the experimental part of this thesis. The results showed that ammonium was converted without the presence of nitrite, but the results weren't strong enough to determine that it is due to the bacteria from the Sharon process.

The Anammox was far from being stable and far from the required removal efficiency. To gain these more research needs to be done in this field.

10.3.2 Pig manure Anammox reactor

There were several factors showing that the Anammox process was not yet fully functioning. There was no conversion of ammonium in the reactor when it should be converted in an Anammox reactor. The conversion of nitrate should not occur in the reactor, it should be formed as one of the products of an Anammox reaction (equation 9).

The increase of inorganic carbon also is a sign that the Anammox process is not taking place in the reactor. The Anammox bacteria consume HCO_3^- (equation 9) present in the wastewater as a carbon source and thus there should be a decrease in the inorganic carbon instead of the increase.

Experiments performed with the pig manure Anammox reactor showed that the start-up of an Anammox reactor takes a long period of time. The reactor was operated for 1,5 months, but no Anammox activity was seen so far. The estimate is that it takes at least 3 months to start an Anammox reactor.

10.4 Combined Sharon/Anammox process

An average removal efficiency of 76% was gained by the combined Sharon/Anammox process with the goal being at 90%. The removal efficiency of 90% was achieved frequently during the experiments.

Aeration in the Sharon reactor is a factor that effects the concentrations of the effluent highly and it should be monitored constantly. The process is also highly dependent on the ratio of $\text{NO}_2\text{-N}:\text{NH}_4\text{-N}$ in the influent of the Anammox reactor. With the ratio of 1-1,3 the process appeared to work efficiently.

The results show that the combined Sharon/Anammox process can be used as a removal method of nitrogen from wastewaters. Results varied frequently and it is evident that the process requires further research to gain a stable process that can be used in larger scale.

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Calibration lines measured for the ion chromatographs for the calculations of the ion concentrations.

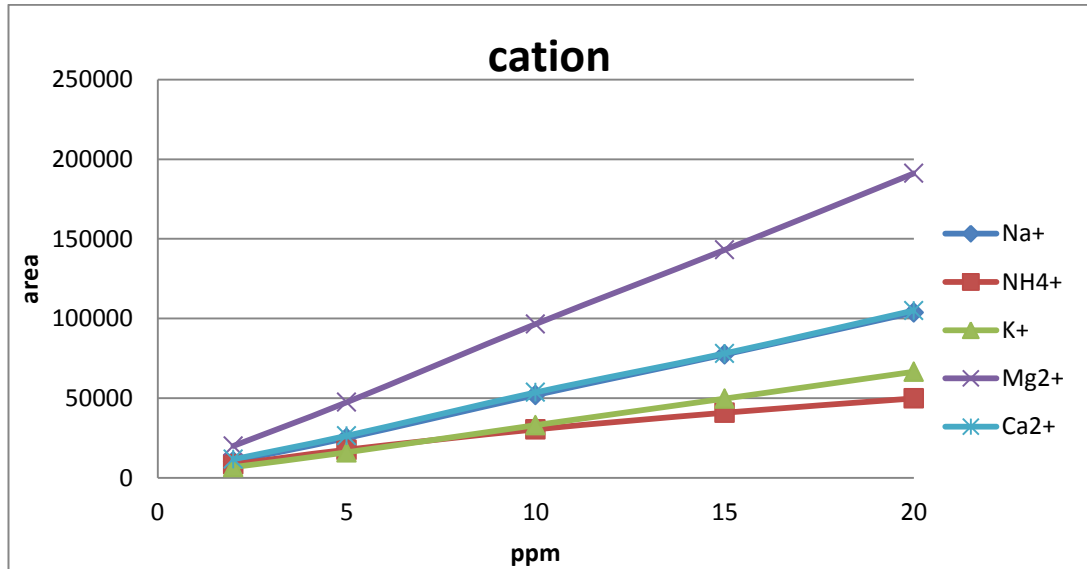


Figure 1. Calibration lines in October for the cations measured with ion chromatograph, a different integrator was used compared to normal situation.

