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Taking advantage of autotrophic nitrogen removal: potassium and phosphorus recovery from municipal wastewater

Sara Johansson

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TAKING ADVANTAGE OF AUTOTROPHIC NITROGEN REMOVAL:

POTASSIUM AND PHOSPHORUS RECOVERY FROM MUNICIPAL WASTEWATER

DOCTORAL THESIS

SARA JOHANSSON
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DOCTORAL PROGRAMME IN WATER SCIENCE AND TECHNOLOGY

Supervisors: Dr. Jesús Colprim, Dr. Maël Ruscalleda, Dr. Bart Saerens

Tutor: Dr. Jesús Colprim

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Girona

To my friends and family who have supported me along the way

The history of men is reflected in the history of sewers
– Victor Hugo (1892) Les Misérables

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CERTIFICATE OF THESIS DIRECTION

Dr. Jesús Colprim, Dr. Maël Ruscalleda from the Laboratory of Chemical and Environmental Engineering (LEQUIA) of the University of Girona, and Dr. Bart Saerens from Aquafin,

DECLARE:

That this work, entitled 'Taking advantage of autotrophic nitrogen removal: Potassium and phosphorus recovery from municipal wastewater', presented by Sara Johansson to obtain the title of Doctor of Philosophy, has been carried out under our supervision and that it meets the requirements for an International Doctorate.

For all intents and purposes, we hereby sign this document.

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Girona,

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SUMMARY

Each year, millions of tons of mineral fertilizer are applied in agriculture. Despite large losses on the way between field and plate, municipal wastewater is a concentrate of the nutrients consumed by a society and a point source of nutrients to receiving water bodies. Conventional wastewater treatment has focused on the removal of nutrients to avoid detrimental environmental effects, but increasing awareness on the limited nature of the raw materials for mineral fertilizer is pushing for a shift from removal to recovery of nutrients at municipal wastewater treatment plants to decrease the dependence on imported raw material for mineral fertilizer production.

Within the wastewater treatment plant, digested sludge liquor (centrate) is a small stream rich in nutrients that is re-circulated to the entrance of the plant for treatment in the main line. During the past decade, two technologies have been implemented for the treatment of this stream in order to decrease the nutrient content and thus the load to the plant: struvite precipitation for phosphorus removal and recovery, and partial nitritation-anammox (PNA) as an energy-efficient alternative for nitrogen removal. However, the implications of coupling these two technologies has not been fully explored. In this PhD thesis, two routes taking advantage of autotrophic PNA for the recovery of nutrient-rich products that can be returned to soils are investigated.

Chapter 4.1 focuses on biologically induced precipitation occurring inside PNA granules. Unlike chemical precipitation of struvite, which is induced by addition of a magnesium source and where the pH is controlled either by CO_2 stripping through aeration or addition of a base, biologically induced precipitation is induced by pH and substrate gradients created by the physical and biochemical properties of the biomass.

Granules with a high inorganic content were harvested from a lab-scale PNA reactor fed with centrate, and characterized for chemical composition. Analysis by emission spectroscopy showed that the granules had a phosphate content of 36 wt% P_2O_5, similar to that of phosphate rock, and a Ca/P ratio close to the one of hydroxyapatite. Crystalline hydroxyapatite was accordingly confirmed by X-ray diffraction. Emission spectrometry further showed that the content of heavy metals complied with proposed EU limits for fertilizer, as well as requirements from the phosphorus industry.

Due to the high inorganic content of harvested granules, their removal does not interfere with demands for PNA sludge for inoculation purposes, nor with the bioactivity of the reactor, and harvest is easy due to gravitational settling. Because the mineral forms without the addition of chemicals it represents a novel alternative to phosphorus recovery from wastewater.

Chapter 4.2 investigates the recovery of potassium together with phosphorus in the form of potassium struvite, an analogue to the more commonly known ammonium struvite. Ammonium has a negative effect on the formation of potassium struvite and precipitation needs to be preceded by a nitrogen removal step. In this chapter PNA is suggested and proven to be a suitable technology for nitrogen removal prior to potassium struvite precipitation from centrate. Lab- and pilot-scale PNA reactors removed up to 85% of ammonium, which allowed for potassium struvite formation. Co-precipitation of ammonium struvite resulted in the recovery of a multi-nutrient product containing all three macronutrients N, P and K. Bicarbonate consumption by the autotrophic biomass reduced the alkalinity by up to 90%, which far surpasses the capacity for CO_2 stripping through aeration. PNA prior to struvite precipitation could therefore drastically lower alkali dosing for pH control.

Although commonly growth-limiting in terrestrial ecosystems, potassium is not considered to contribute to eutrophication and is therefore, unlike phosphorus and nitrogen, not regulated on

the European, nor on the national level. Consequently, the faith of potassium within wastewater treatment plants in not well-documented. Chapter 4.3 presents the results of a sampling campaign conducted over the sludge line of a Bio-P plant, with the aim to the map nutrient flows, especially potassium, in order to better understand where to best implement potassium recovery.

The results showed that the three macronutrients takes three distinctly different routes within the plant due to the characteristics of each compound. Potassium is a small ion that is easily leached, nitrogen can take many forms, including gaseous states, and phosphorus in the form of phosphate readily forms salts with a low solubility in water. It was estimated that from the daily load, 80% of the incoming potassium leaves the plant with the effluent while 85% of incoming phosphorus ends up in the sludge fraction and exit the plant through the biosolids. Incoming nitrogen is to 80% removed in the biological step and leaves the plant as nitrogen gas.A solids mass balance was used to calculate the flow of centrate to 198 m^3 d^{-1} (<1% of the incoming flow to the plant) and a daily flow of 49 $P\text{-}PO_4^{3-}$, 241 $N\text{-}NH_4^+$ and 85 kg K^+.

PNA today is successfully implemented as an energy-, carbon- and cost-efficient alternative for nitrogen removal in the treatment of centrate. This PhD dissertation strives to expand the view on what PNA granular sludge can do. The autotrophic nature of PNA sludge serves as a biological CO_2 stripper of high efficiency, while the biochemistry and physical properties of granular PNA sludge functions as a biological crystallizer. Taking advantage of autotrophic nitrogen removal can lead to both energy and chemicals savings while producing nutrient-rich compounds that can be returned to soils as fertilizer. Thus PNA can play an important role in the conversion of wastewater treatment plant into resource recovery facilities within the circular economy framework.

Furthermore the thesis hopes to broaden the discussion on nutrient recovery to go beyond phosphorus and nitrogen, to bring awareness to the current heavy dependency on imported minerals for fertilizer production and advocate a more sustainable food production and consumption system.

RESUM

Cada any l'agricultura aplica milions de tones de fertilitzants minerals als conreus. Malgrat les grans pèrdues de nutrients que es produeixen entre el camp i la taula, l’aigua residual concentra els nutrients consumits per la societat i esdevé una font important d’aquestes substàncies cap als medis receptors d’aigua. Per això els tractaments convencionals d’aigua residual fins ara s’han focalitzat en l’eliminació de nutrients per evitar-ne els efectes ambientals negatius. No obstant, aquests nutrients representen una font potencial de recursos reciclats i la necessitat de conscienciar sobre el caràcter finit de les matèries primeres ens aboca a un canvi de paradigma en les estacions depuradores d’aigües residuals (EDARs): cal passar de l’eliminació a la recuperació de nutrients.

En les EDARs l’efluent de la digestió de fangs, el “centrat”, és el corrent més ric en nutrients. En els darrers anys, s’han implementat dues tecnologies diferents per a tractar-lo de manera sostenible: la precipitació de l’estruvita per a recuperar fòsfor i la nitritació parcial-anammox (PNA) com a alternativa d’eliminació de nitrogen més eficient energèticament. No obstant això, les implicacions d’acoblar aquestes dues tecnologies encara no s’ha explorat del tot. En aquesta tesi doctoral s’han investigat dues rutes per aprofitar les possibilitats de la nitritació parcial-anammox autotròfica cares a la recuperació de nutrients.

El capítol 4.1 se centra en la precipitació biològica induïda que té lloc en els grànuls PNA. Els resultats obtinguts en un reactor PNA a escala laboratori alimentat amb centrat, demostren que es poden formar grànuls amb un alt contingut de matèria inorgànica, que presenta un percentatge de fòsfor molt similar al del fosfat natural (fonts minerals). Aquest producte recuperat pot ser considerat com a hidroxiapatita i el seu contingut en metalls pesants compleix tant la normativa europea per a fertilitzants com els requeriments de la indústria. La precipitació PNA va ser induïda per les propietats físiques i bioquímiques del fang granular sense necessitat d'afegir productes químics per forçar la precipitació, com en altres processos convencionals. Així, la precipitació bio-induïda en grànuls PNA representa una alternativa innovadora per recuperar fòsfor d’aigües residuals. Degut a l’alt contingut de matèria inorgànica dels grànuls obtinguts, la seva eliminació no interfereix ni amb les demandes de fang PNA per inoculació ni amb la bioactivitat del reactor. El producte generat (granulat) es recupera fàcilment del fons del reactor degut a la seva pròpia decantació gravitacional.

El capítol 4.2 tracta la recuperació conjunta de potassi i fòsfor en forma d'estruvita potàssica (k-estruvita), un mineral que pot ser retornat al sòl en forma de fertilitzant verd. L’amoni inhibeix la formació de k-estruvita, de manera que la precipitació ha d’anar precedida per una fase d’eliminació del nitrogen. En aquest capítol es demostra que la PNA és una tecnologia adequada per a l’eliminació del nitrogen prèvia a la precipitació de k-estruvita del centrat. Així, en experiments duts a terme en reactors a escala laboratori i pilot, es va aconseguir eliminar el 85% de l’amoni, la qual cosa va permetre la formació posterior de k-estruvita. D’altra banda, es va produir co-precipitació d’estruvita amònica, afavorint la recuperació d’un producte multi-nutrient que contenia N, P i K. El consum de bicarbonat per part de la biomassa autotròfica va reduir l’alcalinitat fins al 90%, superant així la capacitat d’extracció del CO_2 per *stripping* convencional amb aeració. D’aquesta manera, la PNA prèvia a la precipitació d’estruvita disminueix dràsticament la dosificació d’àlcali necessària per al control del pH.

Malgrat la seva importància com a nutrient, fins ara la recuperació de potassi ha despertat un interès limitat, la qual cosa fa que la seva presència en plantes de tractament d’aigua residual no estigui ben documentada. El capítol 4.3 d’aquesta tesi aporta els resultats d’una campanya de mostreig duta a terme en una planta amb eliminació biològica de P, amb l’objectiu de fer un

mapping dels fluxos de nutrients amb especial èmfasi en el potassi. A diferència del fòsfor, que principalment acaba a la fracció de fangs, el potassi està present sobretot a la fracció líquida. Aquests resultats també constitueixen una base per a calcular la quantitat de potassi que pot ser recuperada del centrat, per exemple, a través de la precipitació d'estruvita potàssica.

Avui en dia la PNA està implementada de manera exitosa com a alternativa amb major eficiència energètica per a l'eliminació de nitrogen en el tractament del centrat. Aquesta tesi vol expandir la visió sobre el que es pot fer amb el fang granular PNA. El caràcter autotròfic del fang PNA serveix com un element biològic d'extracció del CO_2 d'alta eficiència, mentre que les propietats bioquímiques i físiques del fang granular PNA fan que funcioni com un cristal·litzador biològic. Aprofitar-se de l'eliminació autotròfica del nitrogen pot comportar estalvi d'energia i productes químics i a la vegada produir compostos rics en nutrients que poden ésser retornats al sòl com a fertilitzant. Així, la PNA pot jugar un paper important en la conversió de les plantes de tractament d'aigua residual en instal·lacions de recuperació de recursos.

