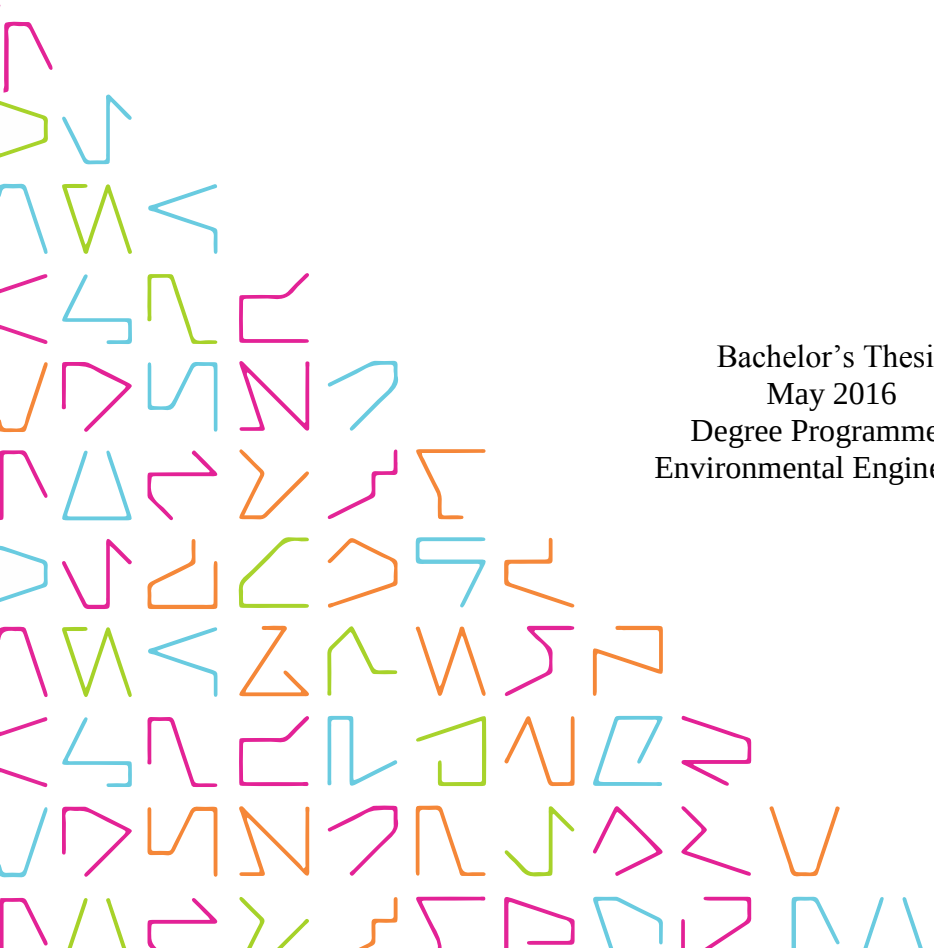
TAMPEREEN
AMMATTIKORKEAKOULU

NITROGEN RECOVERY FROM STRUVITE PRECIPITATION REJECT WATER

Laura Puurunen



Bachelor's Thesis
May 2016
Degree Programme in
Environmental Engineering

TIIVISTELMÄ

Tampereen ammattikorkeakoulu
Degree Programme in Environmental Engineering

PUURUNEN LAURA
Typen talteenotto struviitin saostusprosessin rejektivedestä

Opinnäytetyö 37 sivua, liitteitä 3 sivua
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Maaperän köyhtyminen on maailmanlaajuinen ilmiö, joka johtuu ravinnekiertojen hajoamisesta: ravinteet päätyvät vesistöihin maaperän sijaan aiheuttaen mm. vesistöjen rehevöitymistä. Ihmisvirtsa sisältää kaikki kasvuun tarvittavat ravinteet kasveille käyttökelpoisessa muodossa, joten se on erinomainen kierrätysravinne. Virtsasta voidaan saostaa myös fosforipitoista struviittia, mutta prosessin rejektiveteen jää edelleen paljon typpeä ja muita hivenravinteita. Tämän opinnäytetyön tavoitteena oli tutkia typen talteenottoa struviitin valmistusprosessin rejektivedestä testaamalla erilaisia adsorbenttejä. Tutkimus toteutettiin Tampereen Ammattikorkeakoulussa huhti-toukokuussa 2016.

Adsorbentteina tässä tutkimuksessa testattiin halloisiittia, lehtipuuhiitä sekä biohiiltä pajusta. Halloisiitti on silikaattimineraali, joka helposti muodostaa vettä läpäisemättömän pinnan, joten se sekoitettiin testausta varten kevytsoraan vettä läpäisevän seoksen luomiseksi. Kaikki materiaalit valittiin, koska aiemman tutkimustiedon mukaan niillä on potentiaalia ravinteiden talteenottoon. Lehtipuuhiili ja biohiili ovat hyviä adsorbenttejä huokoisen rakenteensa ja siitä johtuvan laajan pinta-alan ansiosta.

Tutkimukset osoittivat, että halloisiitti-kevytsoraseoksesta vapautui runsaasti typpeä itsessään: typen määrä näytteissä lisääntyi. Lehtipuuhiilen ja biohiilen kyky adsorboida typpeä oli jossain määrin parempi. Tulokset viittaavat siihen, että mitä pidempi oli adsorbentin viipymäaika näytteessä, sitä enemmän ravinteita siihen sitoutui. Lehtipuuhiili näytti tulosten mukaan adsorboivan typpeä parhaiten: typen määrä väheni parhaimmillaan 18 % neljän tunnin viipymällä. Lisätutkimuksia aiheesta tarvitaan, sillä tulokset eivät olleet yksiselitteisiä.

Korkeamman reliabiliteetin saavuttamiseksi testejä pitäisi toistaa lisää. Jatkotutkimusmahdollisuuksia on useita: viipymäajan kasvattaminen, adsorbenttien koostumuksen muokkaus ja adsorbentin sekoittaminen näytteessä.

Asiasanat: typen talteenotto, ravinteiden kierrätys, struviitti, virtsa

ABSTRACT

Tampereen ammattikorkeakoulu
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PUURUNEN LAURA
Nitrogen Recovery from Struvite Precipitation Reject Water

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Soil fertility is depleting due to incomplete nutrient cycles globally, which lead nutrients from soils to water bodies causing water eutrophication and its many consequences. Human urine contains all the necessary nutrients in a form which plants can immediately use as their nutrition, which makes it an excellent candidate for nutrient recycling. Struvite production from source-separated urine is one way of nutrient recycling. Previous research has shown that phosphorous can be efficiently recovered from struvite, but nitrogen mainly remains in the reject water. The aim of this thesis was to study different ways of nitrogen recovery from the effluent of struvite production process using different adsorbent materials. The study was conducted in Tampere University of Applied Sciences during April and May, 2016.

The materials tested were halloysite mineral, charcoal and willow biochar. The halloysite had to be mixed with LECA-pebbles to allow water penetrate the surface. The two last ones have been found efficient adsorbents of water and nutrients due to their extremely porous structure with a very high surface area.

The results indicated that the halloysite-LECA pebbles leached a significant amount of N. Therefore, the amount of N in the samples increased instead of reducing. Charcoal and willow biochar were able to adsorb N to some extent. The results suggest that with increasing retention time more nitrogen is adsorbed. Charcoal had the highest nitrogen adsorption rate, up to 18 % with 4-hour residence time.

More repeated experiments should be conducted to reach higher reliability. Further studies on the subject could include increasing the residence time, changing the consistency of the materials and instead of soaking the material in the filtrate, stirring the adsorbent continuously.

Search words: nitrogen adsorption, nutrient recovery, struvite, urine

CONTENTS

GLOSSARY

LECA	Light expanded clay aggregate
N	Nitrogen
NH_2^-	Nitrite
NH_3^-	Nitrate
NH_3^+	Ammonia
NH_4^+	Ammonium
P	Phosphorous
RO	Reverse Osmosis
TAMK	Tampere University of Applied Sciences
TKN	Total Kjeldahl Nitrogen
TN	Total Nitrogen
TP	Total Phosphorous
WHO	World Health Organization

1 INTRODUCTION

Human urine contains all the necessary nutrients for plant growth: nitrogen (N), phosphorous (P) and potassium (K) as well as a number of micronutrients. This characteristic makes it a potentially excellent fertiliser. Moreover, in urine these nutrients could appear in the same ratio as in commercial fertilisers. Especially P, which is mined from mineral phosphate rock, is depleting and it is estimated that within 50-100 years we might be facing the end of it (Schönning, C. 2001. 7 and Kemacheevakul. 2012. 1). Due to this fact, a real need has occurred for the development of methods for more efficient nutrient cycles which would answer to the growing demand of nutrition for a constantly growing number of people.

Still today in many parts of the world, wastewaters are released untreated from sewage networks to water bodies, which leads to excess nutrient strain, causing eutrophication. This reduces oxygen levels in water, leading in severe cases even to fish deaths. Algal blooms, a common consequence of eutrophicated waters, tend to contain bacteria which can be harmful for humans as well, and therefore the use of severely eutrophicated waters is often restricted by authorities. (EPA. Nutrient Pollution. 2016) Even if the nutrients would be neutralized before releasing them back to water bodies, the waste water treatment systems most often lose the valuable nutrients instead of capturing them for further use. (World Bank Group. 2016.)