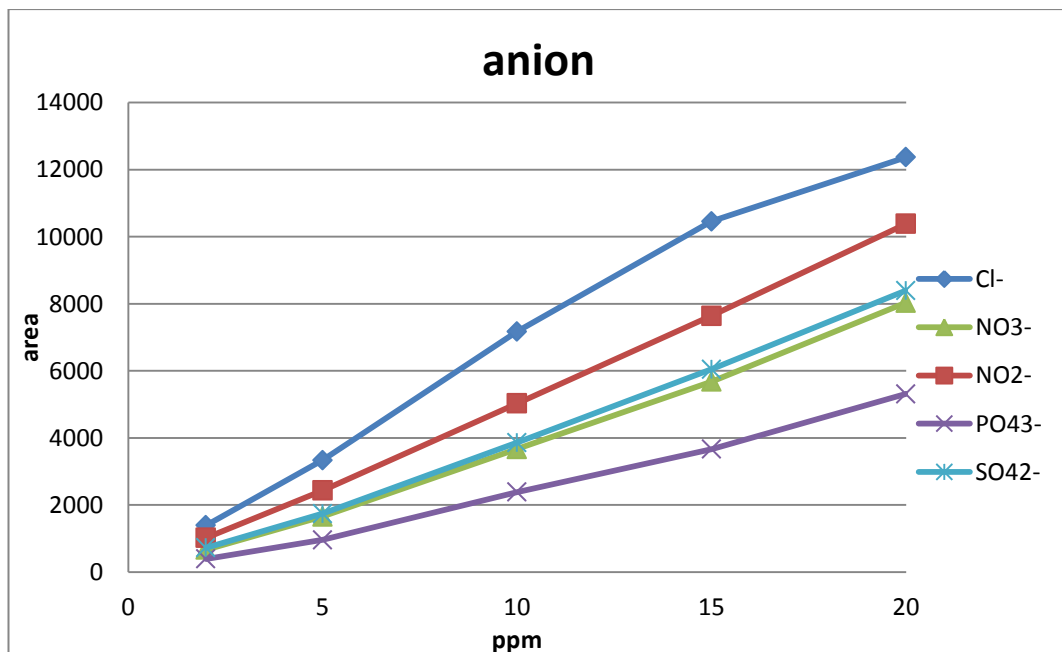


Figure 2. Calibration lines in October for the anions measured with ion chromatograph.

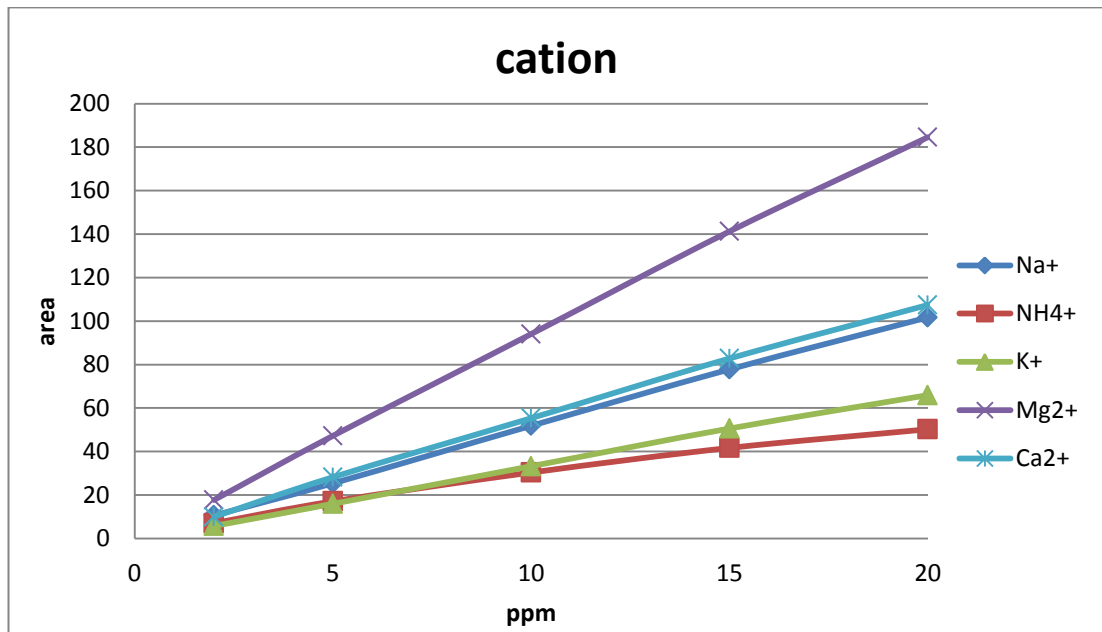


Figure 3. Calibration lines in November for the cations measured with ion chromatograph.