RESUMEN

Cada año se aplican millones de toneladas de fertilizantes minerales en cultivos agrícolas. A pesar de las grandes pérdidas de nutrientes que se producen entre el campo y la mesa, el agua residual concentra los nutrientes consumidos por la sociedad y se convierte en una fuente importante de esas sustancias hacia el medio receptor de agua. Hasta la fecha, los tratamientos convencionales de aguas residuales se han focalizado únicamente en la eliminación de nutrientes para evitar sus efectos negativos sobre el medio ambiente. No obstante, estos nutrientes representan una fuente potencial de recursos reciclados y la necesidad de concienciar sobre la naturaleza finita de las materias primas, nos empuja hacia un cambio de paradigma en las estaciones depuradoras de aguas residuales (EDARs): hay que pasar de la eliminación a la recuperación de nutrientes.

En las EDARs el efluente de la digestión de lodos, el “centrado”, es el flujo más rico en nutrientes. En los últimos años se han implementado dos tecnologías distintas para tratarlo de forma sostenible: la precipitación de la estruvita para recuperar fósforo y la nitritación parcial-anammox (PNA) como alternativa de eliminación de nitrógeno más eficiente energéticamente. No obstante, las implicaciones de acoplar estas dos tecnologías todavía no se han explorado totalmente. En esta tesis doctoral se han investigado dos rutas para aprovechar las posibilidades de la nitritación parcial-anammox autotrófica con vistas a la recuperación de nutrientes.

El capítulo 4.1 se centra en la precipitación biológica inducida que tiene lugar en los gránulos PNA. Los resultados obtenidos en un reactor PNA a escala laboratorio alimentado con centrado, demuestran que se pueden formar gránulos con un alto contenido de materia inorgánica, que presenta un porcentaje de fósforo muy similar al del fosfato natural (fuentes minerales). Este producto recuperado puede ser considerado como hidroxiapatita y su contenido en metales pesados cumple tanto la normativa europea para fertilizantes como los requerimientos de la industria. La precipitación en la PNA fue inducida por las propiedades físicas y bioquímicas del propio lodo granular, sin necesidad de añadir productos químicos para forzar la precipitación, como en otros procesos convencionales. Así, la precipitación bio-inducida en gránulos PNA representa una alternativa innovadora para recuperar fósforo de aguas residuales. Debido al alto contenido de materia inorgánica de los gránulos obtenidos, su eliminación no interfiere ni con las demandas de lodo PNA por inoculación ni con la bioactividad del reactor. El producto generado (granulado) se recupera fácilmente del fondo del reactor debido a su propia decantación gravitacional.

El capítulo 4.2 trata la recuperación conjunta de potasio y fósforo en forma de estruvita potássica (K-estruvita), un mineral que puede ser devuelto al suelo como fertilizante verde. El amonio inhibe la formación de K-estruvita de forma que la precipitación vaya precedida de una fase de eliminación del nitrógeno. En este capítulo se demuestra que la PNA es una tecnología adecuada para la eliminación del nitrógeno previa a la precipitación de la K-estruvita del centrado. Así, en experimentos llevados a cabo en reactores a escala laboratorio y piloto se consiguió eliminar el 85% del amonio permitiendo la formación de K-estruvita. Por otro lado, se produjo co-precipitación de estruvita amónica, favoreciendo la recuperación de un producto multi-nutriente que contenía N, P y K. El consumo de bicarbonato por parte de la biomasa autotrófica redujo la alcalinidad hasta el 90%, superando así la capacidad de extracción del CO_2 por *stripping* convencional con aeración. De este modo, la PNA previa a la precipitación de estruvita disminuye drásticamente la dosificación de álcali necesaria para el control del pH.

A pesar de su importancia como nutriente, la recuperación de potasio ha despertado hasta la fecha un interés limitado. Por ello su presencia en plantas de tratamiento de agua residual no está bien documentada. El capítulo 4.3 de las tesis aporta los resultados de una campaña de muestreo

llevada a cabo en una planta con eliminación biológica de P, con el objetivo de realizar un *mapping* de los flujos de nutrientes con especial atención en el potasio. A diferencia del fósforo, cuyo principal destino es la fracción de lodos, el potasio constituye una base para calcular la cantidad de potasio que puede ser recuperada del centrado, por ejemplo, a través de la precipitación de estruvita potásica.

Actualmente la PNA está implementada de forma exitosa como alternativa de mayor eficiencia energética para la eliminación de nitrógeno en el tratamiento del centrado. Esta tesis persigue expandir la visión sobre lo que podemos hacer con el lodo granular PNA. El carácter autotrófico del lodo PNA sirve como un elemento biológico de extracción del CO_2 de alta eficiencia, mientras que las propiedades bioquímicas y físicas del lodo granular PNA lo hacen funcionar como un cristalizador biológico. Aprovecharse de la eliminación autotrófica del nitrógeno puede comportar ahorro de energía y productos químicos y a la vez producir compuestos ricos en nutrientes que pueden ser devueltos al suelo como fertilizante. Así, la PNA puede jugar un papel importante en la conversión de las plantas de tratamiento de agua residual en instalaciones de recuperación de recursos.

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LIST OF PUBLICATIONS

This thesis has been written following the traditional monograph format, including the results in the form of articles, according to the regulatory basis of the University of Girona in regards to the Doctoral Programme in Water Science and Technology.

The following scientific contributions form an integral part of the thesis:

1. Johansson, S., Ruscalleda, M., Colprim, J.. Phosphorus recovery through biologically induced calcium phosphate precipitation by partial nitritation-anammox granular biomass. *Chemical Engineering Journal*, 2017, 327:881-888.
2. Johansson, S., Ruscalleda, Saerens, B., M., Colprim, J.. Potassium recovery from centrate: Taking advantage of autotrophic nitrogen removal for multi-nutrient recovery. *Journal of Chemical Technology and Biotechnology*, 2019, 94(3):819-828
3. Book chapter Nutrients recovery from wastewater streams in *Innovative Wastewater Treatment & Resource Recovery Technologies: Impacts on Energy, Economy and Environment.*(2017), edited by Juan M. Lema and Sonia Suarez Martinez to which S. Johansson contributed as co-author. Published by IWA.

LIST OF ABBREVIATIONS AND ACRONYMS

Anammox	Anaerobic ammonium oxidation
ACP	Amorphous calcium phosphate ($Ca_3(PO_4)_2 \cdot xH_2O$)
AOB	Ammonia oxidizing bacteria
Bio-P	Biological phosphorus removal
Bio-P PNA	PNA fed with centrate from a Bio-P plant
Chem-P	Chemical phosphorus removal
Chem-P PNA	PNA fed with centrate from a Chem-P plant
DCPD	Dicalcium phosphate dihydrate (brushite) ($CaHPO_4 \cdot 2H_2O$)
DO	Dissolved oxygen
EBPR	Enhanced Biological Phosphorus Removal
IAP	Ion activity product
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
K_{sp}	Solubility product
MAP	Magnesium ammonium phosphate $MgNH_4PO_4 \cdot 6H_2O$ (ammonium struvite)
MLSS	Mixed liquor suspended solids
MPP	Magnesium potassium phosphate $MgKPO_4 \cdot 6H_2O$ (potassium struvite)
NOB	Nitrite oxidizing bacteria
NLR	Nitrogen loading rate
OCP	Octacalcium phosphate ($Ca_4H(PO_4)_3 \cdot 2.5H_2O$)
Ω	Degree of saturation
p.e.	Population equivalents
PE	Poly-electrolyte
PNA	Partial nitritation-anammox
poly-P	Polyphosphate
SEM-EDX	Scanning Electron Microscopy with Energy Dispersive X-ray analysis
SBR	Sequencing batch reactor
SI	Saturation index
TCP	Tricalcium phosphate $Ca_3(PO_4)_2$
TKN	Total Kjeldahl nitrogen

TSP	Triple Super Phosphate
TSS	Total Suspended Solids
UWWTD	Urban Waste Water Treatment Directive
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant
XRD	X-ray diffraction

1 INTRODUCTION

This section includes some paragraphs extracted from Johansson et al. (2017) as well as from the book chapter Nutrients recovery from wastewater streams in *Innovative Wastewater Treatment & Resource Recovery Technologies: Impacts on Energy, Economy and Environment.*(2017), edited by Juan M. Lema and Sonia Suarez Martinez to which S. Johansson contributed as co-author. Published by IWA.

1.1 Nutrient flows in the global food production and consumption system

1.1.1 Historical development of synthetic fertilizers

There has passed some 10,000 years since early agriculturalists planted the first domesticated crops, to today's intensified agriculture. The aim throughout the years has remained the same though: to secure yields. Farmers need to replenish the soils with the nutrients that are removed through harvest.

The earliest attempts to do so were through slashing and burning woodlands. Although the fires vaporized a large part of the nitrogen, remaining minerals were sufficient to sustain a few harvests [1]. With more permanent settlements other techniques to add nutrients to soils emerged, such as crop rotation with leguminous species and spreading of manure and human excreta [1,2]. These were strictly local practices where the cycle of nutrients between food production and consumption took place within the community. With the emergence of cities, the distance between production and consumption of nutrients increased and the nutrient cycling was in parts broken. Still, there are several examples on how human excreta, so called "night soil", was collected in cities and returned to farmland [3,4].

During the 18th and 19th century, fertilizers started do be obtained over further distances. Russia for example, became an important exporter of potassium-rich wood ash, due to its extensive forests, while Scotland produced ashes of kelp, another potassium-rich plant [2]. England on the other hand imported large amounts of bones in order to supply fields with phosphorus [3]. Like potassium and phosphorus, nitrogen was still supplied by biological means trough the fixation of nitrogen by clover and legumes, which was recognized by Jean-Baptiste Boussingault in 1838 although the process was not yet understood [5].

This changed in the 19th century; in 1840, the German chemist Justus von Liebig published his book Die organische Chemie in ihrer Anwendung auf Agricultur und Physiologie (Organic Chemistry in its Application to Agriculture and Physiology) where he advocated that plants can grow on solely inorganic compounds. He has later been crowned the founder of the artificial fertilizer industry [5]. Following ideas of Liebing, production of P fertilizer by treating first bones and then P-containing rocks with sulphuric acid started in the 1840s [6]. With the growth of this industry, the search for phosphate rock deposits took off and eventually overtook the short-lived practice of using guano as a fertilizer [3]. High-quality apatite was found in Norway and phosphate mining also started in the US. In the 1870s phosphoric acid substituted sulphuric acid and yielded what is today known as triple superphosphate (TSP) [6]. Between the two world wars extraction of phosphate rock began in two other major deposits: Morocco and the former USSR.

Extensive potash deposits made Germany the leading producer of potassium fertilizer during nearly 100 years from 1868 until the 1970s [7]. There were various attempts to extract potash during the early 20th century, but in the aftermath of WWII potash cartels were broken up. Instead, Soviet on the one hand (with resources in the Ural mountains and Belarus) and Canada on the other side came to dominate the market [2].

A second discovery, with even larger implications than those of Liebig, was made in 1909 when Fritz Haber managed to synthesise ammonia in the laboratory [1,5]. This became the foundation for the crop production that allowed for the exponential population growth seen during the 20th century. Haber's discovery was made commercial by Carl Bosch and the first plant of the Haber-Bosch process opened in Germany in 1913. Due to WWI, the initial production mainly supplied ammonia for Germany's munition, and the food rationing following the two WWs further delayed the large-scale application of synthetic nitrogen fertilizer until mid-20th century when production started to increase rapidly. From the opening of the first plant in 1913 to the end of the 20th century the world saw a 125-fold increase in average global rates of application of inorganic nitrogen fertilizer, although 50% of Haber-Bosch synthesized ammonia was consumed solely in the last two decades of the 20th century.