Urine has a lot of potential in nutrient recycling, and further research and development is needed in urine diversion and urine nutrient recovery technologies. Also cultural attitude shifts related to human waste reuse has to take place before any major transformations in this matter can happen. Related to an ongoing project of Tampere University of Applied Sciences called Biourea – Innovative fertiliser product in closed nutrient cycle implementation 2015-2016, which focuses on studying these respective urine fertilizing properties, a small-scale struvite reactor has been built in the university laboratory premises. The vision is that in the future, dry urinals and dry toilets could replace the currently most often used chemical toilets as mass events' sanitation solution, where nutrients could be captured from the waste with simple technology. (Global Dry Toilet Association of Finland. BIOUREA.) The struvite reactor used in this study is low-cost, low-tech, but a sufficient model for preliminary tests.

This thesis focuses on studying the reject water of the struvite production process. It has been studied that in struvite production process, phosphorous from the urine can be efficiently recovered. Nitrogen, on the other hand, will not be captured in struvite in large quantities and will mostly remain in the effluent of the process. (EAWAG. 2015. 14) In excess, nitrogen is a main pollutant of our water bodies, a necessary nutrient for all plant growth and in a readily available form for plants' use in urine (Schönning, C. 26). Therefore, studying methods to capture the nitrogen and return it back in nutrient cycle from the effluent of struvite production process is a much needed technology.

1.1. Aims

The aim of the struvite project conducted in TAMK is to optimize struvite production for small scale production and test different methods for capturing nitrogen from the effluent.

The main aim of this research is to study different adsorption methods of N recovery from the reject water of struvite production. The availability of the adsorbent in question was an important factor when considering which adsorbents to test, because it is important that the substance is easily accessible and affordable to make the nutrient capturing process viable. The adsorbent materials chosen for this study are:

- halloysite mixed with light expanded clay aggregate, LECA, pebbles
- charcoal
- willow biochar

The indicators in nutrient removal will be Total Nitrogen, TN, which will be measured of the influent (reject water) and effluent - before and after the adsorption process to find out how much was adsorbed in the material. As already mentioned, the presumption is that most of the P has been captured in the struvite and partly N and micronutrients will be left in the effluent. Therefore, the focus will be on nitrogen, and tests will be optimized on the direction which seem the most efficient and promising in N capture. Experimental setup and duration of the tests were adjusted according to the results of each test run.

2 THEORETICAL BACKGROUND

2.1 Introduction to nutrients and their properties

Today's agriculture relies heavily on external nutrients to reach optimal crop yields. It is also needed, because the UN estimates, that an increase of 70 % in global food production has to be achieved by year 2050 to be able to feed the constantly growing population. To reach this, the food production in developing countries has to grow by 50 % (UNFPA. 2015).

The essential primary nutrients for all plant growth are nitrogen (N), phosphorous (P) and potassium (K). These main nutrients are needed in higher quantities than the rest of the essential nutrients acquired from the soil. Thus mostly N-P-K-labelled fertilisers are used in agriculture. The management of the primary nutrients is especially important for optimal plant growth. (Miransari, M. 2012. 237-238.)

The primary nutrients combined with intermediate nutrients sulphur, magnesium and calcium form the category macronutrients. In addition to these six macronutrients, also micronutrients are required for all plant growth, but in very small amounts. These micronutrients are iron, boron, manganese, molybdenum, copper and zinc. Even though some nutrients are needed in a larger amount than the others, it should not be understood as an order of importance. A lack of any nutrient, be it macro- or micronutrient, restricts plant growth and prohibits it from reaching maximum yield. (Miransari, M. 2012. 237-238.)

A nutrient cycle is a loop of nutrients that circle in nature. The nutrients are uptaken from soil by plants and returned to the soil and air when decomposition of plant matter takes place. This is nutrient cycle in its simplest form. Today, the human-influenced nutrient cycles are less rarely closed loops; more often they concern humans using the nutrients uptaken by plants from soils by consuming the plant or using it as cattle feed. Instead of returning the nutrients back to soils, they end up in water bodies, where they become in excess and cause versatile environmental problems, such as eutrophication and oxygen depletion of waters. Meanwhile, the soil nutrient content keeps on reducing globally which creates poorer soils and smaller crops due to the lack of soil's own nutri-

ents. (Conradin, K. 2010) By upkeeping closed nutrient cycles, the natural nutrient balance of the soil can be supported and optimal crop yields achieved while minimizing the need for external fertilizers. (Food Industry Watch. Environmental Soil Science. 2010.)

2.2 Nitrogen

Nitrogen, N, is the fifth most abundant element on Earth. 78 % of air consists of gaseous nitrogen, N_2. In soil, nitrogen fixing bacteria uptake N_2 from air (fixation) and turn it into ammonia, NH_3 and ammonium, NH_4^+. This is called ammonification. Soil bacteria then turn the ammonia and ammonium first to nitrite, NO_2^- , and then to nitrate, NO_3^- , in a process called nitrification. A part of the ammonium volatilizes back to N_2. The nitrogen partly returns to the soil with decomposing organic matter, by nitrogen fixing plants and commercial fertilizer use. This natural cycle is called the nitrogen cycle, as described in IMAGE 1 below. (Lenntech.com. 2016)

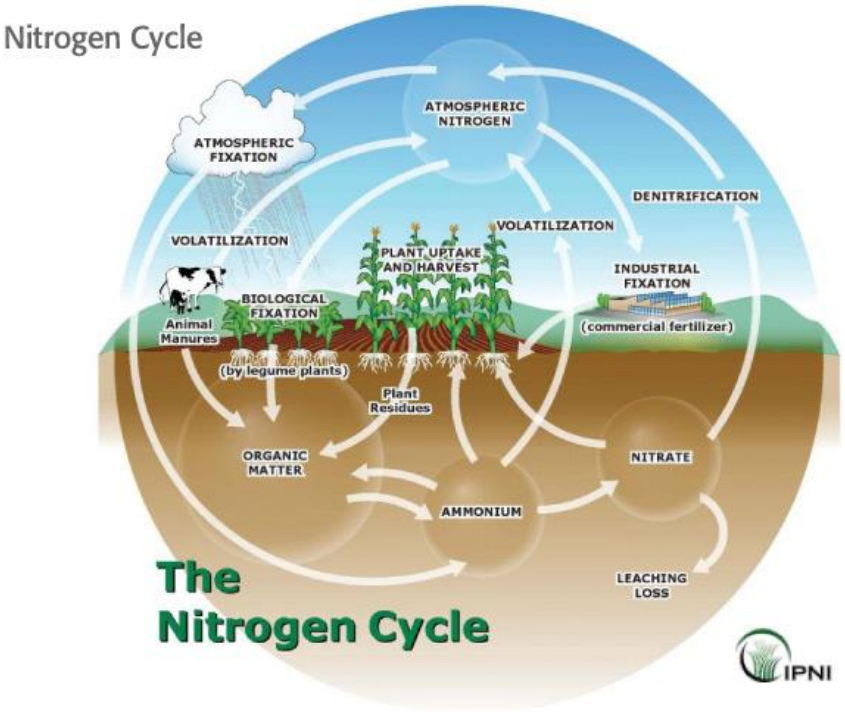


IMAGE 1. The Nitrogen Cycle. (Cropnutrition.com)

Nitrate is plants' main source of nitrogen and nitrate fertilisers are heavily used for that reason. Nitrogen in water appears as ammonia, NH_3^-, nitrite NH_2^-, nitrate NH_3^- , ammonium NH_4^+ and atmospheric nitrogen N_2. Most plants cannot feed on atmospheric nitrogen, but some algae can. Inorganic nitrogen compounds are usable nutrient for algae

in general, most commonly nitrates and ammonium. (Niinimäki, J. & Penttinen, K. 2014. 17)

Nitrate is one of the most water soluble inorganic compounds and can cause heavy pollution of ground water (Wright, J. 2014. 328). A connection between the use of nitrate fertilisers and the amount of nitrate in natural waters has been found (Hester, R.E., & Harrison, R.M. 1996. 1). In itself nitrate is not harmful for humans, but can convert to the toxic NO_2^- in infant and some animals' stomachs. There, it causes for example the so called 'blue baby syndrome', *methaemoglobinaemia*, which reduces the amount of oxygen carried by the child's blood and can lead to lethality by suffocation. Still today the 'blue baby syndrome' is a problem in areas where drinking water is mainly gotten from dwells. (Wright. 2014. 328). Research also suggests, that there is a connection between adult stomach cancer and the amount of nitrate in natural waters (Hester & Harrison. 1996. 2).

In addition to ground water pollution, nitrates cause eutrophication of water bodies when in excess. Increased amount of nitrates in water encourages extra growth of water organisms, such as algae, causing visible algal blooms. When algae die, it is decomposed by bacteria which use oxygen to do so, and therefore the process can cause oxygen depletion in waters and lead even to fish deaths. (Hester & Harrison. 1996. 5)

2.3 Phosphorous

Phosphorous, P, is another crucial nutrient for plant growth. Ii is most often the limiting nutrient in water bodies. Therefore, if there is too little P available, it restricts plant growth. In nature, phosphorous can appear as soluble phosphate phosphorous and particle-like phosphorous attached to solid matter. These two forms together are called total phosphorous, TP. Phosphorous is mined from mineral phosphorous, and in addition to fertilizer use, phosphates are used today especially in detergents. (Niinimäki & Penttinen. 2014. 13-15.)