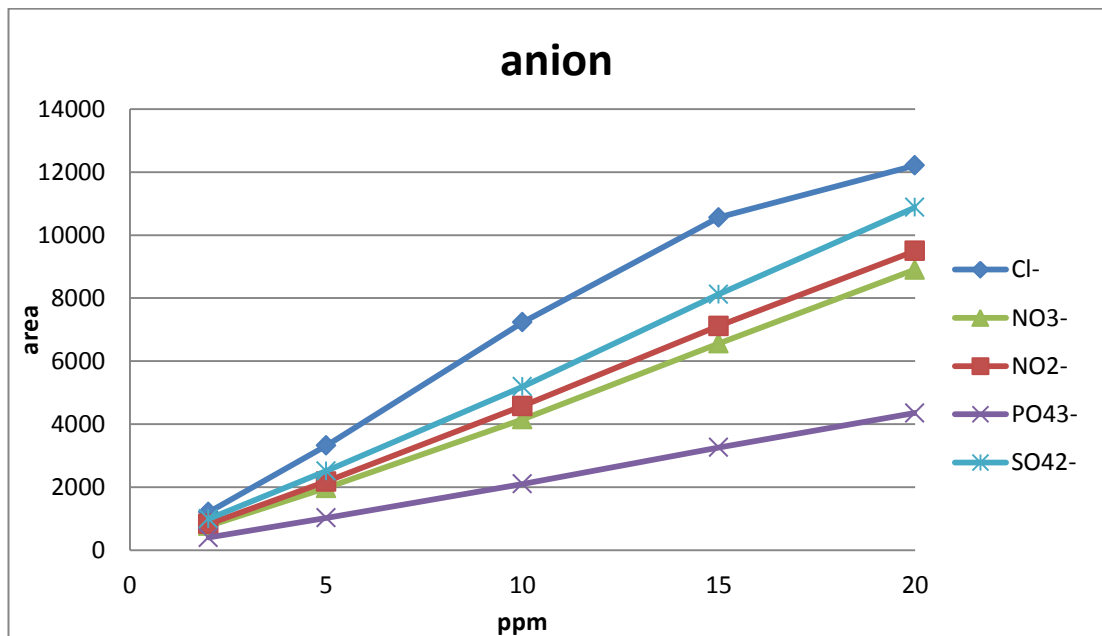


Figure 4. Calibration lines in November for the anions measured with ion chromatograph.

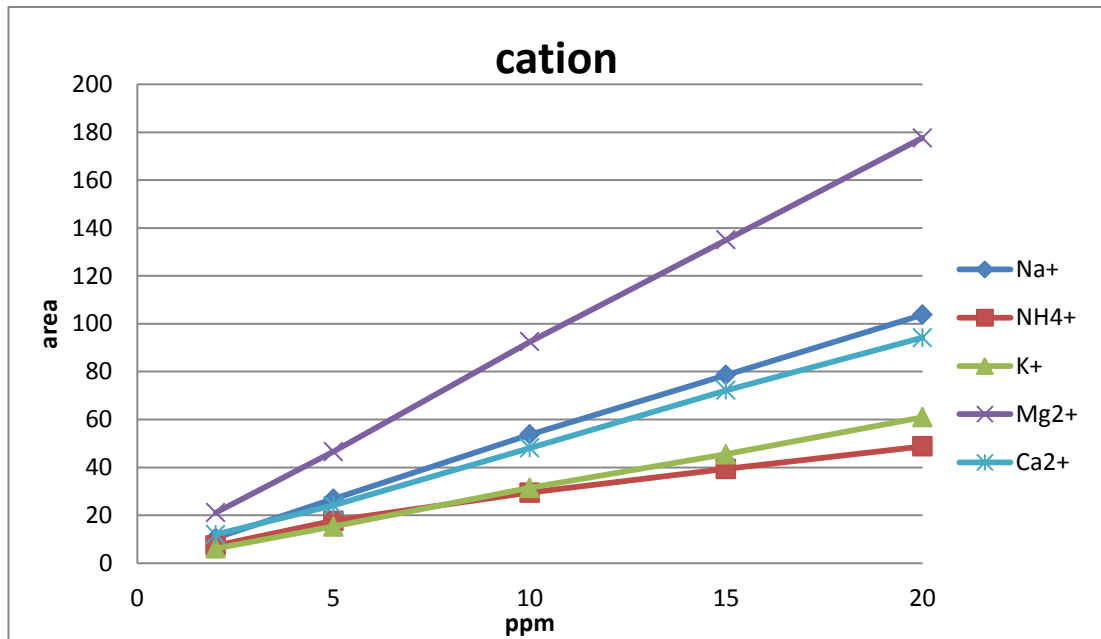


Figure 5. Calibration lines in December for the cations measured with ion chromatograph.