1.1.2 Nutrient flows through the food production and consumption system

The introduction of inorganic fertilizer has profoundly changed agricultural practice and global nutrient flows. Yields have increased; it is estimated that the number of humans that can be supported by one hectare of arable land increased from 1.9 to 4.3 persons between 1908 and 2008 due to Haber-Bosch nitrogen [8]. Haber-Bosch synthesized ammonia has also become a major supplier of protein; it is estimated that around half the human population is currently sustained by Haber-Bosch nitrogen [8]. This has allowed the world population to grow from 1.6 billion people in 1900 to more than 7 billion today. On the global scale, agriculture is today highly dependent on synthetic fertilizer. 50-60% of P fertilizer origins from phosphate rock [6] and it is estimated that industrial N-fixation (~125 Mton N y^{-1}) is reaching almost half of the biological N-fixation (~300 Mton N y^{-1}) [9]. Similar figures on the share of organic and mineral potassium fertilizer are lacking. On a yearly basis 109 Mton N, 21 Mton P and 32 Mton K are added to fields as fertilizer [10].

There are large losses of nutrient throughout the global food production and consumption chain; only 20% of the phosphorus mined as phosphate rock makes its way to the plate [3] while as little as 4 – 14% of nitrogen used in agriculture ends up as consumable protein [11]. The corresponding numbers for potassium are unknown. While this is a waste of resources, it also has adverse effects on the environment. Phosphorus, as a growth-limiting nutrient, is promoting algal growth and eutrophication when added to waterbodies [6,12]. Reactive nitrogen (N_r, all nitrogen species except N_2) released to the environment contribute to a range of negative environmental effects, including acid rain, eutrophication, greenhouse effect, stratospheric ozone depletion and nitrate pollution of groundwater [13]. In addition, one molecule of N_r can have multiple adverse effects as it moves from one environmental system to another, a phenomena known as the “cascade effect” [14].

Human-induced flows of phosphorus and nitrogen are already beyond levels of uncertainty as defined by the planetary boundary approach (Table 1.1), the safe operating space for humanity based on the biophysical processes that regulate the stability of the Earth’s system [15]. Transgressing these boundaries means driving the Earth away from the Holocene epoch, the only state of the planet that so far safely has harboured humans. Although the boundaries are trespassed globally, it is a few regions with high fertilizer application rates that are responsible for the main part [15].

Table 1.1 Control variables for P and N biogeochemical flows (adapted from [15])

Control variable	Planetary boundary (zone of uncertainty) **[15]**	Current value of control variable
N global: Industrial and intentional biological fixation of N	62 Tg yr^{-1} (62-82 Tg yr^{-1})	109 Tg yr^{-1} [10]
P regional: P flow from fertilizers to erodible soils	6.2 Tg yr^{-1} (6.2-11.2 Tg yr^{-1})	21 Tg yr^{-1} [10]

1.2 Conventional nutrient removal in WWTP

Although diffuse sources, such as runoff from fields, represent the major contribution of nutrients to the natural environment, the concentration of people to cities, together with the growing implementation of centralized wastewater collection and treatment makes sewage a considerable point-source. Changing consumption patterns, with higher ratios of meat and dairy have further increased the loads from households [16].

The implementation of the EC Urban Waste Water Treatment Directive 97/271/EC (21st May 1991) imposed some fundamental changes for wastewater treatment. The main purpose of the directive is to protect the environment from adverse effects of urban and certain industrial wastewaters [17]. The directive set minimum standards for the collection and treatment of wastewaters in urban settlements of >2000 people and imposed nitrogen and phosphorus discharge limits (Table 1.2). Although potassium commonly is a limiting factor for plant growth in terrestrial ecosystems [18], it is generally abundant in surface waters and therefore not considered to contribute to eutrophication. Thus, there is no policy pressure to remove potassium from waste water.

Table 1.2 Discharge limits for municipal WWTPs [17]

Parameter	Concentration	Min. percentage of reduction
Total phosphorus	2 mg/L (10,000-100,000 p.e.) 1 mg/L (>100,000 p.e.)	80
Total nitrogen	15 mg/L (10,000-100,000 p.e.) 10 mg/L (>100,000 p.e.)	70-80

1.2.1 Phosphorus removal

1.2.1.1 Chemical phosphorus removal

The most common strategy for phosphorus removal in municipal WWTPs is by chemical precipitation with metal salts, typically iron or aluminium [19]. In Flanders for example, 91% of the plants that remove phosphorus are applying chemical removal. On a p.e. basis though, 27% of the load is treated by biological phosphorus removal [20].

The precipitation can be placed before or after the biological step, but since ortho-phosphate is more easily removed than poly-phosphate or organic phosphorus, there is an advantage to place the phosphorus removal step after the secondary treatment. The phosphate binds to the metal and form ferric or aluminium phosphate. The actual removal of the phosphorus then occurs when the sludge is separated from the water fraction. This can be done by sedimentation or filtration and polymers may be dosed to facilitate the flocculation.

Chemical P-removal accomplishes well with discharge limits, but the chemical cost is high, and the process results in a bulky sludge that needs to be disposed of [6]. More than 3 million tons of sludge (measured as dry weight) is produced in the EU each year, and to dispose of the sludge is a concern for WWTPs. Due to national legislation and conditions, the sludge disposals routes vary widely within the European Union (Figure 1.1). A straightforward way to return nutrients to soils is application of sludge to fields after anaerobic digestion and/or composting. However, application of sludge to agricultural land is prohibited in certain countries and/or regions due to concerns about pollutants [21].

Due to the efficient removal of phosphate from the water fraction and the stability of the formed metal phosphates, the phosphate content in digestate and centrate is limited at plants that apply chemical phosphorus removal. It is therefore not viable to apply struvite recovery in side-stream at such plants.

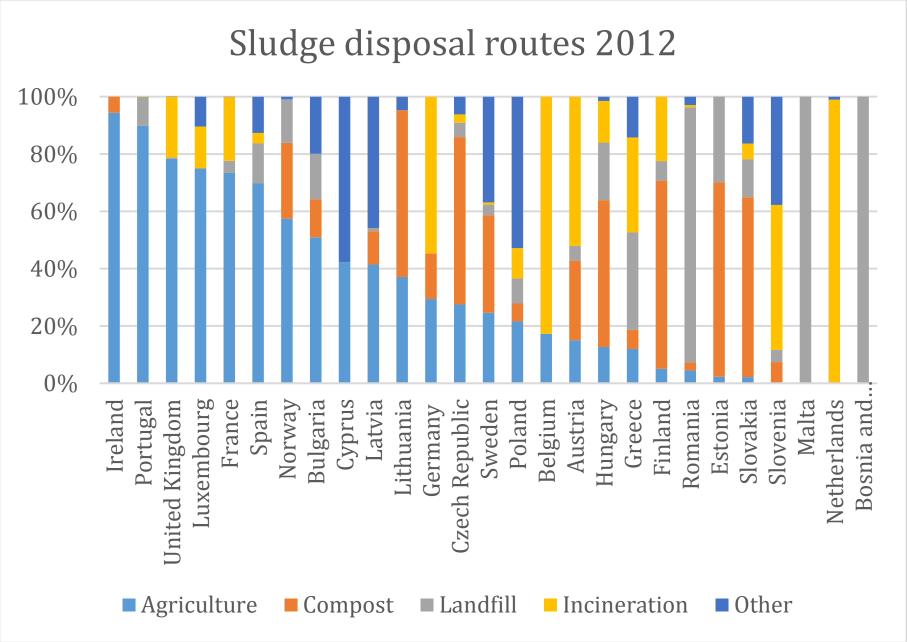


Figure 1.1 Sludge disposal routes in Europe 2012 [22]

1.2.1.2 Biological phosphorus removal

Biological phosphorus removal was introduced in wastewater treatment in the late 1970s as an alternative to chemical phosphorus removal [19]. The process is known as enhanced biological phosphorus removal (EBPR) and relies on the incorporation of phosphate in intracellular polyphosphates (poly-P) by phosphorus accumulating organisms (PAOs). The excess phosphorus is then removed with the wasted sludge.

The most simple process configuration for BOD and P-removal consists of an anaerobic reactor followed by an aeration tank, and a settler from where sludge is returned to the anaerobic reactor [19,23].

The PAOs have a competitive advantage over other heterotrophic organisms in that they are able to take up volatile fatty acids (VFA) during the anaerobic phase and store them as polyhydroxyalkanoates (PHA). The energy to do this is generated by the cleavage of poly-P and is thus accompanied by a release of phosphate [23]. The excess phosphate is taken up in the aerobic tank where it is synthesized into poly-P by PAOs.

The main advantages compared to chemical precipitation are:

- Reduced chemical costs
- Reduced sludge production

The main part of the poly-P is hydrolysed during anaerobic digestion with subsequent release of phosphate. Potassium and magnesium play important roles in EBPR and are co-transported with phosphorus into bacterial cells and are incorporated into the poly-P structure (general formula $(K_aMg_bPO_3)_n$) [24]. Thus the K and Mg that is stored as poly-P is also released during anaerobic digestion.

The release of phosphate, ammonium and magnesium during anaerobic digestion has augmented problems with struvite scaling in pipes downstream of the anaerobic digester. Scaling can be so severe that it affects the flow and require replacement of piping systems [25].

1.2.2 Nitrogen removal

Conventional nitrogen removal consists of biological nitrification/denitrification. First, ammonium is oxidized to nitrite and further to nitrate with molecular oxygen as electron acceptor (Eq. 1.1). This step requires extensive aeration to supply the two moles of oxygen needed for each mole of ammonium oxidised and is thus an energy demanding process. In the denitrification step, nitrite and nitrate are reduced to nitrogen gas under anoxic conditions with NO_x^- as electron acceptors (Eq. 1.2). The organic carbon ($C_{10}H_{19}O_3N$) present in the wastewater is used as electron donor, but an external source, such as methanol or waste glycerine, can be added in order to sustain or accelerate denitrification [19].

$$NH_4^+ + 2HCO_3^- + 2O_2 \rightarrow NO_3^- + 3H_2O + 2CO_2 \qquad \textbf{Eq. 1.1}$$

$$C_{10}H_{19}O_3N + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^- \qquad \textbf{Eq. 1.2}$$

Sewage treatment has been identified as an important factor for decreasing reactive nitrogen in the environment as it converts reactive nitrogen to nitrogen gas [13].

1.2.3 Anaerobic digestion and reject water

Anaerobic digestion has long been used to decrease sludge volumes. An additional advantage is that the methane gas produced can be used internally for heat and electricity production. If the digester is fed with external sludge or the sludge is co-digested with i.e. food waste, the surplus gas can be used for heat and power production, fed to the grid or upgraded to vehicle fuel.

After digestion, the digested sludge (digestate) is dewatered before disposal. The WWTPs in relation to this thesis all apply centrifugation, but screw press can also be applied for solid-liquid separation. The water fraction (centrate) is returned to the main water line. Even though the centrate is a small stream compared to the incoming flow to the plant, typically < 1% on a volumetric basis, it can represent up to 25 % of the nitrogen and phosphorus loads [19,26,27]. During anaerobic digestion a part of organic P, K, Mg and Ca is released due to degradation of organic matter [28]. In the case of digestion of EBPR sludge, there is also a complete hydrolysis of the poly-P structure with subsequent release of phosphate, magnesium and potassium.