Phosphate fertilizers are heavily used in agriculture, because phosphorous is often also a limiting nutrient and it is important that the plants receive enough of it. Phosphates are slowly soluble, which reduces leaching to the environment. Therefore, particulate phosphorous may have more negative environmental impacts than phosphates, because when

introduced to water bodies, up to 65 % of the solid phosphorous may be available as algae feed and therefore accelerate eutrophication. (Niinimäki & Penttinen. 2014. 16-17.)

In water bodies, phosphorous is usually bound in the sediment. P leaching is very dependent on the pH of water because the higher the pH, the more phosphorous is released to waters. In heavily eutrophicated waters the pH may be higher than 9, which creates an unwanted cycle, as more P is then released from the sediments, which feeds algae and accelerates eutrophication even further. (Niinimäki & Penttinen. 2014. 16.)

2.4 Nutrient removal in waste water purification process

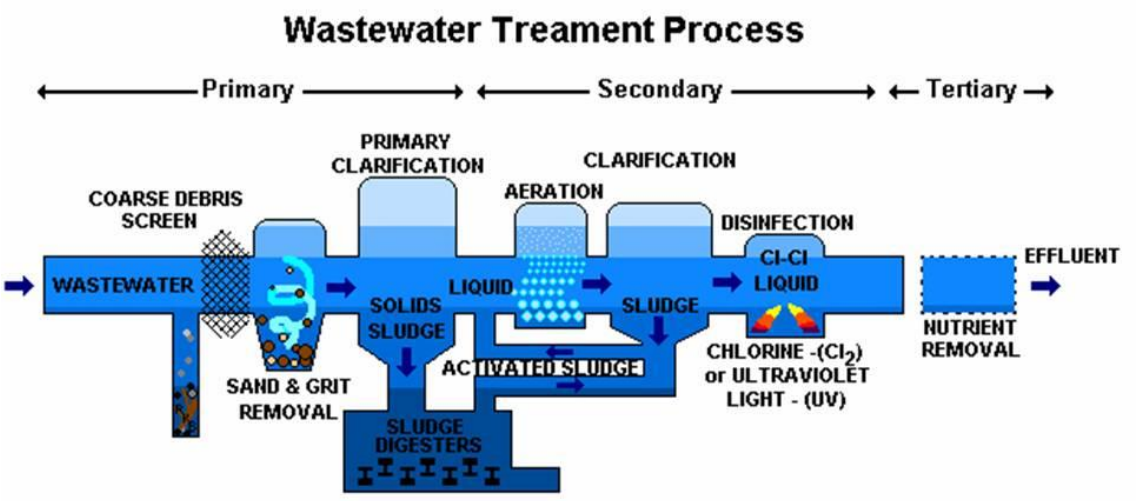


IMAGE 2. Wastewater Treatment Process. (The Water Treatments)

In municipal waste water treatment facilities, the aim is to reduce the amount of pollutants and foreign objects in waters, and finally release the purified waters back to the nature. The process is described in IMAGE 1 above. Generally, the purification process has three stages, called primary, secondary, and tertiary phase. (Park, C. 2013) During the primary stage of the process, the coarse particles are removed, the secondary phase uses aerobic biological treatment in breaking down the remaining organic matter further, whereas at the third stage, microstraining is used to further purify the wastewater. The third stage is conducted when a really high standard for the purified water is required: not always, and for that reason it is also called the advanced stage. (Wright, J. 2014. 318-321)

In this traditional waste water purification process, the processes of nutrient removal is taking place as one of the last measures of the three-stage process. The methods that are usually used for nutrient removal from wastewaters in industrial scale are air stripping and aeration, denitrification and phosphate precipitation, of which the latter one is not used for nitrogen removal. (Wright, J. 2014. 321) Also other methods, which are in use to a varying extent, such as ion-exchange and adsorption, membrane processes, chemical oxidation and algae cultivation have been studied. (Viotti, P. & Gavasci, R.) Some of these methods which focus on nitrogen removal from wastewaters are presented here.

2.4.1 Air stripping

Air stripping utilizes mass transfer and volatile substances' transition between liquid and gaseous forms to change from water to air or vice versa. Air stripping is one of the most common ways of desorption, which refers to the capture of volatile substances from water to air. Removal of NH_3 can be achieved through gas-liquid equilibrium, where the gas is transferred from air to water until equilibrium is reached (Howe & al. 2012. 437-438.) Below the IMAGE 2 describes the process of air stripping in more detail.

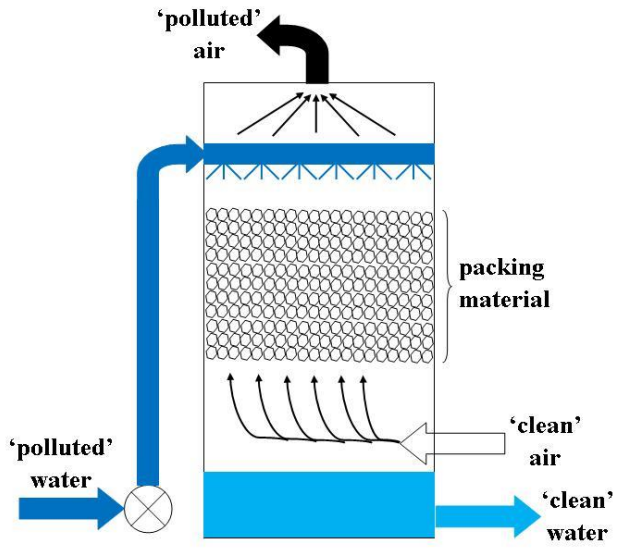


IMAGE 3. Air stipping process. (Aquatreat)

In nitrogen removal, the process is called ammonia stripping. It is used to convert ammonium ions, NH_4^+, to gaseous ammonia NH_3, which can be removed from waste waters by the process of bubbling air through the waste water. Ammonium is a highly wa-

ter soluble substance, and a high pH as well as warm temperatures are required to optimize ammonium volatilization to air and to prevent dissolving in the process water. The pH increase can be done by adding lime to the stripping process. The reaction is as follows:

$$NH4^{+} + OH^{-} \leftrightarrow NH_4OH \leftrightarrow NH_3 + H_2O \quad (1)$$

(O'Farrell & al. 1972)

2.4.2 Adsorption and Ion Exchange

Adsorption of nutrients is based on the removal of the particles from water by adsorbing them to the surface of the solid, the adsorbent material. It is a common procedure in drinking water treatment in removing certain pollutants. The most common adsorbent is activated carbon. Ion exchange refers to a two-way procedure between water and substance whereas in adsorption it is only the surface of the substance that is attracting particles and there is no transfer to the other direction. A key feature in adsorbents is a porous structure which creates a lot of inner surface area where the particles can attach to. (Howe & al 2012. 369-371.)

Charcoal, especially activated carbon, and some minerals have shown potential in nutrient capture. In the following the materials used as adsorbent test materials in this study are described in more detail.

Halloysite is a clay mineral with a chemical formula $Al_2Si_2O_5(OH)_2 \cdot n\ H_2O$. Halloysite is made up of fine particles with a high absorption capacity towards certain substances, such as heavy metals. The permeability for liquids is low due to a tubular structure, which results to a huge surface area. This property is excellent in nutrient adsorption point of view, and the reason for choosing halloysite for a test material for this research as well. As a result of a study by Liuskanto (2015.), which focused on halloysite use in nutrient and moisture retention in soils, halloysite showed potential in nutrient (phosphate, nitrate and potassium) capture. (Liuskanto. 2015. 17-31) The main problem with the halloysite as an adsorbent is the fact that it creates easily a thick, non-penetrable layer of particles and therefore has to be mixed with another substance to allow water flow between the particles.

Industrial applications for halloysite include its use as a coagulant in wastewater purification, as a catalyst, nanocomposite technologies as well as environmental remediation. (Rawtani, D. & Agrawal, Y. K. 2012. 1)

PICTURE 1. Halloysite (on the right) and light expanded clay aggregate, LECA, pebbles (on the left).

Charcoal is a substance which is created from animal or plant material (for example wood or bones) by burning it in conditions where oxygen levels are low. The result is a highly porous charred material. (Merriam-Webster dictionary) In different studies, charcoal has shown potential in nutrient and water capture. Due to its porous structure, it has a huge surface area in a small amount. Charcoal can be activated to create a substance with the highest known physical adsorption forces and a surface area of up to 1500 m^2 / g, called activated charcoal or activated carbon. In charcoal adsorbance research, activated charcoal is of main interest today. (Shoba, J.)