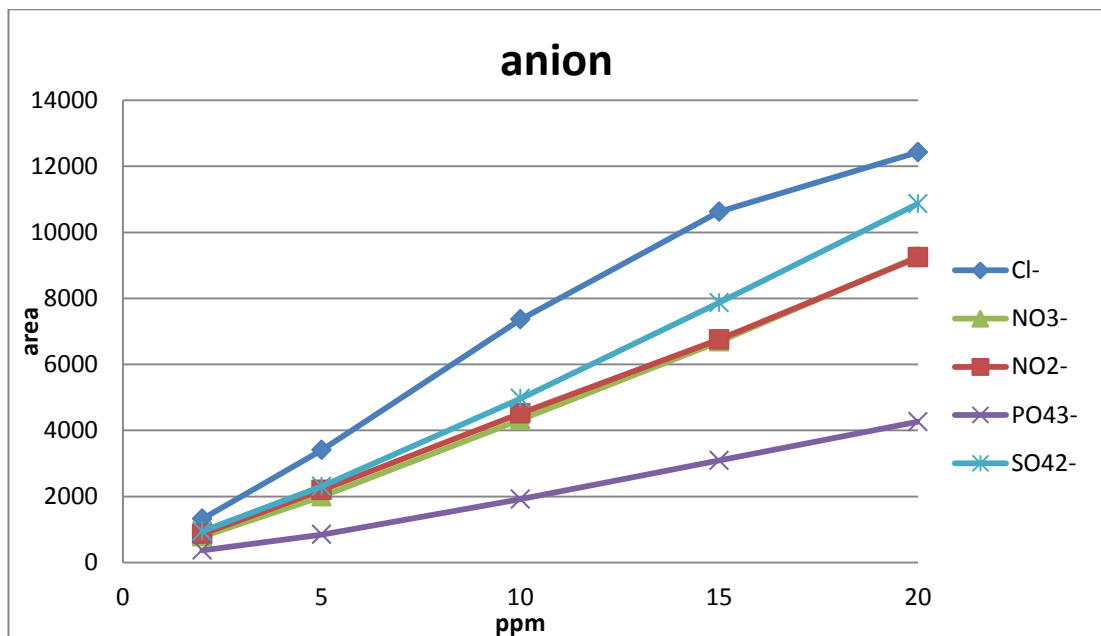


Figure 6. Calibration lines in December for the anions measured with the ion chromatograph.

APPENDIX 2

Calibration equations used to calculate the concentration of ions in the samples.

Table 1. Equations used for calculations of cations and anions in October. A different integrator was used compared to normal situation.

cations			anions		
	y=	R ²		y=	R ²
Na ⁺	5208,8x-482,54	0,9999	Cl ⁻	629,74x+398,7	0,9871
NH ₄ ⁺	2291,4x+5581,5	0,9909	NO ²⁻	521,19x-116,32	0,9996
K ⁺	3340,4x-334,98	0,9999	NO ³⁻	409,05x-311,67	0,9975
Mg ²⁺	9525,4x+587,44	0,9999	PO ₄ ³⁻	274,06x-304,89	0,9954
Ca ²⁺	5190,1x+969,93	0,9997	SO ₄ ²⁻	428,47x-301,02	0,9981

Table 2. Equations used for calculations of cations and anions in November.

cations			anions		
	y=	R ²		y=	R ²
Mg ²⁺	9,2884x+0,3751	0,9996	Cl ⁻	632,48x+329,3	0,981
Ca ²⁺	5,4112x+0,4723	0,9991	NO ²⁻	484,71x-200,45	0,9997
Na ⁺	5,1011x+0,4178	0,9997	NO ³⁻	454,68x-254,99	0,9991
K ⁺	3,367x-0,7117	0,9995	PO ₄ ³⁻	220,59x-67,368	0,9997
NH ₄ ⁺	2,3938x+4,3839	0,9878	SO ₄ ²⁻	552,81x-208,61	0,9995

Table 3. Equations used for calculations of cations and anions in December.

cations			anions		
	y=	R ²		y=	R ²
Na ⁺	5,1722x+0,9013	0,9996	Cl ⁻	636,71x+405,6	0,9833
NH ₄ ⁺	2,2518x+5,1139	0,9887	NO ²⁻	463,88x-110,43	0,9996
K ⁺	3,0407x+0,2618	0,9995	NO ³⁻	471,97x-293,1	0,9988
Mg ²⁺	8,7279x+3,8136	0,9998	PO ₄ ³⁻	219,05x-179,47	0,997
Ca ²⁺	4,6278x+1,9979	0,9995	SO ₄ ²⁻	554,22x-372,79	0,9981

APPENDIX 3 (1/2)

Measurement results for the phosphorus removal reactor.