A separate treatment of the reject water is therefore an efficient way to decrease the nutrient load to the water line. Apart from a high nutrient concentration the centrate is characterized by elevated temperatures (around 30°C), low organic carbon content and rather high alkalinity (between 2000 and 5000 mg L^{-1} typically [19]).

The past decade has seen the introduction of two processes for nutrient removal and recovery in side-stream: anammox-based processes for nitrogen removal, and struvite precipitation for phosphorus recovery, which are introduced in the following two sections.

1.3 Advanced reject water treatment

1.3.1 Anammox: a shortcut in the nitrogen cycle

The discovery of the anaerobic ammonium oxidation (anammox) in the late 1980s was a revolution in the understanding of the biological nitrogen cycle. Until then, fixation, nitrification and denitrification were thought to be the major flows in the nitrogen cycle [1], and ammonium had only been known to be oxidised under aerobic conditions. Then, anaerobic, or more correctly anoxic, conversion of ammonium was noticed in a pilot-plant at a yeast and penicillin producing company in Delft, the Netherlands [29]. The discovery of anammox confirmed previous predictions by Broda, who in 1977 suggested that there should exist lithotrophic denitrifiers that can use ammonium as electron donor [30].

Anammox organisms oxidise ammonium directly to nitrogen gas with nitrite as electron acceptor. The process is autotrophic with bicarbonate as only carbon source. The anammox stoichiometry was deducted by [31] on granular sludge:

$$\begin{aligned}\boldsymbol{NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+}\\ \boldsymbol{\rightarrow 1.02N_2 + 0.26NO_3^- + 2.03H_2 + 0.066CH_2O_{0.5}N_{0.15}}\end{aligned} \qquad \textbf{Eq. 1.3}$$

Two decades later Lotti et al. calculated the stoichiometry of floccular anammox biomass in a membrane bioreactor (MBR) [32]:

$$\begin{aligned}&NH_4^+ + 1.15NO_2^- + 0.071HCO_3^- + 0.057H^+\\&\rightarrow 0.99N_2 + 0.16NO_3^- + 0.071CH_{1.74}O_{0.31}N_{0.20} + 2.0H_2O\end{aligned}$$ **Eq.** 1.4

The advantages of nitrogen removal with anammox over conventional nitrification-denitrification are many and include reduced sludge production, drastically reduced requirements for aeration and no need for external organic carbon for denitrification [33,34]. The anammox organisms have a natural tendency to form granules and the compact nature of granular sludge allow for high loading rates and small footprints.

The anammox process requires 1.2-1.3 moles of nitrite for each mole of ammonium oxidised (Eq. 1.3 and 1.4). In waste streams such as centrate, where close to all nitrogen is present as ammonium, about half of the ammonium needs to be oxidized to nitrite, a process called partial nitritation. The partial nitritation can either take place in a separate reactor previous to the anammox reactor, or in a mixed culture of aerobic ammonia oxidizing bacteria (AOB) and anammox organisms in a one-stage partial nitritation-anammox (PNA) configuration. In granular PNA sludge the anammox organisms are found in the inner, anoxic part of the granules, covered by a layer of AOB [35,36]. The presence of nitrite oxidizing bacteria (NOB) is unwanted as they compete with anammox organisms for nitrite and with AOBs for oxygen. However, as the NOBs are subjected to a double competing pressure their presence is normally naturally suppressed in PNA reactors operated in side-stream.

The majority of the full-scale anammox installations have been implemented in the side-stream treatment at municipal WWTPs [37]. Much of the success can be ascribed to the characteristics of centrate. Centrate typically has a low organic carbon to nitrogen ratio making conventional autotrophic nitrification-heterotrophic denitrification too costly (due to the need of aeration and addition of organic carbon), and an elevated temperature (around 30 °C) at which AOB has a higher growth rate than NOB [27]. Anammox have been shown to be more sensitive to inorganic carbon limitations than AOB or NOB [38], but the inorganic carbon:ammonium ratio in centrate is typically sufficiently high, while the alkalinity is high enough to buffer the acidifying effects of AOB activity. After the start-up of the first full-scale plant in 2002 [39,40] the number of installations has increased steadily and in 2014 there were over 100 full-scale installations in place, the majority of them one-stage systems treating centrate [37].

Anammox organisms have been notoriously known as slow-growing with a doubling-time of 11 days [31]. Although it has been shown that under specific operational conditions, anammox organisms can increase their kinetics [41], most full-scale installations rely on biomass retention to maintain the biological activity in the reactor. The two major ways to retain biomass is to use carriers or to work with granular sludge. To take advantage of the natural tendency of anammox biomass to form granules instead of relying on carrier materials has many advantages: they allow for a higher surface area and thus a higher loading rate compared to carriers, the cost of carrier material is avoided and the mixing is easier [42].

PNA granules are characterized by gradients in microflora, dissolved oxygen (DO) concentration, pH and substrate concentration [35,36]. The stratification allows for partial nitrification and anammox to take place in the same reactor, although the anammox require anoxic, and the partial nitrification aerobic conditions.

1.3.2 Controlled precipitation for phosphorus recovery

1.3.2.1 Why controlled precipitation?

Struvite scaling that severely diminished the flow in the pipes downstream of the anaerobic sludge digester was reported in the 1960s at a WWTP in Los Angeles [43]. Maintenance to keep pipes clear, or in the worst case, replacement of entire pipe systems are substantial costs and to reduce or avoid scaling is therefore a main incitement for WWTPs to invest in a controlled phosphorus precipitation step in side-stream. At the same time it reduces the phosphorus load to the main line, which decrease the need for organic carbon that might be needed to sustain EBPR and has the added benefit of the recovery of a recovered phosphorus product that is easier to handle than sludge [26,44]. This is similar to manure treatment plants which state reduced sludge volumes and decreased effluent concentrations of phosphorus, while the recovery of struvite is an added benefit [45]. If struvite precipitation is placed directly on the digestate, reported additional benefits include improved dewaterability and a lower P content in the dried sludge, the latter being important if the dried sludge is used in the cement industry [26,46].

The most commonly applied strategy for phosphorus recovery in WWTPs is the precipitation of struvite. Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a mineral that precipitates according to the following equation:

$$\boldsymbol{HPO_4^{2-} + Mg^{2+} + NH_4^+ + 6H_2O \rightarrow NH_4MgPO_4 \cdot 6H_2O + H^+} \qquad \textbf{Eq. 1.5}$$

Phosphorus can also be recovered in the form of calcium phosphates. The formation of calcium phosphates is complex and depending on the conditions a number of different calcium phosphates may form. However, the formed pre-cursor phases are likely to eventually transform into the thermodynamically more stable hydroxyapatite ($Ca_5(PO_4)_3OH$) [47–49]. Once formed, hydroxyapatite has a very low solubility in water.

1.3.2.2 Applications of recovered struvite

Recovered struvite contain nitrogen, phosphorus magnesium and can be used as a fertilizer, either as is, or blended with other fertilizers [46]. The recovered product is a close to water-free, except for the crystal water, and has shown a high purity and low content of heavy metals [26,44,50,51].

Struvite is poorly soluble in water (1-5%), while TSP is 90% soluble in water [52,53]. High water solubility has been a quality mark of superphosphate fertilizer (among else with the implementation of the European Union fertilizer regulation of 1976), but high water solubility has been proven to not be a prerequisite for plant availability [54]. Furthermore, the application of soluble fertilizers is associated with phosphorus losses from cultivated lands to watersheds [12] where it contributes to eutrophication. The low water-solubility of struvite was early recognized as advantage from a fertilizer perspective as the slow release of nutrients avoid damage to roots by overdosing of fertilizer, a phenomena commonly known as root burn [55], but high production costs limited its introduction on the market until waste streams were recognized as a free source of nutrients from which struvite can be harvested.

1.3.2.3 Full-scale installations

Early experiments to remove phosphorus from secondary effluent by calcium phosphate formation were started in the 1970s using a column packed with phosphate rock [56]. The first full-scale phosphate recovery installation (the Crystalactor®) was developed by DHV Consultants in the Netherlands. It was taken into operation in 1988 for dephosphorization of WWTP effluent and allowed for the recovery of phosphorus in different forms, including calcium phosphate, and ammonium and potassium struvite [57,58]. The plant comprised of a CO_2 stripper followed by a fluidized bed reactor and two pressure filters [57]. To reach an efficient CO_2 stripping, the pH was lowered to around 5 by dosing of sulphuric acid. In the crystallizer the pH was increased to 10.0–10.5 by dosing of milk of lime.

The number of full-scale phosphorus recovery installations didn't start to grow until the past decade (Figure 1.2). Since then, a number of technologies have been developed for phosphorus precipitation in side-stream. Figure 1.3 gives an overview of some of the technologies currently on the market. Phosphorus precipitation can be applied either on the digested sludge before dewatering, or on the centrate. There are also technologies for leaching of phosphorus from incinerated sludge ash, but this lies outside the scope of the thesis.

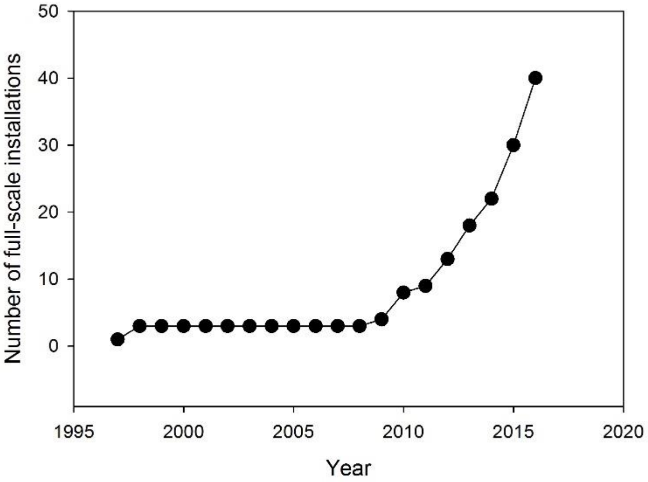


Figure 1.2 Cumulative development of on-site full-scale phosphorus recovery installations from sludge or centrate, adapted from Kabbe (2017)

Phosphorus crystallizers operating on centrate can be divided between fluidized bed reactors (FBRs) or mixed reactors. The mixed reactors can be either one-stage (Phospaq) or two-stage (NuReSys and Anphos). In the two-stage configuration, the first tank is a CO_2 stripper for pH increase, while in the one-stage configuration the aeration is supplied directly to the crystallizer tank [46]. Further pH control can be supplied by addition of sodium hydroxide to the crystallization tank. FBRs are fed with wastewater from the bottom of the reactor and the upflow supply the mixing. The reactor can either be cylindrical or have a gradually larger diameter in order to allow for particle size separation within the reactor. The most common magnesium sources are $MgCl_2$, MgO and $Mg(OH)_2$. $MgCl_2$ has the advantage to be easily soluble, while MgO and $Mg(OH)_2$ are cheaper alternatives and also have the advantage that they increase the pH and thus reduce the need for CO_2 stripping and/or NaOH addition. However, they are less soluble and need to be prepared as a suspension.

Crystallizers operated directly on digestate can be either mixed (NuReSys) or operated as air-lift reactors (AirPrex). Similar to crystallizers operated on centrate they can be either in a two-stage (NuReSys) or one-stage (AirPrex) configuration with the same strategies for pH control (CO_2 stripping and/or NaOH dosing for pH control and addition of a magnesium source for correcting the Mg:P ratio). However, in contrast to crystallizers operating on centrate, a crystal washing step to remove organics from the sludge [21,26,46].