A fertilizing practice called Terra Preta, was used already among the native Amazonians up to 2500 years ago. In Terra Preta method, charcoal is used to cover human excreta and bind the nutrients to avoid leaching, sterilize the excreta and keep the environment hygienic. Finally mixing of the nutrient-rich charcoal with crop soil was done. The fertility of the Terra Preta soil has been measured to be up to 500 times higher than the fertility of a natural soil of the same area, which gives an indication on the fact that the characteristics of charcoal on nutrient adsorption have been known for a long time. (Schmidt, H.-P. & Wilson, K. 2014)

Willow is a tree which grows extremely fast in nature – up to 3 cm a day in optimal conditions. Due to the rapid growth, the structure of willow is very porous. Willow is native all over Finland and is therefore an excellent source of supply for biochar in Finland. (Pajupojat) Biochar refers to biomass which has been artificially created by pyrolysis in temperatures under 700 degrees Celsius, with a low oxygen level. (Granatstein, D. & al. 2009)

The research on biochar is blooming globally. Its many possible applications due to its excellent adsorption properties interest scientists around the world. According to the Biochar journal, in recent environmental research, biochar has been found promising in for example many applications for decontamination of water, soil and air. Carbon sequestration, waste water treatment, air purification and drinking water filtration are just a few examples on the multiple possibilities of biochar that are based on the porous structure offering excellent adsorption properties. (Schmidt, H.-P. & Wilson, K. 2014)

2.4.3 Reverse Osmosis

Reverse osmosis (RO) is a water purification technique which uses a semi-permeable membrane technology to separate dissolved solids from the water. The principle is, that the membrane is permeable to certain particles while it is non-permeable to others. It is a constant process where the influx is pressurised, some water passes through the membrane while a concentrated reject stream that cannot pass the membrane is created and directed elsewhere. (Howe & al 2012. 327-328)

According to Garud, R.M., Kore, S. V., Kore, V. S. & Kulkarni, G. S. (2011) reverse osmosis procedure is an alternative method to traditional wastewater purification methods. For example, organic contaminants, colour, dissolved solids as well as nitrates and bacteria can be removed with RO membrane technology. Even drinking water has been produced from waste water purification with RO technology. As separation is achieved with no state change, thermal energy use nor chemicals, RO technology is an e
nergy efficient alternative to be used in nutrient recovery processes. (Garud & al 2011. 233-236)

2.4.4 Algae Cultivation

Algae cultivation is one of the upcoming ways of wastewater purification that have been studied in recent years. Cai & al discuss in their paper (2013) that certain type of algae has been found to have a high capacity for nutrients and heavy metal recovery. If these types of algae are managed to be used for biofuel production by feeding them with key nutrients, such as nitrogen, the nutrients are removed from the wastewaters. This also leads to a reduced growth of unwanted phytoplankton. (Cai & al. 2013)

According to the abstract book of a UNESCO First International seminar on Algal Technologies for Wastewater Treatment and Resource Recovery (2015), algae has potential to recover nutrients through both aerobic and anaerobic digestion processes from waste waters. A study, which presented algae cultivation for urine nutrient recovery stated that the respective algae cultivation method provided up to 50 % N and 75% P recovery rates from urine. (Tuantek, K. & al. 2013)

2.5 Fertilisers

Fertilisers are divided in two main groups: inorganic and organic fertilisers. The organic group contains fertilisers such as manure and compost, when inorganic fertilisers, also known as chemical fertilisers, can come in any form that is suited for the purpose. Usually organic fertilisers tend to be less convenient in forms of transport and use of space, as they tend to take more space in transport and storing. The inorganic fertilisers are therefore often more convenient for transport as well as having the nutrients in a readily available form for the plants' use. (Refsgaard, K. & al. 2005. p. 2-4)

2.5.1 Urine as a fertiliser

According to Refsgaard et al., human urine contains 88 % of the nitrogen produced by humans, so it is a very nutrient-rich substance. In addition to this, it has an even higher nutrient content than animal urine, and saves costs which makes it an excellent source for a recycled nitrogen-rich fertiliser. (Refsgaard & al. 2005. 10) In addition to the macronutrients nitrogen, phosphorous, potassium and sulphur, urine contains most of the micronutrients in smaller fractions. The traditional fertilisers can often be considered to

be replaced by the nitrogen-rich urine as it normally produces equally high crop yields. (Richert, A. & al. 2010. 9)

Source separation is an effective way of urine collection, which also keeps the urine pathogen-free, as most of the pathogens are in the feaecal matter. There are certain precautions which are required for safe urine use as fertilizer. Generally, urine should be spread on soil and not on the plant itself. Proper hygiene should be taken care of while spreading. (Richert, A. & al. 2010. 9-10) WHO guidelines state that urine fertilizing can be recommended for all single household crops, as long as one month safe barrier is kept between the fertilization and harvesting. 6 months storage time of urine in ambient temperature (20 degrees Celsius) removes pathogens from urine and after this period of time, the urine can be used for fertilization of all crops. (WHO. 2006. xvii-xviii)

2.5.2 Struvite Production

Struvite is a mineral with a chemical formula of ($MgNH_4PO_4 * 6H_2O$). The basic method of struvite production is a fairly simple chemical procedure between urine and an added salt, such as magnesium chloride or magnesium oxide. The precipitation of struvite crystals starts to occur after the addition of salt, which is enforced by mixing of the urine for a defined period of time. The precipitate is then gathered separate from the effluent, and dried. The end result is grey powder with a high phosphorous content, which can be diluted in water and used as a phosphorous fertiliser. (VUNA Final Report. 2015. 14)

By today, struvite production has been stated to be a functional method for phosphorous recovery from urine and waste waters. Through struvite production, up to 99 % efficiency in phosphorous recovery has been reached, but it is not an efficient method in nitrogen removal. It has been studied (VUNA Final Report. 2015. 14) that nitrogen is mostly not precipitated in the struvite, but stays in the effluent of the process.

3 METHODS

This study was started by designing the first version of experimental setup (PICTURE 2). Many adjustments and optimization of the process was needed before the experimental system was functional. At first, funnels were placed in the holes of a funnel holder as seen in the picture. Similar 2 l bottles were collected, holes drilled in the caps and silicone used to attach a piece of hose to each cap. The bottles were initially whole with a screw tightened in the top of them to adjust air flow and to prevent bubbling, and the adsorbents were placed in a filter in the funnel below the bottle. Clamps were attached on burette holders on top of the funnels, and the bottles attached to the clamps upside down. Then by adjusting the flow rate of the effluent from the bottle to the beaker under the funnel, approximately 900 mL of effluent was let to flow through the adsorbent into the beaker under it. Nitrogen concentration of the struvite process reject water was then analysed before and after the adsorption treatment.

Picture 2. The initial test set-up.

After the first material trial with this method, it was realized that soaking the absorbents in the effluent for a defined period of time might work better. At this phase the resi-

dence times were decided to be 2, 4 and 6 hours. The bottles were cut in half for this purpose, so the absorbent in question could be placed in the bottle. A small paper filter was cut to fit the bottle cap and placed there to prevent solid particles from entering the effluent. After doing one experiment like this, as seen in PICTURE 3 it was realized that the lighter substances were floating on the top of the reject water and therefore the maximum absorption capacity could not be reached.

PICTURE 3. Charcoal soaking in the samples, partly floating on the top.

For a third trial, the materials were placed a small, thin bag which would hold the absorbents in place and prevent floating of them on top of the liquid, after which the effluent was poured on top.

PICTURE 4**.** Third trial. Adsorbents soaking in the reject water in a thin fabric bag.

All of the test subjects were also tested for leaching capacity to make sure they will not leach nitrogen themselves and distort the results. For this, a 0,13 mg/L sodium hydroxide solution, where the test subjects were to be staying overnight, was prepared. It was calculated that with a concentration of 0,13 mg / L NaOH, the pH could be adjusted to approximately pH 8,5 – 9, which is the pH of the urine and struvite precipitate effluent, which would indicate the leaching capacity of each substance. The 0,13 mg / L NaOH mixture was prepared by two 1/100 dilutions for maximum accuracy: first there was 1,3 g / L NaOH, which was mixed 1/100 with deionized water to 13 mg / L. Then this was once more diluted 1/100 to form 0,13 mg / L NaOH. NaOH was poured on a beaker and placed on a magnetic stirrer for approximately 20 hours with a material sample. A parafilm was used to cover the top to avoid evaporation. 50 mL of the mixture for 1 g of halloysite and 500 mL of it for 10 g of LECA was used.

3.1 Halloysite-LECA-mixture

Halloysite and light expanded clay aggregate, LECA, mixture was tested first as seen in PICTURE 1. Two different experiments were conducted, where the variables were the filter (coffee filters and fabric filters) and the ratio between halloysite and LECA. Mass ratios (LECA:halloysite) were 1:1 (15g each) and 1:2 (10 g LECA and 20 g halloysite) .

The reason why LECA was mixed with was that even though as a mineral it has good nutrient absorption capabilities it was expected to form a close to non-penetrable surface and that the flow rate would be extremely low. (Liuskanto. 2015. 17.)

PICTURE 5**.** Trial 1: Halloysite and LECA pebbles in a filter through which the struvite filtrate was let.