date		24.11.2010	26.11.2010	29.11.2010	1.12.2010	2.12.2010
flow rate	l/h	0,54	0,672	0,672	0,684	0,684
HRT	d	0,23	0,19	0,19	0,18	0,18
pH influent		8,08	7,87	8,06	8,1	7,8
pH effluent		8,06	8,24	8,36	8,28	7,93
NH₄⁺ influent	mg/l	183,4	151,8	139,61	197,9	185,46
NH₄⁺ effluent	mg/l	330,75	248,9	267,08	290,02	236,21
Mg₂⁺ influent	mg/l	45,54			42,31	40,8
Mg₂⁺ effluent	mg/l	26,98			253,34	233,48
PO₄³⁻ influent	mg/l	175,05	177,08	168,88	165,4	164,77
PO₄³⁻ effluent	mg/l	67,86	52,56	112,55	31,9	56,15
IC influent	mg/l	293,2	305,7	328,1	277,4	275,1
IC effluent	mg/l	347,3	319,6	362,7	312,8	296
TSS	mg/l		9750			8720
VSS	mg/l		2180			1990
date		6.12.2010	7.12.2010	9.12.2010	13.12.2010	15.12.2010
flow rate	l/h	0,66	0,66	0,66	0,624	0,66
HRT	d	0,19	0,19	0,19	0,20	0,19
pH influent		7,89	7,97	7,51	7,97	7,56
pH effluent		8,11	8,26	7,85	8,28	8,08
NH₄⁺ influent	mg/l	186,17	147,8	193,27	191,35	180,27
NH₄⁺ effluent	mg/l	252,92	259,24	291,3	273,85	274,61
Mg₂⁺ influent	mg/l	36,25	33,26	33,21	29,19	34,39
Mg₂⁺ effluent	mg/l	122,1	256,68	231,81	231,9	211,56
PO₄³⁻ influent	mg/l	133,26	164,72	178,75	145,52	171,72
PO₄³⁻ effluent	mg/l	19,26	45,99	77,85	23,15	55,13
IC influent	mg/l			244,2		
IC effluent	mg/l			271,7		
TSS	mg/l					
VSS	mg/l					

APPENDIX 3 (2/2)

date		17.12.2010
flow rate	l/h	0,654
HRT	d	0,19
pH influent		7,79
pH effluent		8,16
NH₄⁺ influent	mg/l	203,86
NH₄⁺ effluent	mg/l	295,31
Mg₂⁺ influent	mg/l	32,89
Mg₂⁺ effluent	mg/l	224,65
PO₄³⁻ influent	mg/l	168,65
PO₄³⁻ effluent	mg/l	49,58
IC influent	mg/l	
IC effluent	mg/l	
TSS	mg/l	
VSS	mg/l	

APPENDIX 4 (1/2)

Measurement results for the Sharon reactor.

date		8.10.2010	11.10.2010	14.10.2010	18.10.2010	19.10.2010
flow rate	l/h		0,552	0,456	0,354	0,552
HRT	d		1,74	2,10	2,71	1,74
pH influent		8,07	7,85	7,93	8,17	8,32
pH effluent		8,04	8,06	8,01	8,2	8,25
NH₄⁺ influent	mg/l	221,82	197,21	161,13	225,35	253,6
NH₄⁺ effluent	mg/l	162,51	154,92	90,16	126,54	148,59
NO₂⁻ influent	mg/l	0	0	52,63	0	0
NO₂⁻ effluent	mg/l	201,35	232,2	228,92	285,25	291,25
NO₃⁻ influent	mg/l	30,82	0	38,6	31,91	31,85
NO₃⁻ effluent	mg/l	32,45	31,01	26,08	30,9	31,99
IC influent	mg/l		245,9	234,3	296,6	
IC effluent	mg/l		204,1	161,7	162,9	
date		3.11.2010	4.11.2010	8.11.2010	10.11.2010	15.11.2010
flow rate	l/h	0,54	0,552	0,534	0,54	0,54
HRT	d	1,77	1,74	1,79	1,77	1,77
pH influent		7,87	7,88	7,85	7,95	8,11
pH effluent		8	7,62	7,69	7,71	7,88
NH₄⁺ influent	mg/l	121	102	105	157,82	145,68
NH₄⁺ effluent	mg/l	120	65	43	42,49	18,21
NO₂⁻ influent	mg/l	55,35	67,1	76,99	76,95	78,37
NO₂⁻ effluent	mg/l	336,54	391,03	544,91	539,13	594,28
NO₃⁻ influent	mg/l	105,85	177,41	32,16	31,99	39,67
NO₃⁻ effluent	mg/l	53,17	98,59	41,05	53,7	38,94
IC influent	mg/l	211,1	125,8	202	209,4	236,6
IC effluent	mg/l	182,2	98,93	79,09	90,6	77,41
date		17.11.2010	19.11.2010	23.11.2010	25.11.2010	26.11.2010
flow rate	l/h	0,582	0,582	0,744	0,756	0,732
HRT	d	1,65	1,65	1,29	1,27	1,31
pH influent		8,15	8,27	8,18	8,19	8,2
pH effluent		7,95	7,62	8,08	8,15	8,18
NH₄⁺ influent	mg/l	236,55	218,52	253,59	203,17	206,38
NH₄⁺ effluent	mg/l	107,39	18,21	108,42	173,38	139,61
NO₂⁻ influent	mg/l	69,07	0	0	0	0
NO₂⁻ effluent	mg/l	463,58	614,74	338,92	237,14	184,39
NO₃⁻ influent	mg/l	3,81	3,86	4,88	4,43	4,38
NO₃⁻ effluent	mg/l	21,53	26,34	61,72	18,32	6,51
IC influent	mg/l	258,2	263,8	335,5	309,7	307,6
IC effluent	mg/l	129,5	73,87	182,6	221,2	241,3