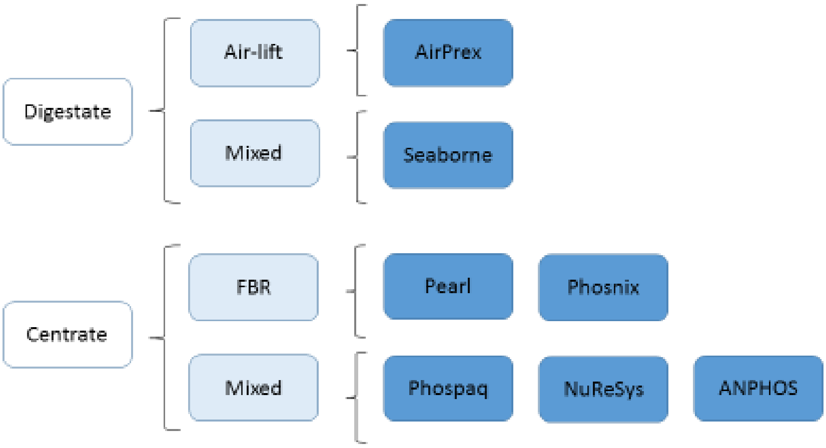


Figure 1.3 Overview of phosphorus recovery technologies from digestate and centrate (adapted from Desmidt et al. (2015) and Kabbe et al. (2015))

1.3.2.4 Theory of crystallization

For a chemical compound to precipitate, the solution from which it is forming needs to be supersaturated in respect to the formed material. A supersaturated solution contains more of the dissolved material than it can hold at a given condition. A supersaturated solution is unstable and precipitation will occur until equilibrium concentrations are reached. Sometimes a template for crystallization, such as a seed crystal or other small particles, is needed to initiate the precipitation. In the case of an open system, such as a wastewater treatment plant, where new ions continuously are added, precipitation will continue indefinitely. Crystallization is separated into two phases: nucleation and growth. Nucleation is the formation of ions into crystal embryos, nuclei, and growth is the development of crystals by incorporation of ions into the crystal lattice.

The degree of saturation describes how far a solution is from equilibrium and can thus be seen as the driving force for precipitation. The degree of saturation also determines whether crystallization will occur mainly as nucleation or as growth. Higher supersaturation promotes nucleation while lower nucleation promotes growth of crystals.

Precipitation occurs when a solution is saturated with respect to a solid phase. The degree of saturation, Ω, id defined as:

$$\boldsymbol{\Omega = \frac{IAP}{K_{sp}},} \qquad \textbf{Eq. 1.6}$$

where IAP is the ion activity product and K_{sp} is the solubility constant of the precipitated mineral.

Commonly the term saturation index (SI) is used to describe whether a system is saturated or not. SI is the logarithm of Ω, and thus:

$$SI = log\,\Omega = log\,IAP - log\,K_{sp}, \qquad \textbf{Eq. 1.7}$$

A solution is considered to be oversaturated when the SI is above zero, saturated when zero, and undersaturated when less than zero.

1.4 Motivations and objectives for nutrient recovery

1.4.1 Legal structures and policy

The implementation of the UWWTD imposed some fundamental changes for wastewater treatment, previous practices such as dumping of sewage sludge at sea became prohibited, while the stricter discharge limits results in that a larger fraction of phosphorus is removed from the water phase and consequently ends up in the sludge fraction. This in turn augments the risk of unwanted struvite precipitation after anaerobic digestion. It should be noted that the UWWTD only regulates the nitrogen and phosphorus discharge and omits potassium. Thus, there is no policy pressure to remove or recover potassium from waste water.

The current EU legislation on fertilizer (Regulation (EC) No 2003/2003 relating to fertilizers) excludes around 50% of fertilizers currently on the market, including most fertilizers from organic materials such as animal or other agricultural by-products, and recycled bio-waste from the food chain. It also fails to state limits for contaminants, such as cadmium and heavy metals in fertilizer. To address these points, the current legislation is now under revision [60]. The proposed revision would allow recovered nutrient products such as struvite to enter the EU internal market.

The European Union has adapted an action plan for the Circular Economy as an aim to transition into a sustainable and resource efficient economy. In the action plan, recycled nutrients are recognized as an important category of secondary raw materials that can be returned to the soils as fertilizer [61].

The European Commission has created a list of critical raw materials that are of high importance to the EU economy and that are associated with a risk of supply. The list aims to create awareness of potential raw materials supply risks and to enhance mining and recycling activities within the EU. The raw materials in the list include a range of raw materials divided into the categories: heavy rare earth metals, light rare earth metals and platinum group metals. Each material is evaluated according to its economic importance and the supply risk. The first list was created in 2011 and the idea is to update it every three years. Phosphate rock was added to the list in 2014 and elemental phosphorus was added in 2017.

1.4.2 Ensuring food security: supply and clean sources of nutrients

The main supply of the three macronutrients nitrogen, phosphorus and potassium all rely on geological sources; phosphorus and potassium are mined, while nitrogen is synthesised via the

Haber-Bosch process that uses natural gas. The amount of remaining phosphate rock reserves has been highly debated during the past decade, following the discussion about an approaching "peak phosphorus". Concerns have been voiced over the fact that data on reserves are supplied by mining companies and/or states, and is not independently verified [62]. As an example, China´s reported reserves jumped from 2 to nearly 8 billion tonnes when they joined the World Trade Organization in 2001 [63]. There was another great increase in 2010 following "significant revisions" of reserves data for Morocco, and revised data for Algeria, Senegal and Syria [64] (Figure 1.4). Since 2017, the USGS reports that there are no imminent shortages of phosphate rock [65]. Yet, it is widely recognized that phosphorus is a limited resource, and consequently phosphate rock was added to the EU list of Critical Raw Materials in 2014 [66]. The presence of cadmium and other heavy metals in remaining reserves of phosphate rock has been recognized as a concern both by the European Commission as well as the elemental phosphate industry [60,67]. It is also a fact that the phosphate content (commonly expressed on a P_2O_5 basis) in phosphate rock is decreasing [6].

At the same time, reported reserves for potash dramatically plunged after 2013 (Figure 1.4) due to revised reporting [68,69]. Similar to phosphate rock, reserves data from certain countries are uncertain as they are provided by official government sources or fertilizer companies. Yet, the diminishing reserves of potash has gone relatively unnoticed by researchers and policy makers. More concern have been payed to the limited geographical distribution of potash mines, which has given rise to cartelization and overprizing of potash on the market [70]. Up until 2013 the potash market was dominated by two export cartels; one made up of Canadian producers and the other involving a company in Russia and in Belarus, but in 2013 the Russian company Urakali withdrew [70,71]. This event was followed by falling potash prices.

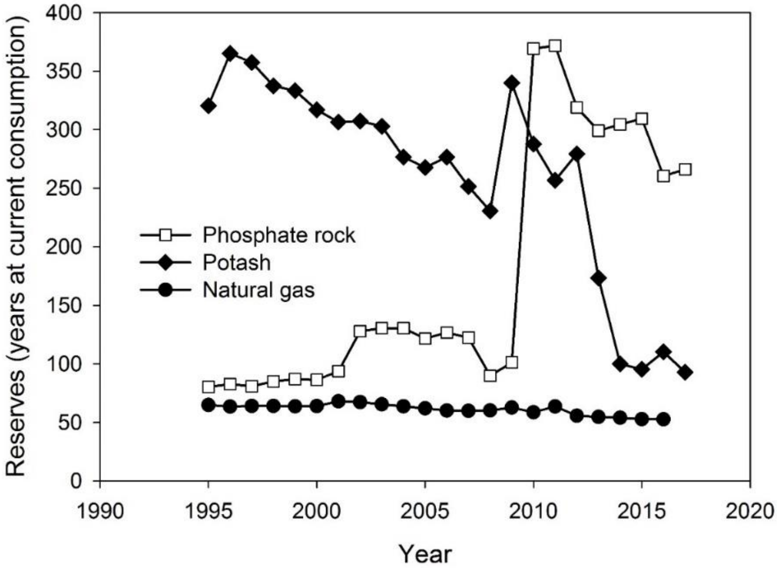


Figure 1.4 Estimated remaining reserves of phosphate rock, potash and natural gas (at current consumption rate) [72,73]

The European Union is highly dependent on imports of minerals for fertilizer production. Europe only have a small phosphate rock mine in Finland [21] and the EU is currently importing more than 90% of the phosphate fertilisers used [60]. Germany accounts for 7% of the global potash production, and there are also smaller mines in Spain and in the UK [65], but the EU is importing 70% of the potash used for fertilizer production [74]. Five countries account for more than 80% of world production of potash and phosphate rock (China, Morocco and West Sahara, the US, Russia and Jordan) respectively (Figure 1.5).

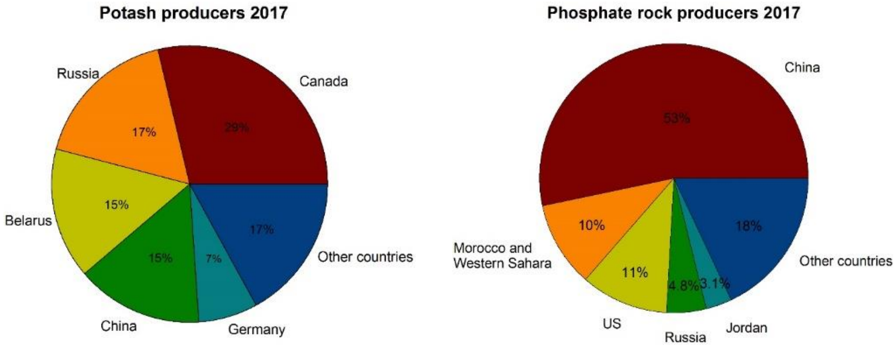


Figure 1.5 Distribution of potash and phosphate rock producing countries 2017 [75,76]

1.5 Recovery of potassium in the form of potassium struvite

Potassium can replace ammonium in the struvite crystal lattice and form potassium struvite ($MgKPO_4 \cdot 6H_2O$, MPP). Potassium struvite precipitates similar to ammonium struvite and allows for the recovery of a mineral containing potassium and phosphorus that can be returned to soils as fertilizer. Similar to ammonium struvite, potassium struvite exhibits a low solubility in water and thus a slow release of nutrients [77]. This is one of the characteristics that make struvite attractive as a fertilizer as it decreases the risk of overload of nutrients to plants, and the risk of leaching of fertilizer during heavy rains.

Few installations have been targeted at the recovery of potassium in the form of potassium struvite, but a full-scale plant treating calf manure after nitrogen removal (nitrification/denitrification) in Putten, the Netherlands has been in operation for several years [45]. The recovered potassium struvite has been used as a secondary raw material and to upgrade the phosphorus content of organic manure (from 20 to 50 kg P_2O_5/ton manure) [78]. Due to the presence of ammonium in regular ammonium struvite, concerns have been expressed over the use of MAP as a secondary raw material as this poses problems for the processing of phosphate rock via the thermal route. This problem is by-passed when potassium struvite is used as it contains potassium instead of ammonium in the crystal structure and MPP has been successfully been tested as a secondary raw material by Thermphos in their thermal phosphorus production plant [79].