Total of 30 grams of the test material was placed in a test filter in the funnel, and approximately 900 mL of filtrate was measured in a bottle above the funnel. Triplicate tests were done on each treatment. A clamp was used to manage the water flow and prevent overflowing of the funnel. After all the water had flown through to a beaker underneath the funnel, the sample beaker was placed on a magnetic stirrer and mixed properly for approximately 15 minutes. Samples were taken from the stirred filtrate and also from influent (reject water after struvite process) to a volumetric flask where a ratio of 1/500 sample on ion-exchanged water was prepared. This was done to set the amount of nitrogen and phosphorous on the measuring range of the HACH-device where the amounts of P and N have to be over 1 mg / L for an accurate reading. HACH-device was used to do the final analysis of TP and TN amounts. Each adsorbent mixture test was done as triplicate for recording the variation between samples. Part of the halloysite-LECA samples were not tested with HACH method but with Kjeldahl Total Nitrogen method. Three batches of the struvite reject water (influent) was tested on random and reject water from the same batches were used for the rest of the tests to have directly comparable values.

3.1.1 Total Kjeldahl Nitrogen

The Total Kjeldahl Nitrogen was determined based on the instructions booklet Nitrogen Determination according to Kjeldahl by R. Hoegger (1998). The effluent tested, was diluted to 1/10 with ion-exchanged water as opposed to the 1/500 dilution made for the HACH-device. Sometimes the sample size was less than required 50 ml, but then the exact sample size was written down and taken into account in the FORMULA 1 presented before. Also the concentration of the H_2SO_4 used in the titration was 0.05 mol. Otherwise the procedure followed the process presented by Hoegger. There are two major parts of the Kjeldahl procedure: the digestion and distillation, which can be seen in PICTURE 4 and 5 below.

3.1.2 Determination of nitrogen content

Total Nitrogen is the total amount of nitrogen in the sample; a combination of NH_2^-, NH_3, and NH_3^+ as well as organically bonded nitrogen. Two methods can be used for determining the TN: HACH spectrophotometer and Kjeldahl method. Both methods are based on the hydrolysis of all forms of nitrogen to ammonia, NH_4^+. In Kjeldahl method, an acid titration is performed and based on the consumption of acid, and the following FORMULA 1, the amount of TN in the sample can be determined. In analysis, HACH device uses the principles of spectrophotometry: it detects the unique spectra of an element, in this case N, and determines the amount of it in the studied sample.

The following formula 1 will be used to determine the amount of Total Kjeldahl Nitrogen from the samples.

$$x = \frac{(V_1 - V_{BI}) \cdot c \cdot f \cdot M(N) \cdot 1000}{V} \quad (2)$$

where:

x = total nitrogen concentration of the sample

V1 = consumption of acid in titration (mL)

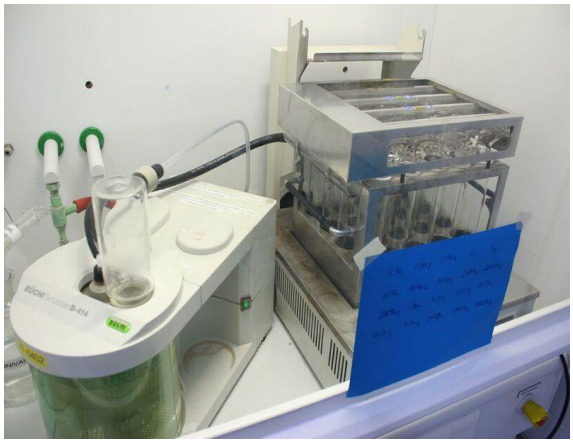
VBI = consumption of acid in blank reading determination (mL)

c = concentration of sulphuric acid (here: 0.05 mol/ L)

f = factor of acid (here: 2)

M (N) = molar mass of nitrogen (14 g/ mol)

V = original sample volume (mL) (Hoegger, R. 1998)



PICTURE 6. Kjeldahl digestion device and scrubber.

PICTURE 7. Kjeldahl distillation device

3.2 Charcoal

For another test round charcoal was tested. At first it was blended very fine and sieved, but it was realized that the particles were really difficult to deal with because the fine charcoal powder blocked all filters and was difficult to test. Therefore, whole charcoal pieces were tested. 30 g of charcoal was placed in the bottles in pieces and 900 mL of struvite effluent was poured on top, as seen already in PICTURE 4 in page 18. Before, the effluent had been mixed carefully in the canister it was taken from. The caps of the bottles had been insulated this time with a paper filter. The urine was let to soak in the

bottle for a determined amount of time and then the clamps around the hoses were opened and filtrate released to beakers. Afterwards the mixtures were still mixed on a magnetic stirrer, 3 samples of each were taken and 1/10 dilutions prepared for TN testing with the Kjeldahl method. Different residence times of struvite filtrate was tested: 2, 4 and 6 hours. There were three different batches of effluent tested, each in triplicate.

It can be seen in the previous PICTURE 4 in page 18 that the charcoal pieces were floating at the top as it is such a lightweight material, and the following tests were decided to be conducted with a thin bag to prevent floating. After the soaking time of 2, 4 and 6 hours had ended, the struvite filtrate was released in a beaker below the funnel, stirred on a magnetic stirrer and triplicate samples of each were stored for Total Kjeldahl Nitrogen analysis to be conducted later on.

It was also tested if there was any ion exchange. This was done by adjusting the pH of the solution close to neutral. Sulphuric acid was used to adjust the struvite filtrate pH to 7 ± 0,05 on another set of struvite effluent samples. The original pH of the samples was measured to be approximately 8,5. After this the samples were mixed on a magnetic stirrer and acid added until a desired pH was reached. After that the test of 2 and 4 hour residence times was repeated as presented previously. Due to restricted space in the Kjeldahl digester and the fact that it takes two working days to do all phases of Kjeldahl testing, it was decided that all of the samples were not done in triplicate. This was also acceptable because the sample results had been consistent and it was not expected that this would change. Therefore, biochar 4 h pH 8,5 samples and charcoal 4 h pH 7 of the samples in the last test round were only done in duplicate.

Charcoal samples were also tested for leaching overnight (approximately 20 hours) by mixing them on a magnetic stirrer in 0,13 mg/L NaOH as described on page 18. For charcoal, 500 ml for 10 g of charcoal was used.

3.3 Willow biochar

The willow biochar was tested in a similar way to the charcoal test. The 6 hour samples were not conducted due to an indication of the previous results that the 6 h residence time would not increase the removal compared to the 4 h residence time. Time for the study was limited as well and had to be taken into account. The same effluents were

tested as with the charcoal, with and without pH modification to see whether there is a difference with the N capture for residence times of 2 and 4 hours. Some biochar samples were also done only in duplicate due to the reasons presented previously.

Also biochar was tested for leaching the same way as the previous samples. 10 g of biochar was measured on 500 mL of 0,13 mg / L NaOH and placed in a beaker on a magnetic stirrer for approximately 20 hours.

4 RESULTS

4.1 Halloysite & LECA-mixture

As seen in TABLE 1 and FIGURE 1 below, the removal rate of nitrogen in halloysite-LECA-pebble mixture is negative in all cases except for one sample. This means that in most cases, the amount of nitrogen was increasing in the samples. Two different filter types were tested, but it is unclear whether there was a difference in the removal rate due to the filter.

TABLE 1. Concentration of N in influent and effluent and the N removal rate of halloysite-LECA—pebbles mixture. Tests were conducted on two samples, and a mean value of triplicates is presented.

	INFLUENT N conc. (mg/ L)	EFFLUENT N concentration (mg/ L)	Reduction INFLUENT _ EFFLUENT N conc. (mg/ L)	Reduction INFLUENT - EFFLUENT N conc. (%)
Coffee filter 1:1, R1	2185,00	1088,33	1096,67	50,19
Coffee filter 1:1, R2	2185,00	3600	-1415,00	-64,76
Fabric filter 1:1, R1	2185,00	2743,33	-558,33	-25,55
Fabric filter 1:1, R2	2185,00	3113,33	-928,33	-42,49
Coffee filter 1:2, R1	2185,00	3000	-815,00	-37,30
Coffee filter 1:2, R2	2185,00	4540	-2355,00	-107,78
Fabric filter 1:2, R1	2185,00	3588,33	-1403,33	-64,23
Fabric filter 1:2, R2	2185,00	3047,5	-862,50	-39,47