APPENDIX 4 (2/2)

date		29.11.2010	1.12.2010	3.12.2010	6.12.2010	9.12.2010
flow rate	l/h	0,72	0,732	0,672	0,54	0,54
HRT	d	1,33	1,31	1,43	1,77	1,77
pH influent		8,23	8,11	7,95	8,19	7,99
pH effluent		8,19	8,17	8,03	8,09	8,07
NH₄⁺ influent	mg/l	218,52	260,79	244,23	158,08	246,89
NH₄⁺ effluent	mg/l	151,75	197,85	131,85	113,56	195,1
NO₂⁻ influent	mg/l	0	0	0	0	0
NO₂⁻ effluent	mg/l	172,42	128,2	144,41	230,25	206,11
NO₃⁻ influent	mg/l	11,62	4,41	15,59	25,66	30,98
NO₃⁻ effluent	mg/l	4,24	0	16,92	19,8	26
IC influent	mg/l	405,2	330,1	265,2		253,8
IC effluent	mg/l	292,8	277	166,6		184,8
date		13.12.2010	15.12.2010	17.12.2010		
flow rate	l/h	0,492	0,6	0,6		
HRT	d	1,95	1,60	1,60		
pH influent		8,07	7,88	8,02		
pH effluent		7,65	7,82	8,06		
NH₄⁺ influent	mg/l	206,53	232,91	250,95		
NH₄⁺ effluent	mg/l	29,38	103,36	191,7		
NO₂⁻ influent	mg/l	0	15,76	16,51		
NO₂⁻ effluent	mg/l	611,1	394,79	432,6		
NO₃⁻ influent	mg/l	9,2	7,78	6,74		
NO₃⁻ effluent	mg/l	0	0	0		
IC influent	mg/l					
IC effluent	mg/l					

Measurement results for the vegetable Anammox reactor.

cond = conductivity, I = influent, E = effluent

<i>date</i>		8.10.2010	12.10.2010	14.10.2010	18.10.2010	19.10.2010
flow rate	l/h		0,102	0,102	0,102	0,102
HRT	d		1,02	1,02	1,02	1,02
cond/I	mS/cm	5,04	5,06	5,1	4,7	5,19
cond/E	mS/cm	4,83	4,94	4,9	4,7	5,09
pH/I			7,99	7,78	8,14	8,16
pH/E			8,23	8,21	8,48	8,51
NH₄⁺/I	mg/l	113,32	126,5	72	99,49	118,16
NH₄⁺/E	mg/l	0	0	0	17,89	26,98
NO₂⁻/I	mg/l	296,39	268,98	267,87	209,53	238,75
NO₂⁻/E	mg/l	141,3	112,67	132,86	77,75	101,21
NO₃⁻/I	mg/l	26,66	9,44	26,37	38,85	46,23
NO₃⁻/E	mg/l	92,52	94,19	88,11	91,5	93,39
IC/I	mg/l		142,9	163	132,4	
IC/E	mg/l		136,6	142,6	120,9	
<i>date</i>		3.11.2010	4.11.2010	8.11.2010	10.11.2010	15.11.2010
flow rate	l/h	0,108	0,108	0,108	0,108	0,108
HRT	d	0,96	0,96	0,96	0,96	0,96
cond/I	mS/cm	4,42	4,16	4,22	6,2	6,31
cond/E	mS/cm	4,31	4,32	4,26	5,66	5,88
pH/I		7,87	7,72	7,77	7,79	7,53
pH/E		8,17	8,2	8,3	8,24	8,09
NH₄⁺/I	mg/l	82	72	23	42,49	297,43
NH₄⁺/E	mg/l	1,5	0,4	0,3	1,214	89,836
NO₂⁻/I	mg/l	225,4	203,03	306,53	521,9	395,26
NO₂⁻/E	mg/l	35,64	0	77,73	217,58	94,89
NO₃⁻/I	mg/l	57,07	54,83	85,86	86,17	97,78
NO₃⁻/E	mg/l	114,85	102,09	199,68	198,84	239,22
IC/I	mg/l	112,6	108,4	67,72	84,87	62,5
IC/E	mg/l	114,6	107,7	76,4	82,82	71,65