Ammonium has a negative effect on the formation of MPP [80] due to that the solubility product for MAP is slightly smaller than the one for MPP. Reported values of the negative logarithm of the solubility product (pKsp) for MPP range between 10.6–12.2 [81–83] (Table 1.2), while the most commonly used value for MAP is 13.26 [25]. Consequently, when struvite precipitation is applied on streams with high ammonium concentrations, such as centrate, only traces of K are detected in the recovered product [84], while if the struvite precipitation is preceded by a nitrogen removal step, such as the case of the calf manure plant in the Netherlands, a close to pure potassium struvite can be obtained [45].

Table 1.3 Different reported values of pKsp of potassium struvite and the most commonly used pKsp value of ammonium struvite

Struvite compound	pK_{sp}	Source
MAP	13.26	[85]
MPP	12.2	[81]
	11.7	[82]
	10.6	[83]

1.6 Limitations of struvite as a secondary raw material

The majority (80%) of mined phosphate rock is used for the production of fertilizer, while the remaining fraction is used for the production of detergents or (animal) food additives [6,67].

Phosphate rock is processed either via the “wet” (chemical) route or the “thermal” (electric furnace) route. In the thermal route, phosphate rock is first sintered, a step during which fluoride is driven off, and then the pellets are baked in an oven at 1200 – 1500°C (Eq. 1.7). Phosphate melts at 44°C and boils at 280°C and is evaporated from the apatite and then condensed and harvested as elemental phosphorus (P_4). The majority of the impurities ends up in the calcium silicate slag. The phosphorus obtained via this route is of high purity, but the process is highly energy intensive and elemental phosphorus is a relatively expensive product reserved for the production of agrochemicals, plastic additives and pharmaceutical intermediates [67,86].

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO \qquad \textbf{Eq. 1.8}$$

The wet route is less energy intensive than the thermal route, but the resulting phosphoric acid is not as pure. The process consists of the treatment of phosphate rock with sulphuric acid, which produces phosphoric acid and crystals of calcium sulphate (Eq. 1.8) [67]. The calcium sulphate is then filtered off from the phosphoric acid, which is recovered and concentrated before being sold. The efficiency of the process depends on the growth of large crystals of calcium sulphate that can be easily removed. The wet route requires much less energy than the thermal route, and is therefore used for bulk production of fertilizers. Unfortunately, the majority of the impurities present in the phosphate rock end up in the phosphoric acid and subsequently in the fertilizer.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4 + 3H_2O \qquad \textbf{Eq. 1.9}$$

The elemental phosphorus industry has expressed concern about the increasing levels of impurities in phosphate rock, and the associated costs for removing them, and expressed interest in the use of recycled secondary raw materials [67,86]. The fertilizer sector has been less concerned about the level of impurities, but it has been predicted that stricter limits to the level of impurities, most notably cadmium, in fertilizer will apply stronger pressure also on this sector [67]. Both the wet and the thermal route are designed for the processing of phosphate rock, which is mainly composed of apatite, a calcium phosphate with the general formula $Ca_{10}(PO_4)_6X_2$, $X = OH^-, F^-, Cl^-$. The main requirement from the manufacturers of elemental P via the thermal route is a low (< 1%) iron content, while the wet route requires low contents of cadmium, iron and magnesium. Aluminium poses problems for both processes.

Struvite contains magnesium, which causes problems for the wet route by interfering with the formation of large crystals of calcium sulphate, and ammonium that causes problem for the thermal route [67]. Additionally, the P content of struvite is 12.6% (28.9% P_2O_5), which is lower than most phosphate rock sources, which typically have P content of 35% P_2O_5 (15.2% P) [67]. Therefore, struvite is not the perfect product as a secondary raw material to substitute phosphate rock in the existing phosphate rock infrastructure, but is limited to direct fertilizer use. Potassium struvite has been used by Thermphos as a secondary raw material. Because potassium struvite does not contain ammonium, it has been possible to use it in the thermal route [79].

The recovery of phosphorus in the form of calcium phosphate could be a better alternative for the recycling and reuse of phosphorus in the existing phosphate industry for the processing to fertilizer or other commodities.

2 OBJECTIVES

2.1 Problem definition

Phosphorus recovery and recycling has been recognized by the industry, policy makers and the scientific community as an important step towards food security within the Circular Economy framework. Less attention has been paid to the recovery and recycling of another macronutrient, namely potassium. Phosphorus and potassium are found in wastewater and can be precipitated in the form of potassium struvite, a mineral that can be returned to soils as fertilizer and decrease the dependence on imported mineral fertilizer. However, the presence of ammonium, a third nutrient found in wastewater, is inhibitory to potassium struvite formation and needs to be removed. Conventional nitrification-denitrification treatment of centrate is expensive due to the high energy consumption and the need for organic carbon. The use of partial nitritation-anammox is a proven economically more feasible technology for nitrogen removal in side-stream, but has not yet been assessed as a pre-treatment for subsequent potassium struvite recovery.

The recovery of phosphorus through ammonium struvite precipitation is a proven technology, but requires input in terms of aeration energy and chemicals. Precipitation can also be induced biologically by gradients within biofilms without the addition of chemicals. The phenomena is quite known, but the feasibility biologically precipitated calcium phosphate by partial nitritation-anammox granular sludge has not been assesed as a recovered phosphorus product from wastewater.

2.2 Objectives

The main objective of the thesis was to evaluate the combination of partial nitritation-anammox and phosphorus recovery in the treatment of digested sludge liquors (centrate). The specific objectives were the following:

- To assess the possibility to recover potassium together with phosphorus in the form of potassium struvite from municipal wastewater, using PNA as a nitrogen-removal step
- To assess the potential of biologically induced precipitation by granular anammox sludge as a possible phosphorus recovery product
- Assessing PNA as an alternative to conventional CO_2 stripping by aeration
- Assessing the faith of nitrogen, phosphorus and potassium through the sludge line in order to estimate the amount of nutrients available for recovery and the best point where to recover potassium

3 MATERIALS AND METHODS

3.1 Operation of the lab-scale Chem-P PNA reactor

A lab-scale PNA reactor was started up and operated in order to provide effluent for precipitation experiments conducted to assess the viability of potassium recovery from centrate. Granules with a high inorganic content were harvested from the reactor and analysed and evaluated as a possible phosphorus recovery product.

The PNA was started up with 1 L of inoculum from a lab-scale granular PNA reactor operated under mainstream conditions. The reactor consisted of a stainless steel container fitted with a top-stirred mixer (Figure 3.1a) and was operated as a sequencing batch reactor (SBR). Three taps on the side were used for effluent, influent and MLSS sampling respectively (Figure 3.1b). Granules with a high inorganic content that settled in the bottom of the reactor were sampled from the bottom tap. The minimum working volume of 10 L was regulated by the location of the effluent tap. The maximum volume was determined by the amount of centrate fed in each cycle and was continuously increased to increase the nitrogen loading rate. The temperature was kept at 25°C using a water jacket. Air was supplied via a aeration stone at the bottom of the reactor. The air flow was regulated by an airflow meter. pH and dissolved oxygen (DO) were monitored using probes (Orbipac CPF81 and Oxymax W COS41 respectively, Endress +Hauser) connected to an online monitoring system (Liquisys M, Endress +Hauser).

A 6-hour batch cycle was configured as follows: 10 repeated sequences of aerated feed and reaction (30 min each), followed by anoxic reaction (40 min), settling (10 min) and drawing (10 min) (Figure 3.2). The nitrogen load was increased by lengthening the feed and simultaneously decreasing the aerated reaction phase while maintaining the total length of 30 minutes.

The reactor was fed with centrate collected from WWTP Terri (Cornellà de Terri, Catalonia, Spain) every three weeks. After collection, the centrate was kept in a cold storage tank at 4°C from where it was fed to the reactor via a peristaltic pump.

Effluent was sampled twice a week, while the influent was sampled on the day of collection and then once a week from the cold storage tank. MLSS samples were taken once a week in the beginning of the aerated feed and reaction phase. This represents the minimum volume of the reactor, and was chosen as it remains constant while the maximum volume change depending to the volume of centrate fed to the reactor.

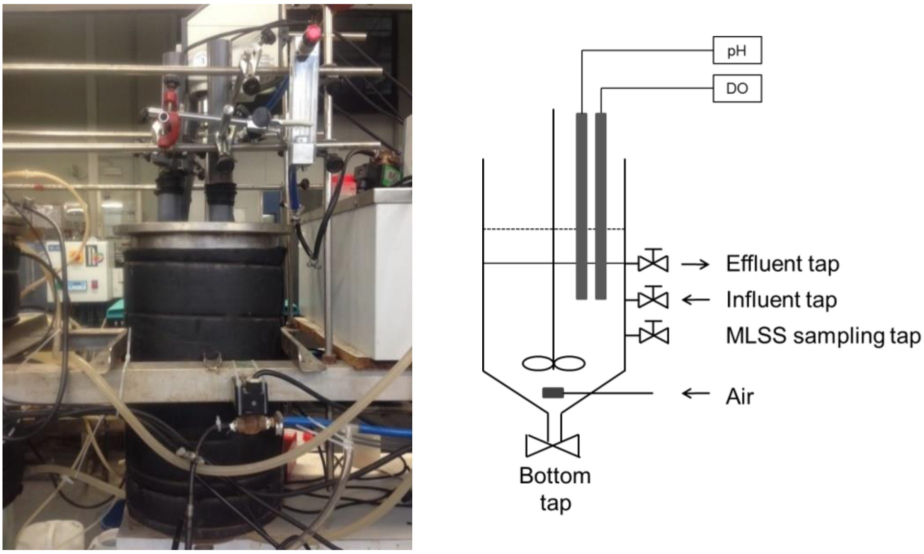


Figure 3.1 Photo and outline of the lab-scale PNA reactor

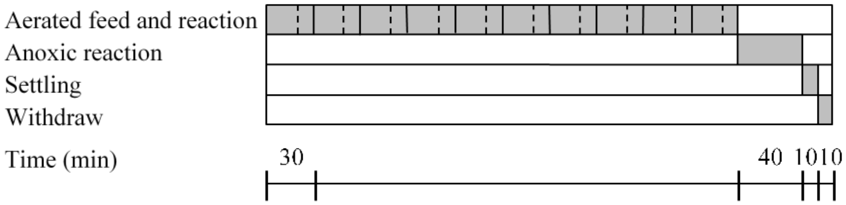


Figure 3.2 Reactor operation configuration

3.2 Origin and collection of centrate fed to the Chem-P PNA reactor

WWTP Terri treats 10 000 m^3 of urban and industrial wastewater per day (design load 186 560 p.e.). Primary and secondary sludge is sent to a mesophilic digester (37°C) with a residence time of approximately 40 days. Phosphorus is removed chemically using iron chloride, which is dosed prior to the entrance of the secondary settler. The composition of the Chem-P centrate together with the Bio-P centrate is presented in Table 3.1.

Table 3.1 Composition of the Chem-P and Bio-P centrates

Species	Unit	Concentration	
		Chem-P centrate	Bio-P centrate
$P\text{-}PO_4^{3-}$	mg L^{-1}	57±27	246±16
$N\text{-}NH_4^+$	mg L^{-1}	966±130	1218±115
Ca	mg L^{-1}	79±33	108±24
Alkalinity	mg $CaCO_3$ L^{-1}	4401±479	3407[a]

a) Converted from meq L^{-1} (single sample)

3.3 Origin and collection of Bio-P PNA effluent

Effluent was collected from the pilot-scale PNA reactor operated by Aquafin and placed at WWTP Antwerp South. The reactor has a volume of 2.0 m^3, consists of floccular biomass and is fed with centrate. Effluent from the pilot was brought to the lab in plastic containers where it was stored at room temperature until the date of the precipitation experiment (maximum two days).