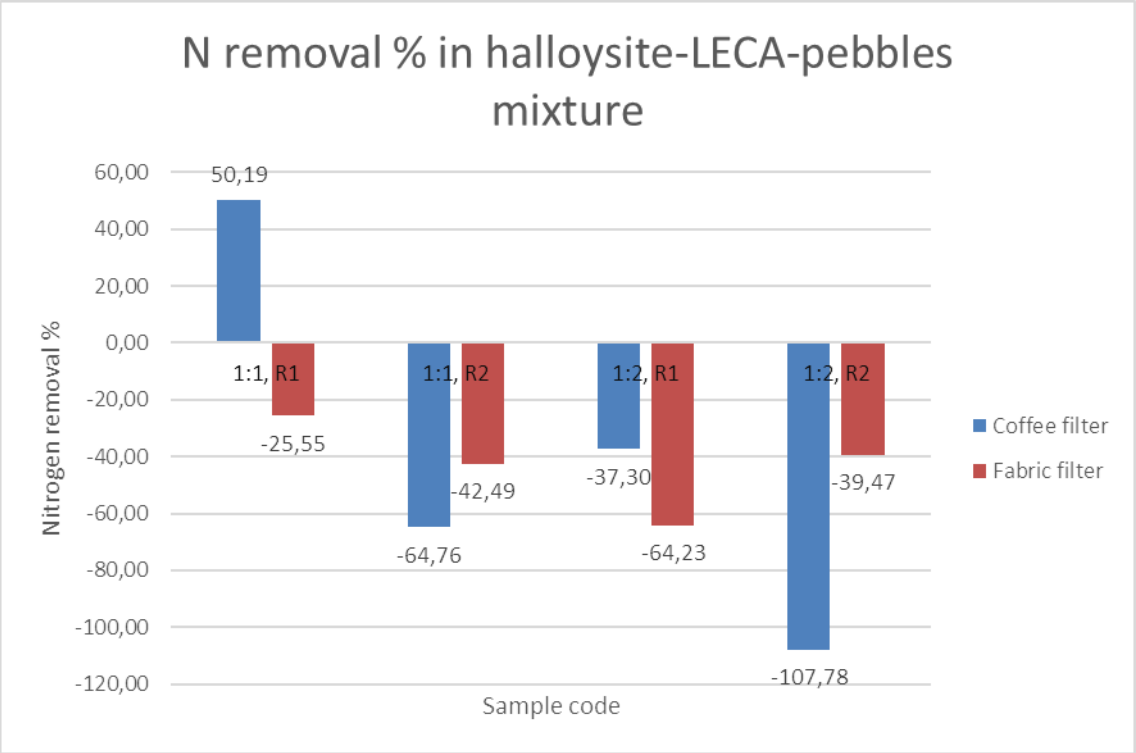


Figure 1. N removal rate in halloysite-LECA-pebble mixture. Variables were filter (coffee filter and fabric filter) and halloysite-LECA-ratio. Mean values of triplicates are presented.

The results in TABLE 2 below indicate, that nitrogen leaching from both halloysite and LECA-pebbles was significant when stirred overnight in a NaOH-mixture.

Table 2. The amount of TN leaching (mg of nitrogen / g of material) from halloysite and LECA-pebbles during an overnight mixing in pH 8.5 deionized water and 0,13 mg / L NaOH mixture.

	Max. amount of N leaching (mg N/ g material)	**Max amount of N leaching from absorbents in mixture 1:1 (mg)**	**Max amount of N leaching from absorbents in mixture 1:2 (mg)**
LECA-pebbles	24,52	367,73	245,15
Halloysite	195,30	2929,50	3906,00
TOTAL		3297,23	4151,15

4.2 Charcoal

TABLE 2 and FIGURE 2 below present the results of charcoal soaking in pH 8.5 effluent for 2, 4 and 6 hours. The results indicate that the lowest removal, actually an increase of N, has the 2 hour samples, where all of them have a negative removal rate. Four hour samples are the most efficient in N recovery, the highest removal rate being 17,75. The results are mean values of three replicates.

TABLE 3. Concentrations (mg / L) of N in pH 8.5 influent and effluent samples with 2, 4 and 6 h charcoal soaking. A1, A2 and A3 are batches of influent. Mean values of triplicates are presented.

	INFLUENT N concentration (mg/L)	EFFLUENT N concentration (mg/ L)	N removal (INFLUENT - EFFLUENT) (mg/L)	N removal % (INFLUENT - EFFLUENT)
A1, 2 h	3256,40	3773,65	-517,25	-15,88
A2, 2 h	3131,24	3758,16	-626,92	-20,02
A3, 2 h	3111,64	4240,50	-1128,86	-36,28
A1, 4 h	3131,24	2575,44	555,80	17,75
A2, 4 h	3131,24	2575,44	555,80	17,75
A3, 4 h	3111,64	3110,99	0,65	0,02
A1, 6 h	3256,40	2815,31	441,09	13,55
A2, 6 h	3131,24	2812,51	318,73	10,18
A3, 6 h	3111,64	2918,53	193,11	6,21

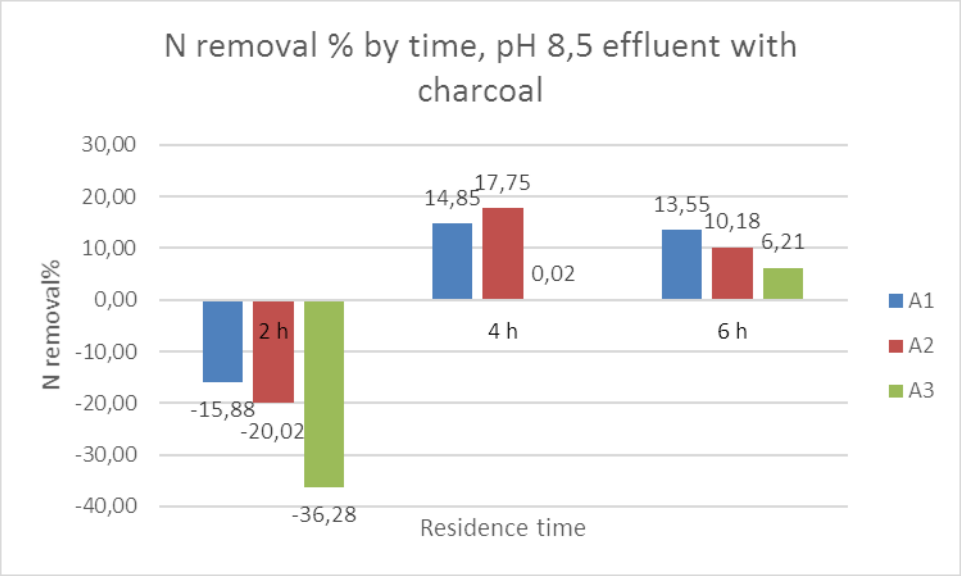


FIGURE 2. N removal % of pH 8.5 effluent, 2, 4 and 6 h residence times with charcoal. A1, A2 and A3 are the different batches of influent tested. Mean values of triplicates are presented.

In FIGURE 3 and TABLE 4 it can be seen that the N removal from 4 h soaking time samples in pH modified effluent (pH 7) is significantly lower than in the pH 8,5 samples (FIGURE 2).

TABLE 4. Concentration of N in charcoal influent and effluent, 4 hours, pH 7. A1, A2 and A3 are batches of influent tested. Mean values of duplicates are presented.

	INFLUENT N concentration (mg/L)	**EFFLUENT N concentration (mg/ L)**	**N removal (INFLUENT-EFFLUENT) (mg/L)**	**N removal % (INFLUENT - EFFLUENT)**
A1	3256,4	2890,16	366,24	11,25
A2	3131,24	3085,32	45,92	1,47
A3	3111,64	3162,88	-51,24	-1,65

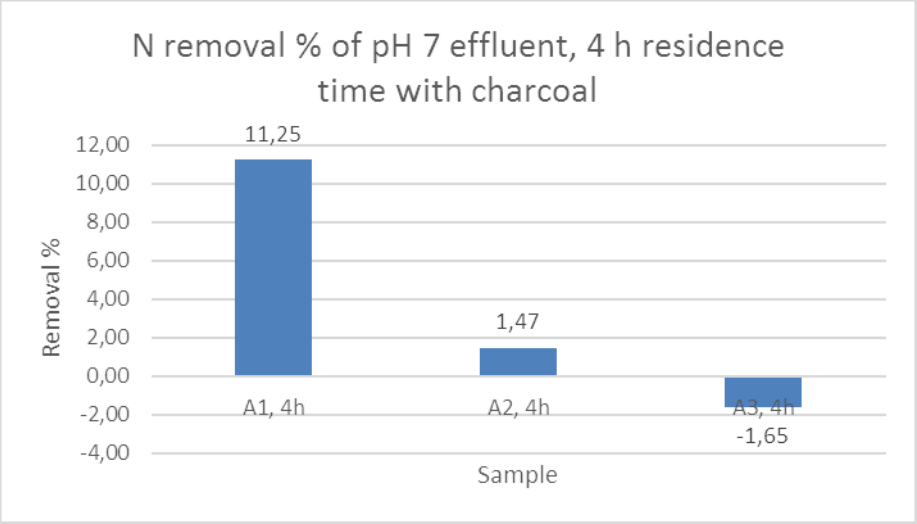


Figure 3. N removal rate of pH 7 effluent, 4 h residence time with charcoal. A1, A2 and A3 are the different batches of influent tested. Mean values of duplicates are presented.

Charcoal leaching test was also conducted to find out whether it can potentially leach N to the samples. The results showed no leaching in the 0,13 % NaOH solution where it was stirred overnight. Therefore, it can be concluded that there is no N leaching from charcoal.

4.3 Willow biochar

From TABLE 5 below the amount of initial and final TN in the 4 h willow biochar samples in original pH struvite precipitate reject waters can be seen. In FIGURE 4 the same removal can be seen graphically. The results show, that the maximum removal rate was 5,30 % for A1 sample. Compared to the charcoal samples where the highest removal rate was close to 18 %, the N removal with willow biochar 4 h residence time is not very high. With these biochar samples, only duplicates were taken.