APPENDIX 5 (2/3)

cond = conductivity, I = influent, E = effluent

<i>date</i>		17.11.2010	19.11.2010	23.11.2010	25.11.2010	26.11.2010
flow rate	l/h	0,108	0,108	0,102	0,102	0,102
HRT	d	0,96	0,96	1,02	1,02	1,02
cond/I	mS/cm	7,11	4,36	4,76	6,49	6,84
cond/E	mS/cm	6,52	6,3	4,74	5,89	6,33
pH/I		7,51	7,47	7,4	8,01	8,03
pH/E		8,01	7,95	7,87	8,11	8,23
NH₄⁺/I	mg/l	236,49	115,33	87,53	149,87	127,47
NH₄⁺/E	mg/l	149,68	115,33	15,93	11,61	26,71
NO₂⁻/I	mg/l	562,83	275,32	328,8	279,67	244,68
NO₂⁻/E	mg/l	269,71	239,48	123,53	96,88	102,27
NO₃⁻/I	mg/l	62,41	65,61	70,99	84,91	75,67
NO₃⁻/E	mg/l	178,95	181,14	179,85	193,85	169,37
IC/I	mg/l	67,16	60,13	62,19	186,5	200,1
IC/E	mg/l	61,56	52,63	52,37	111,6	152,4
<i>date</i>		29.11.2010	1.12.2010	2.12.2010	3.12.2010	6.12.2010
flow rate	l/h	0,102	0,105	0,105	0,144	0,102
HRT	d	1,02	0,99	0,99	0,72	1,02
cond/I	mS/cm	6,46	6,44	6,56	6,56	3,94
cond/E	mS/cm	6,65	6,58	6,61	6,74	5,76
pH/I		8,11	8,14	8,16	8,22	7,92
pH/E		8,19	8,16	8,18	8,21	8,13
NH₄⁺/I	mg/l	115,33	188,2	168,2	180,56	100,71
NH₄⁺/E	mg/l	26	64,4	49,29	39,28	24,14
NO₂⁻/I	mg/l	219,87	130,86	111,78	105,3	0
NO₂⁻/E	mg/l	156,15	114,44	97,3	84,94	97,03
NO₃⁻/I	mg/l	136,75	77	84,75	94,97	28,9
NO₃⁻/E	mg/l	165,37	151,25	147,86	149,96	121,44
IC/I	mg/l	222,6	243,8	234,2	239,7	
IC/E	mg/l	193,8	191,5	178,4	187,2	

cond = conductivity, I = influent, E = effluent

<i>date</i>		7.12.2010	13.12.2010	15.12.2010	17.12.2010
flow rate	l/h	0,102	0,102	0,102	0,108
HRT	d	1,02	1,02	1,02	0,96
cond/I	mS/cm	3,65	4,27	4,61	4,65
cond/E	mS/cm	4,07	4,17	4,27	4,55
pH/I		7,99	7,94	7,96	8,06
pH/E		8,08	8,02	8,01	8,03
NH₄⁺/I	mg/l	123,86	147,94	152,44	180,47
NH₄⁺/E	mg/l	53,52	57,09	50,39	55,4
NO₂⁻/I	mg/l	0	0	15,01	15,17
NO₂⁻/E	mg/l	62,9	68,49	34,91	37,19
NO₃⁻/I	mg/l	56,91	26,45	23,06	25,34
NO₃⁻/E	mg/l	87,59	48,66	50,68	51,71
IC/I	mg/l	133			
IC/E	mg/l	110,4			

Measurement results for the pig manure Anammox reactor.