WWTP Antwerp South (Antwerp, Belgium) treats 77,570 m3 d^{-1} of municipal wastewater (design load is 190 000 p.e.). The actual load based on BOD5, represents 171 000 p.e.. The plant applies biological P-removal and the water line consists of pre-treatment, anaerobic compartment, four aerobic tanks, and nine clarifiers. The plant receives sludge from other WWTPs and the external sludge is fed to the anaerobic digester together with the thickened sludge from the plant. The digester is mesophilic with a residence time of 21 days.

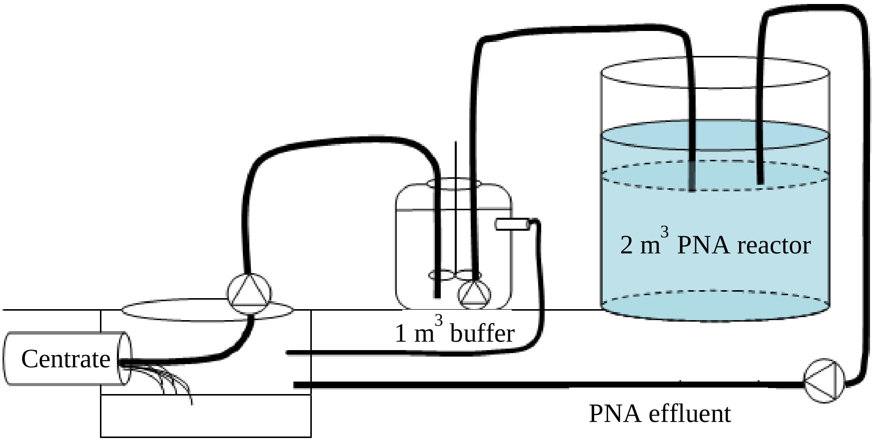


Figure 3.3 Outline of the pilot-scale PNA reactor operated by Aquafin (Antwerp, Belgium)

3.4 Lab-scale precipitation experiments in batch

The influence of Mg:P ratio, pH and temperature on nutrient removal was investigated in lab-scale batch experiments conducted on effluent from two different PNA reactors: i) a lab-scale reactor fed with centrate from a WWTP operated with chemical P-removal (Chem-P) and ii) a pilot-scale reactor fed with centrate from a WWTP operated with biological P-removal (Bio-P). Table 3.2 presents the experimental outline. The experiments were carried out in duplicates in glass reactors fitted with water jackets for temperature control. The pH and Mg:P ratio were adjusted with magnesium chloride and sodium hydroxide respectively. The solutions were mixed for 1 hour using magnetic stirrers. After the experimental time, liquid samples were pipetted from the supernatant. The solids were allowed to settle for 30 min before the supernatant was discarded, and the solids were captured and analysed.

Table 3.2 Experimental conditions for batch experiments assessing the influence of pH, temperature, and Mg:P ratio on nutrient removal

Serial	pH	Temp.	Mg:P ratio
		°C	mol/mol
1	10	25	0.75:1
2	10	25	1.0:1
3	10	25	1.25:1
4	10	25	1.5:1
5	10	25	1.75:1
6	8	25	1.25:1
7	9	25	1.25:1
8	10	25	1.25:1
9	11	25	1.25:1
10	12	25	1.25:1
11	10	20	1.25:1
12	10	25	1.25:1
13	10	30	1.25:1
14	10	35	1.25:1
15	10	40	1.25:1

3.5 Saturation index calculation / Chemical equilibrium simulations

In this work, the saturation index (SI) was used as an indication on what minerals that would precipitation from a given solution. The saturation index (SI) was calculated using the software Visual MINTEQ (version 3.0). The degree of saturation, Ω, and the saturation index, with respect to the mineral phases are defined as follows:

$$\Omega = \frac{\mathrm{IAP}}{K_{\mathrm{sp}}}, \qquad \textbf{Eq. 3.1}$$

$$\mathrm{SI} = \log \Omega = \log \mathrm{IAP} - \log K_{\mathrm{s}}, \qquad \textbf{Eq. 3.2}$$

where IAP is the ion activity product and K_{sp} is the solubility product of the precipitated mineral. The solution is considered to be oversaturated when the SI is above zero, at saturation when zero, and undersaturated when less than zero.

The IAP is the product of activities of the particular ions for the mineral considered. The activity, a, of an ion is calculated according to the following formula:

$$a = \gamma \cdot C \qquad \textbf{Eq. 3.3}$$

where γ is the activity coefficient and C is the molar concentration of the ion. In Visual Minteq the activity coefficient is calculated with the Davies equation (an extension of the Debye-Hückel equation) according to the following formula:

$$-log\gamma_i = \frac{1}{2} z_i{}^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \qquad \textbf{Eq. 3.4}$$

where z is the charge of the particular ion and I is the ionic strength of the solution.

The values for Ks are derived from the Visual Minteq thermodynamic database. Potassium struvite was not included in the standard MINTEQ database and was therefore added with log K_{sp} = -11.68 according to Luff and Reed (1980).

3.6 Analytical techniques

For the operation of the lab-scale PNA reactor, the precipitation experiments on Chem-P PNA effluent and the analysis of the inorganic core of PNA granules, the following analytical techniques were used: Analysis of $N\text{-}NH_4^+$, total suspended solids (TSS), volatile suspended solids (VSS) and alkalinity were performed according to Standard Methods [87]. Concentrations of $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, $P\text{-}PO_4^{3-}$, Mg^{2+} and Ca^{2+} were analysed using ion chromatography (Dionex

IC5000) after being filtered with 0.2 µm filters. In the experiments on Chem-P PNA effluent, Mg^{2+} and Ca^{2+} were analysed using cuvette tests (Hach LCK327) read with a spectrophotometer (Hach DR3900) after being filtered using 0.2 µm filters.

XRD analysis was performed on a Bruker D8 Advance. The EDX analysis was performed with a Bruker X-Flash detector 5010, with a detection limit of 129eV, coupled to an SEM (ZEISS DSM960A). Heavy metals were analysed using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) (Agilent 7500c). Calcium, phosphorus, magnesium, potassium and iron were analysed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Agilent 5100). The samples for ICP were digested with a mix of nitric and hydrochloric acid in duplicate using an Etos Sel microwave from Milestone. The samples were digested in two steps: ramping up to 180°C over 10 minutes and then digested for 20 min at 180°C.

In the experiments on Bio-P PNA effluent, samples for $P\text{-}PO_4^{3-}$ and $N\text{-}NH_4^+$ were immediately filtered using 0.45 µm filters and analysed using cuvette tests (Test 0-79 and Test 0-60, Macherey-Nagel) read with a spectrophotometer (PF-12, Macherey-Nagel). Remaining filtered samples were acidified to pH < 4.5 with HCl in order to prevent further crystallization and analysed for all other ions using ICP-OES (Optima 8300, Perkin Elmer), which was also used to analyse the composition of the recovered precipitates.

4 RESULTS

4.1 Biologically induced precipitation in partial nitritation-anammox granular sludge

Phosphorus recovery by precipitation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) has been implemented in the full-scale treatment of centrate during the past decade. The precipitation of struvite is induced by an increase in pH, through CO_2 stripping and/or addition of alkali, and addition of a magnesium source. However, precipitation can also be induced biologically by gradients in ion concentrations and pH created inside or between cells. In this chapter, biologically induced precipitates formed in PNA granular sludge were analysed for their composition, and evaluated as a potential phosphorus recovery product from municipal wastewater.

Results from this chapter has been published in the following journal:

Johansson, S., Ruscalleda, M., Colprim, J.. Phosphorus recovery through biologically induced calcium phosphate precipitation by partial nitritation-anammox granular biomass. *Chemical Engineering Journal*, 2017, 327:881-888.

4.1.1 Motivation

Phosphorus recovery by precipitation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a well-established technology for phosphorus recovery from wastewater. Precipitation occurs when the IAP exceeds the solubility product of the precipitated mineral (See section 1.3.2.4). The IAP is determined both by the concentration of the corresponding ions, but is also strongly influenced by the pH. In the industrial crystallization of struvite, precipitation is induced by the addition of a magnesium source and increase of the pH by CO_2 stripping and/or alkali dosing. However, precipitation can also be induced biologically by gradients in ions and pH caused by the biochemistry of microorganisms [88]. This phenomena is named biomineralization.

In EBPR, part of the phosphorus removal is indeed considered to be due to precipitation of calcium phosphate initiated by the elevated phosphate concentrations during the phosphorus release in the anaerobic stage [89,90]. Similarly, a part of the phosphate removal by aerobic granular sludge has been shown to be due to the formation of calcium phosphate inside the granules [91,92].

Presence of calcium phosphate has also been confirmed in anammox granular sludge where it has been found to be important for granule mechanical strength [93], as well as functioning as a biomass carrier [94]. Since biomineralization allows for precipitation induced by microorganisms, it offers the possibility of phosphorus precipitation without the addition of chemicals. Furthermore, the accumulation of minerals increases the gravity of granules and leads them to settle to the bottom of the reactor where they can be easily harvested [93]. Therefore, phosphate minerals formed through biomineralization have potential as a phosphorus product recovered from wastewater.

As with any product recovered from wastewater, the presence of harmful substances is a concern, and an evaluation of the metals content in calcium phosphate formed by PNA sludge has been lacking. The current EU fertilizer legislation is being revised and is proposed to include recovered phosphorus products, as well as introducing limits to heavy metals content in fertilizer [60]. Although the majority (85%) of mined phosphate rock is used for fertilizer production [3], there is a small but considerable amount used by the elemental phosphorus industry. This sector has expressed concern about the increasing levels of impurities in phosphate rock and interest in recovered phosphorus products, as long as they fulfil their requirements in terms of purity [67].

4.1.2 Objectives

The objective of this chapter was to characterize the inorganic core found in granular PNA sludge. Granules were harvested and analysed for their composition. Once the mineral had been defined as a calcium phosphate it was evaluated as a potential phosphorus recovery in accordance to the proposed revision of the EU fertilizer legislation and the requirements from the elemental phosphorus industry. The

The biochemistry causing the mineralisation was elucidated and the scope for recovery as well as trade off effects between nitrogen removal and phosphorus recovery were discussed.

4.1.3 Experimental approach

Granules with a high inorganic content were harvested from the bottom of the lab-scale Chem-P PNA reactor and evaluated for their possible application as a recovered phosphorus product. The structure, chemical composition and type of mineral were studied using microscopy, quantitative elemental analysis and direct spectral analysis. The heavy metals content was analysed and compared to the proposed EU limits for P fertilizer and the requirements from the elemental P industry.

The morphology of the granules was observed with a stereomicroscope (ZEISS Stereo Discovery V12). MLSS samples for X-ray diffraction (XRD) analysis were filtered, air-dried over night before and then grinded before analysis.

Sampled granules were rinsed with milliQ water and cracked open for SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray analysis) analysis of the interior of the granules. A group of granules were cut using a cryo-microtome (PowerTome X, RMC Products) to prepare the samples for elemental mapping. The sample for ICP analysis was taken from the bottom of the reactor and rinsed with milliQ water. Subsequently, it was dried at 105°C overnight.

4.1.4 Results and Discussion

4.1.4.1 Reactor performance

A PNA reactor was started up with an initial biomass concentration of 0.7 g VSS L^{-1}. The VSS concentration gradually increased together with the nitrogen loading rate (NLR). Because of the low initial VSS concentration, no sludge was wasted during the 200 days that the reactor was in operation for this study. Mean values of the bulk liquid pH, VSS, VSS/TSS ratio, nitrogen loading rate, as well as the nitrogen removal and the molar ratio of NO_3^- produced over NH_4^+ consumed are all shown in Table 4.1.