TABLE 5. Concentration of N in willow biochar influent and effluent, 4 hours, pH 8,5. A1, A2 and A3 are batches of influent tested. Mean values of duplicates are presented.

	INFLUENT N concentration (mg/L)	EFFLUENT N concentration (mg/ L)	N removal (INFLU-ENT-EFFLUENT) (mg/L)	N removal % (INFLUENT-EFFLUENT)
A1	3256,40	3084,20	172,20	5,30
A2	3131,24	3116,12	15,12	0,48
A3	3111,64	3059,28	52,36	1,68

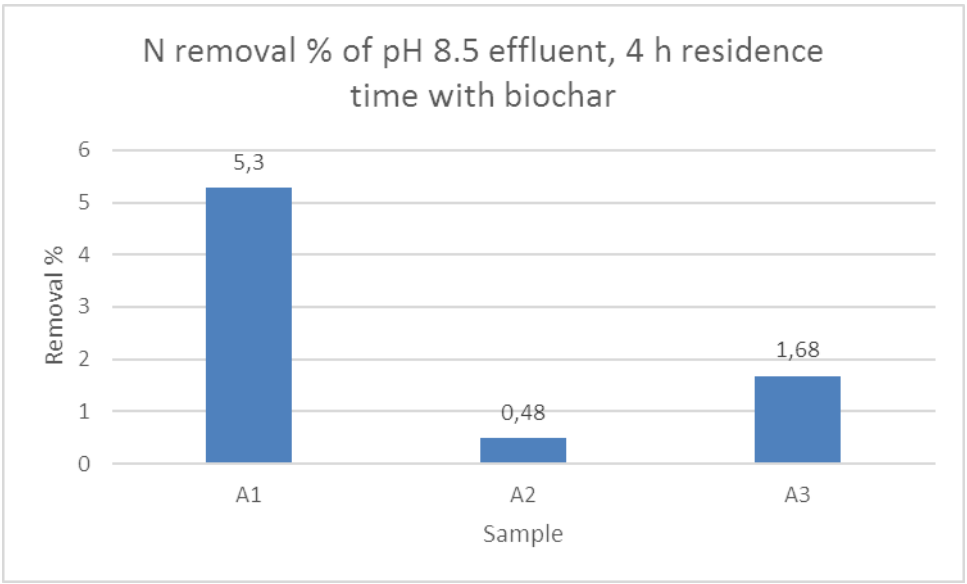


Figure 4. N removal rate of pH 8.5 effluent, 4 h residence time with biochar. A1, A2 and A3 are the different batches of influent tested. Mean values of duplicates are presented.

From FIGURE 5 below it can be seen that the removal rate of N in pH 7 biochar is low in both 2 and 4 h residence times in all samples. Still, it can also be seen that the 4 h residence time is more efficient in all samples. The biggest removal rate can be seen to

be 6,12 % in A1 sample. If we compare the results to the previous original pH results, it can be seen that the N reduction in the samples is linear: A1 has the highest removal rate in both pH's in 4 hour residence time, A2 very low and A3 something in between.

TABLE 6. Concentration of N in willow biochar influent and effluent and removal in 2 and 4 h samples in pH 7. A1, A2 and A3 are the different batches of influent tested. Mean values of triplicates are presented.

	INFLUENT N concentration (mg/L)	EFFLUENT N concentration (mg/ L)	N removal (EFFLUENT- INFLUENT) (mg/L)	N removal % (INFLUENT - EFFLUENT)
A1, 2h	3256,40	3168,39	88,01	2,70
A2, 2h	3131,24	3265,64	-134,40	-4,29
A3, 2h	3111,64	3159,61	-47,97	-1,54
A1, 4h	3256,40	3056,95	199,45	6,12
A2, 4h	3131,24	3118,92	12,32	0,39
A3, 4h	3111,64	2993,48	118,16	3,80

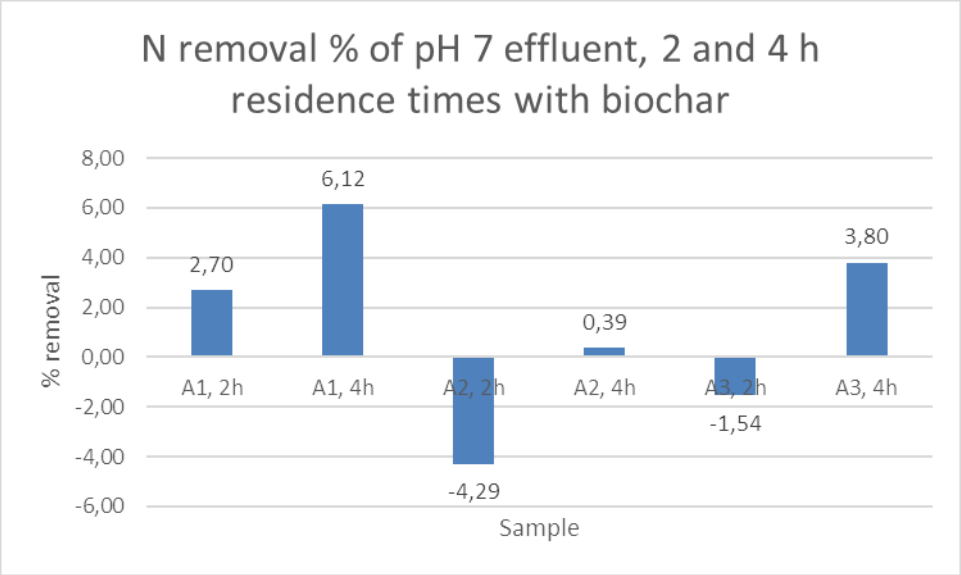


Figure 5. N removal rate of pH 7 effluent, 2 and 4 h residence times with biochar. A1, A2 and A3 are the different batches of influent tested. Mean values of triplicates are presented.

It was also tested, that biochar mixed overnight on a magnetic stirrer leached less than 1 mg of N in the sample, 0,98 mg exactly. Therefore, it can be concluded that biochar does not leach N in itself.

5 DISCUSSION

From the tested materials charcoal and willow biochar seemed most promising. When looking at the biochar and charcoal samples, it can be seen that the 2 h residence time N reduction results are always the lowest compared to 4 and 6 h residence times. The 4 h residence time samples seem to have the most adsorption, resulting in 18 % reduction of nitrogen in the effluent. This is not very high, but suggests that with increasing retention time the adsorption can be increased. It may be due to a statistical error that in some of the 6 h samples the removal is lower than in the 4 h samples. This could be solved by a larger amount of replicates. Looking back, the 6 h sampling should have been done until the end and not leave it out because of such a small amount of samples. The next and most easily taken step could be to increase the residence time of the adsorbent in the struvite reject water, and see whether there is a difference in the removal rate. Then the research could be led to the direction of the most promising residence time and any alterations that will be made, would be about other variables. Also the amount of adsorbent in the mixture could be studied in comparison to the amount of liquid. In this research, the amount was kept stable, but by increasing it could be studied whether there is any difference.

Another suggestion for improvement of the test methods includes stirring the adsorbent in the mixture instead of just letting it soak. That was done for the leaching tests and it seems that the water flow might have an impact in the nutrient removal rate Also, because it was already noticed that letting the effluent flow through the filter and pipe in the bottle cap did not work, as the small particles blocked the filter very easily, the test set-up could be drastically changed to simpler version. A large beaker with a bag of adsorbent in the effluent on a magnetic stirrer might work just as well and even better with the option of stirring it the whole residence time.

Biochar is a very promising material with low environmental impact as an adsorbent. Biochar in general can be made from a number of different materials, of which the one tested here, willow, is definitely worth testing more because of its rapid growth even in Finnish conditions, which make it unbeatable in environmental impacts compared to other trees. There are also other types of materials such as willow chips which can be

tested. In this study, however, charcoal indicated better adsorption results than biochar. This suggest, that charcoal should not be left out of the studied materials in the future.

There were a high number of variables in the test set-up and some of them may have had an impact on the removal even though they were not identified as study parameters. These are for example that during the soaking time of the adsorbent, there would have been evaporation of N from the open bottle tops. It is possible, that the filtrate that was taken for the testing from the canisters contained a different amount of nitrogen than what it was tested to contain beforehand, because of an improper homogenizing of it. The canisters were mixed well before taking a sample but it is possible that an improperly mixed sample was received. This way a distorted removal rate would have gotten.

The N leaching from the absorbents was tested, and the results indicated that there is no leaching from charcoal nor biochar. On the other hand, there was a lot of leaching from halloysite and LECA-pebbles. This was unexpected – halloysite is a mineral and should not contain any nutrients. Therefore, it is somewhat curious that results such as these were gotten. The leaching test was conducted overnight in a sealed container and therefore not even evaporation of water, which would have led to a higher concentration of N in the sample, should have been possible. Also contamination of the original halloysite and LECA-pebbles cannot be ruled out. They have been stored in original containers in a storage room for an unknown period of time, and it cannot be exactly known if a contamination would have happened. On the other hand, if the results of such a high amount of leaching from halloysite and the pebbles are true, that would give an indication of the leaching capacity and explain the increase in N in the samples to a certain extent.