cond = conductivity, I = influent, E = effluent

<i>date</i>		3.11.2010	4.11.2010	8.11.2010	10.11.2010	15.11.2010
flow rate	l/h	0,41	0,330	0,384	0,432	0,444
HRT	d	2,04	2,53	2,17	1,93	1,88
cond/I	mS/cm	2,05	2,02	1,98	2,04	1,74
cond/E	mS/cm	2,06	1,95	1,87	1,82	1,72
pH/I		7,76	7,87	8,35	8,28	8,24
pH/E		8,26	8,35	8,54	8,48	8,31
NH₄⁺/I	mg/l	92,00	98,00	82,00	66,77	78,91
NH₄⁺/E	mg/l	5,50	93,00	75,00	78,91	84,98
NO₂⁻/I	mg/l	215,98	203,17	200,01	161,31	128,94
NO₂⁻/E	mg/l	56,08	27,18	43,00	32,35	3,07
NO₃⁻/I	mg/l	190,55	172,05	123,74	101,38	13,66
NO₃⁻/E	mg/l	47,60	40,65	33,04	14,83	7,77
IC/I	mg/l	81,50	80,49	78,14	86,25	85,21
IC/E	mg/l	119,30	123,00	116,60	108,60	103,80
<i>date</i>		17.11.2010	19.11.2010	23.11.2010	25.11.2010	26.11.2010
flow rate	l/h	0,402	0,366	0,24	0,39	0,414
HRT	d	2,07	2,28	3,47	2,14	2,01
cond/I	mS/cm	1,71	1,66	1,88	1,86	1,87
cond/E	mS/cm	1,68	1,66	1,74	1,78	1,76
pH/I		8,43	8,6	7,87	8,15	8,21
pH/E		8,42	8,51	8,45	8,31	8,40
NH₄⁺/I	mg/l	95,81	78,91	99,19	100,54	91,05
NH₄⁺/E	mg/l	102,56	78,91	86,78	102,78	91,05
NO₂⁻/I	mg/l	106,31	74,9	158,39	137,78	129,94
NO₂⁻/E	mg/l	5,78	11,87	9,11	0	0
NO₃⁻/I	mg/l	16,01	17,89	15,94	137,78	17,46
NO₃⁻/E	mg/l	0	4,06	4,3	0	0
IC/I	mg/l	84,06	88,88	89,50	90,95	92,58
IC/E	mg/l	106,40	106,90	119,80	110,20	112,70

APPENDIX 6 (2/2)

cond = conductivity, I = influent, E = effluent

<i>date</i>		29.11.2010	1.12.2010	2.12.2010	3.12.2010	6.12.2010
flow rate	l/h	0,354	0,42	0,474	0,456	0,438
HRT	d	2,35	1,98	1,76	1,83	1,90
cond/I	mS/cm	1,79	1,68	1,68	1,68	1,67
cond/E	mS/cm	1,72	1,7	1,61	1,58	1,54
pH/I		8,5	7,46	7,57	7,7	8,01
pH/E		8,51	8,52	8,49	8,5	8,48
NH₄⁺/I	mg/l	97,12	85,53	81,55	85,17	70,56
NH₄⁺/E	mg/l	103,19	99,18	88,5	89,1	83,68
NO₂⁻/I	mg/l	102,94	193,05	182	180,28	162,22
NO₂⁻/E	mg/l	0	0	29,18	13,65	19,28
NO₃⁻/I	mg/l	22	27,74	25,69	22,41	27,5
NO₃⁻/E	mg/l	4,89	8,69	6,99	5,99	6,49
IC/I	mg/l	108,70	78,86	82,36	84,57	
IC/E	mg/l	133,40	109,20	102,20	109,60	
<i>date</i>		9.12.2010	13.12.2010	15.12.2010	17.12.2010	
flow rate	l/h	0,42	0,384	0,402	0,378	
HRT	d	1,98	2,17	2,07	2,20	
cond/I	mS/cm	1,64	1,87	1,71	1,81	
cond/E	mS/cm	1,53	1,72	1,75	1,68	
pH/I		8,28	7,68	8	8,24	
pH/E		8,45	8,37	8,36	8,41	
NH₄⁺/I	mg/l	78,85	98,86	99,74	104,14	
NH₄⁺/E	mg/l	80,16	101,4	99,15	99,16	
NO₂⁻/I	mg/l	131,39	161,32	130,22	112,3	
NO₂⁻/E	mg/l	25,33	14,86	17,05	7,67	
NO₃⁻/I	mg/l	34,58	17,44	15,85	10,9	
NO₃⁻/E	mg/l	17,68	8,92	10,84	9,15	
IC/I	mg/l	79,62				
IC/E	mg/l	98,76				