It can be discussed, whether the testing of halloysite alone with the soaking method as was done with charcoal and biochar would have led to improved results with halloysite adsorption. Then using another material, LECA-pebbles, to increase the liquid flow rate through halloysite would have been avoided and one possible result distortion altogether ignored. However, as the test results indicated that the amount of nitrogen increased in the samples, according to this research there is no reason to continue the study with halloysite.

To increase the reliability of the research, more replicates and tests should have been done. With especially the halloysite tests the repeatability of the tests are not good in all cases: the results gotten from halloysite testing did show even significant deviation, with results on very different ends of the scale, as seen in APPENDIX 1. On the other hand, there were more halloysite tests conducted compared to the other experiments: two exactly similar treatments with three replicates. Also the fact that halloysite was the first material to be tested could have had an impact on the success of the testing because of lack of routine. Also different testing method, HACH, was used, compared to Kjeldahl in other samples.

6 CONCLUSIONS

New, effective nutrient recycling applications are needed around the world to tackle the global issue of water eutrophication and soil nutrient depletion. Urine has excellent potential as a recycled fertiliser for example through struvite production, where the phosphorous can be effectively separated. A more challenging task is the nitrogen and micronutrient capture and recovery from the reject water of struvite production process. This thesis aimed at coming up with ways of nitrogen recovery from the reject water. Adsorption to different materials were thus tested. The most promising materials found in this study were charcoal and willow biochar with at least 4 hour retention time with adsorption method.

This study was first of a kind, and thus required a lot of preliminary testing and work. As a result, however, there is now a functional experimental setup and two promising materials to be further tested – charcoal and also willow biochar is worth studying.
It can be concluded that the work succeeded in producing valuable know-how on nitrogen adsorption from the effluent of struvite production process with the tested materials.

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APPENDICES. Appendix 1. Halloysite experiment calculations and results

	Concentration N1 1/500 (mg/ L)	Concentration N2 1/500 (mg/ L)	Concentration N3 1/500 (mg/ L)	Average N concentration 1/500 N (mg/ L)	Undiluted N concentration (mg/ L)	Average final undiluted N conc. (mg/ L)	Initial effluent N conc. (mg/ L)	Reduction INITIAL-FINAL N conc. (mg/ L)	Reduction INITIAL-FINAL N conc. (%)
Coffee filter 1:1, R1	3	1,56	1,97	2,177	1088,33	2344,17	2185,00	-159,17	-7,28
Coffee filter 1:1, R2	1,74	7,96	11,9	7,2	3600				
Fabric filter 1:1, R1	4,22	7,45	4,79	5,49	2743,33	2928,33	2185,00	-743,33	-34,02
Fabric filter 1:1, R2	8,63	8,46	1,59	6,23	3113,33				
Coffee filter 1:2, R1	6,00	7,73	4,27	6	3000	3770,00	2185,00	-1585,00	-72,54
Coffee filter 1:2, R2	8,47	8,99	9,78	9,08	4540				
Fabric filter 1:2, R1	6,88	8,65	6,00	7,177	3588,33	3317,92	2185,00	-1132,92	-51,85
Fabric filter 1:2, R2	6,68	5,51		6,095	3047,5				

	Initial effluent N conc. (mg/ L)	Average final undiluted N conc. (mg/ L)	Difference initial - final conc. (mg/ L)	Reduction final - initial conc. (%)
Coffee filter 1:1	2185	2344,17	159,17	-7 %
Coffee filter 1:2	2185	3770,00	1585,00	-72,50 %
Fabric filter 1:1	2185	2928,33	743,33	-34 %
Fabric filter 1:2	2185	3317,92	1132,92	51,85 %

	Max. amount of N leaching (mg/ g)	Max amount of N leaching from absorbents in mixture 1:1 (mg)	Max amount of N leaching from absorbents in mixture 1:2 (mg)
LECA-pebbles	24,515	367,725	245,15
Halloysite	195,3	2929,5	3906
TOTAL		3297,225	4151,15

Appendix 2. Charcoal experiment calculations and results

Test: Original pH (approximately 8.5) charcoal, 2, 4 and 6 hours residence times. Diluted 1/10 for Kjeldahl analysis

	Acid consumption in titration (mg) R1	Acid consumption in titration (mg) R2	Acid consumption in titration (mg) R3	Average acid consumption in titration (mg)	FINAL diluted N conc. (mg/L)	FINAL undiluted N concentration (mg/ L)	INITIAL undiluted N concentration (mg/L)	N removal (INITIAL - FINAL) (mg/L)	N removal % (INITIAL - FINAL)
A1, 2 h	13,33	13,77	13,90	13,67	377,37	3773,65	3256,4	-517,25	-15,88
A1, 4 h	10,29	10,17	9,82	10,09	277,27	2772,75	3256,4	483,65	14,85
A1, 6 h	10,25	10,41	10,07	10,24	281,53	2815,31	3256,4	441,09	13,55
A2, 2 h	13,65	13,56	13,62	13,61	375,82	3758,16	3131,24	-626,92	-20,02
A2, 4 h	9,67	9,21	9,28	9,39	257,54	2575,44	3131,24	555,80	17,75
A2, 6 h	10,18	10,31	10,21	10,23	281,25	2812,51	3131,24	318,73	10,18
A3, 2 h	15,73	15,42	14,84	15,33	424,05	4240,51	3111,64	-1128,87	-36,28
A3, 4 h	11,38	11,50	11,02	11,30	311,10	3110,99	3111,64	0,65	0,02
A3, 6 h	10,38	10,92	10,53	10,61	291,85	2918,53	3111,64	193,11	6,21

Test: Charcoal, 4 h residence time, adjusted pH (pH 7 ± 0.05), diluted 1/10 for Kjeldahl analysis

	Original pH	Final pH	Acid consumption in titration (mg) R1	Acid consumption in titration (mg) R2	Average acid consumption in titration (mg)	FINAL diluted N conc. (mg/L)	FINAL undiluted N concentration (mg/ L)	INITIAL undiluted N concentration (mg/L)	N removal (INITIAL - FINAL) (mg/L)	N removal % (INITIAL - FINAL)
A1, 4h	**8,52**	**7,04**	9,89	11,13	10,51	289,02	2890,16	3256,4	366,24	11,25
A2, 4h	**8,49**	**7,01**	11,27	11,15	11,21	308,53	3085,32	3131,24	45,92	1,47
A3, 4h	**8,49**	**7,03**	11,36	11,61	11,48	316,29	3162,88	3111,64	-51,24	-1,65

Test: Leaching test 24 hours, 0,13 % NaOH and 30 g charcoal on a magnetic stirrer

	Average acid consumption in titration (mg)	Final N conc. (mg/L) in leachate
R1	0,17	
R2	0,17	
R3	0,158	
Av.	0,166	0

Appendix 3. Biochar experiment calculations and results

Test: Willow biochar, 2 and 4 hours, adjusted pH (pH 7 ± 0.05), diluted 1/10 for Kjeldahl analysis

	Original pH	Final pH	Acid consumption in titration (mg) R1	Acid consumption in titration (mg) R2	Acid consumption in titration (mg) R3	Average acid consumption in titration (mg)	FINAL diluted N conc. (mg/L)	FINAL undiluted N concentration (mg/L)	INITIAL undiluted N concentration (mg/L)	N removal (INITIAL - FINAL) (mg/L)	N removal % (INITIAL - FINAL)
A1, 2h	8,5	7,04	11,3	11,6	11,5	11,47	316,84	3168,39	3256,40	88,01	2,70
A1, 4h	8,5	7,04	11,2	10,7	11,3	11,07	305,69	3056,95	3256,40	199,45	6,12
A2, 2h	8,5	7,02	11,8	11,7	11,9	11,82	326,56	3265,64	3131,24	-134,40	-4,29
A2, 4h	8,5	7,02	11,2	11,2	11,5	11,30	311,89	3118,92	3131,24	12,32	0,39
A3, 2h	8,48	6,98	11,5	11,4	11,4	11,44	315,96	3159,61	3111,64	-47,97	-1,54
A3, 4h	4,48	6,98	11,1	11,2	10,2	10,85	299,35	2993,48	3111,64	118,16	3,80

Test: Willow biochar, 4 hours, original pH (approximately 8.5 pH), diluted 1/10 for Kjeldahl analysis

	Original pH	Final pH	Acid consumption in titration (mg) R1	Acid consumption in titration (mg) R2	Average acid consumption in titration (mg)	FINAL diluted N conc. (mg/L)	FINAL undiluted N concentration (mg/ L)	INITIAL undiluted N concentration (mg/L)	N removal (INITIAL - FINAL) (mg/L)	N removal % (INITIAL - FINAL)
A1	8,5	8,5	11,172	11,172	11,172	308,42	3084,2	3256,40	172,20	5,288048151
A2	8,5	8,5		11,286	11,286	311,612	3116,12	3131,24	15,12	0,482875794
A3	8,48	8,48	10,47	11,696	11,083	305,928	3059,28	3111,64	52,36	1,682713939

Test: Leaching test 24 hours, 0,13 % NaOH and 30 g biochar on a magnetic stirrer

	Average acid consumption in titration (mg)	Final N conc. (mg/L) in leachate
R1	0,158	
R2	0,19	
R3	0,322	
Average	0,223	0,98