Table 4.1 Mean operational parameters during 200 days of start-up and operation

Time period (days)	Reactor pH	VSS (g L^{-1})	VSS/TSS (%)	NLR (g N-NH_4 L^{-1}, d^{-1})	N-removal (%)	$NO_3^-{}_{,prod}/NH_4^+{}_{,cons}$ (mol mol^{-1})
0–50	7.73	0.79	92	0.085	60	0.19
50–100	7.50	0.90	94	0.148	61	0.12
100–150	7.41	1.07	65	0.214	74	0.09
150–200	7.22	1.45	62	0.308	66	0.10

The centrate fed to the reactor had a pH of 8.1 ± 0.2 (Table 4.6). The reactor pH was not regulated, and thus the bulk liquid pH was an effect of the biological activity. Nitrifying AOBs has an acidifying effect, while anammox organisms consume protons. The net effect of the PNA process however, is a production of protons and a decrease in pH (Equations 4.1 – 4.3) show a simplified version of the different processes involved). Due to this, the reactor pH was lower than the centrate (Table 4.1).

Nitritation: $1.3NH_4^+ + 1.95O_2 \rightarrow 1.3NO_2^- + 2.6H^+ + 1.3H_2O$ **Eq. 4.1**

Anammox: $NH_4^+ + 1.3NO_2^- \rightarrow 0.26NO_3^- + 1.02N_2 + 2H_2O$ **Eq. 4.2**

PNA: $NH_4^+ + 0.85O_2 \rightarrow 0.11NO_3^- + 0.445N_2 + 1.43H_2O + 1.13H^+$ **Eq. 4.3**

The ratio between the moles of ammonium consumed over the moles of nitrate produced ($NO_3^-{}_{,\,prod}/NH_4^+{}_{,\,cons}$) can be used as a way to monitor the microflora of the reactor. Theoretically, the combined PNA process produces 0.11 moles of nitrate for each mole of ammonium oxidized. A value above 0.11 indicate growth of NOB ($NO_3^-{}_{,\,prod}/NH_4^+{}_{,\,cons}$ ratio for full nitrification is 1.0).

Such an elevated $NO_3^-{}_{,\,prod}/NH_4^+{}_{,\,cons}$ ratio was noted initially, but after 50 days of operation, a stable microbial community of AOB and anammox with suppressed NOB growth was obtained, as the $NO_3^-{}_{,\,prod}/NH_4^+{}_{,\,cons}$ ratio was close to the stoichiometric of 0.11. The nitrogen load was gradually increased up to 0.308 g N-NH_4^+ L^{-1} d^{-1} and nitrogen removal reached 80%, with specific nitrogen removal of 0.180 g N-NH_4^+ (g VSS)$^{-1}$ d^{-1}.

The feed was stored in a cold storage tank that was initially equipped with a mixer. However, an increase in pH and subsequent precipitation was noted in the tank during storage of the feed. This was assumed to be due to CO_2 stripping caused by the stirring of the feed. Therefore the mixer was disabled on operational day 80 and after this less precipitation was observed in the storage tank. As a consequence of the decreased precipitation in the feed tank, there was an increase of free ions in the feed. After 100 days of operation, a drop in the organic fraction of the MLSS was noted, with a decrease in the VSS/TSS ratio from 92-94% to 65%. The increase in the inorganic fraction of the biomass is therefore considered to have been initiated by the increased concentration of ions in the feed to the reactor following the disabling of the mixer in the storage tank.

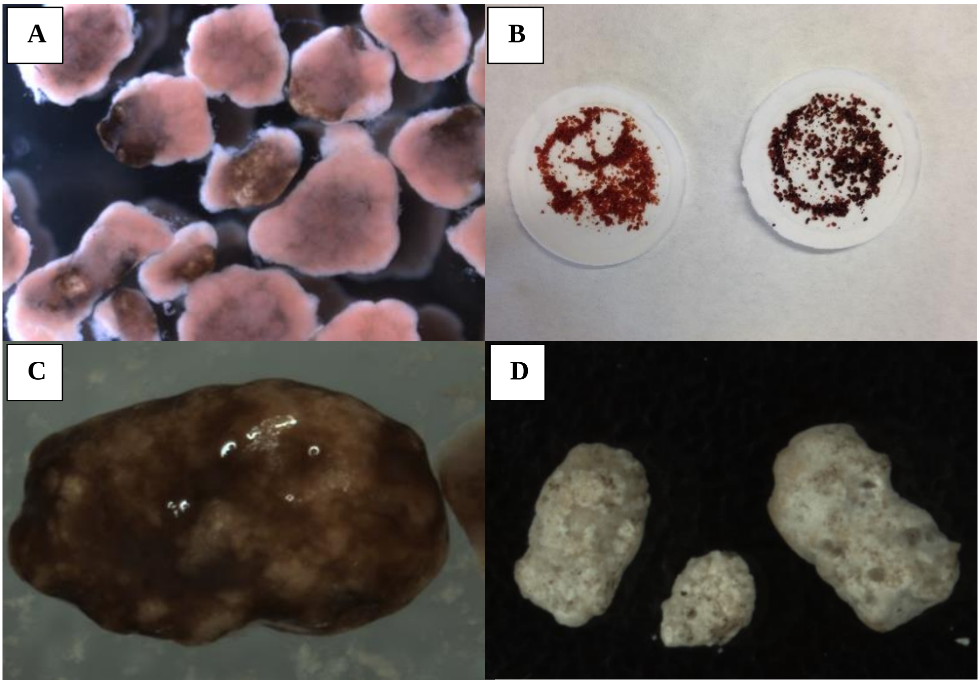


Figure 4.1 Granules from the MLSS (a), granules from the MLSS (left) and bottom of reactor (right) (b), granule from the bottom of the reactor (c), inorganic core after incineration at 550°C (d)

4.1.4.2 Granule structure and distribution in reactor

The granules in the MLSS had the typical orange-red colour of anammox biomass. However, after the drop in the VSS/TSS ratio was noted, granules with a dark and hard core were observed. Figure 4.1a shows a sample from the MLSS (sampled on operational day 199) observed under the stereomicroscope and the mineral core can be seen embedded in the biomass, indicating that the mineralization was biologically induced. This theory is further strengthened by the fact that no precipitation was noted in the bulk liquid nor any scaling on the walls.

Over time, dark-brown granules with a high inorganic content (>70%) accumulated at the bottom of the reactor. Although the reactor was being mixed, the density of these mineralized granules was too high to keep them in suspension by mixing. The MLSS was therefore separated by gravity, with increasing solids concentration and inorganic content towards the bottom (Table 4.2). The stratification could also be seen visually, with reddish coloured granules in the MLSS and dark-brown granules at the bottom of the reactor (Figure 4.1b). Figure 4.1c shows a granule sampled from the bottom of the reactor, with almost no biomass attached, and in Figure 4.1d the mineral core remaining after incineration at 550°C can be seen.

Table 4.2 Suspended solids and inorganic fraction from different sample taps

Sample port	TSS (g/L)	Inorganic fraction (% of TSS)
Effluent tap (top)	1.5 ± 0.05	6.4
Influent tap (middle)	1.9 ± 0.00	10
MLSS sampling tap (lower)	2.2 ± 0.03	15
Bottom tap (bottom)	22 ± 5.1	71

The interior of a granule, as captured by SEM, (Figure 4.2) shows a porous beehive-like structure similar to the one observed by Mañas et al. (2011) in aerobic granules. This is suggested to be due to precipitate formation around cells. *Epicellular* mineralization, that is, the formation of minerals along the surface of the cell wall, is a typical feature of biologically induced mineralization, as the cell wall is the site of metabolic fluxes of ions in and out of the cell [88].

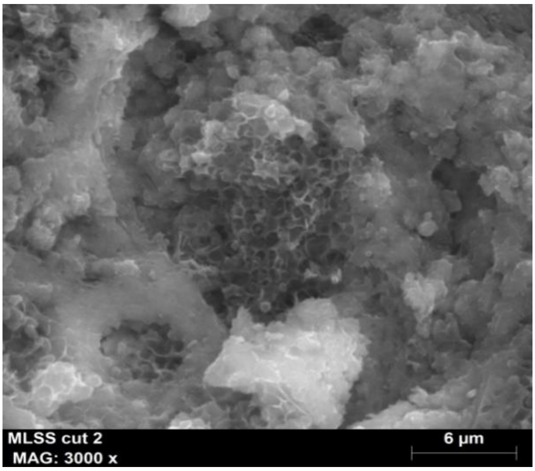


Figure 4.2 SEM picture showing the inner part of a granule

4.1.4.3 Elemental composition and distribution in PNA granules

Table 4.3 presents the composition of the granules as measured by ICP-OES. The main elements were calcium (33.5±1.9 wt%) and phosphorus (15.8±0.99 wt%), with some traces of magnesium (<1 wt%) and potassium (<1 wt%). This indicates the presence of a calcium phosphate mineral, while the low amount of magnesium excludes the presence of struvite in any major quantities. The molar ratio of calcium over phosphorus was 1.64, which is close to the theoretical ratio of 1.67 for hydroxyapatite ($Ca_5(PO_4)_3(OH)$). The composition of the harvested granules were similar to phosphate rock, which is mainly composed of apatite, a calcium phosphate with the general formula $Ca_{10}(PO_4)_6X_2$, X = OH^-, F^-, Cl^- and a phosphorus content of 13-17.5 wt% of P [86].

Table 4.3 Quantitative elemental composition of granules (ICP-OES)

Element	Composition (wt%)
Ca	33.5 ± 1.94
P	15.8 ± 0.99
Mg	0.24 ± 0.00
K	0.12 ± 0.004

In a solution containing calcium and phosphate, a number of calcium phosphates may form, depending on the pH and solution composition [47], but they are likely to transform into the thermodynamically most stable phase, which at standard conditions is hydroxyapatite.

Precursor phases to hydroxyapatite include dicalcium phosphate dehydrate (brushite) (DCPD), octacalcium phosphate (OCP), tricalcium phosphate (TCP) and amorphous calcium phosphate (ACP) [47,49]. They all have lower Ca/P ratios compared to hydroxyapatite (see Table 4.4). The slightly lower Ca/P ratio of the granules compared to hydroxyapatite could be explained by the presence of precursor phases that have not yet matured into hydroxyapatite.

Table 4.4 Calcium phosphates, their molecular formula and solubility product, adapted from Valsami-Jones (2001)

Name	Abbreviation	Formula	pK_{sp}	Ca:P ratio
Brushite	DCPD	CaHPO4·2H2O	6.60	1.0
Monetite	-	CaHPO4	6.90	1.0
Octacalcium phosphate	OCP	Ca4H(PO4)3·2.5H2O	46.9	1.33
Amorphous calcium phosphate	ACP	Ca3(PO4)2	28.9	1.5
Hydroxyapatite	HAP	Ca5(PO4)3OH	58.3	1.67
Tricalcium phosphate	TCP	Ca3(PO4)2	undefined	variable

Figure 4.3 shows the intersection of two cryosected granules and the elemental mapping of the elements of phosphorus (P), calcium (Ca) and carbon (C). The elemental mapping reveals a homogenous distribution of phosphorus and calcium over the intersection surface. Carbon was only sparsely detected in the interior, but was found on the exterior of the granules. The carbon detected can be associated with biomass and is also present in the coating medium used to prepare the samples for the SEM-EDX. The results show that biomass is not incorporated into the inorganic structure.

Apatites have a natural affinity for metals [67]. Therefore, it is not unlikely that some metals would be incorporated into the crystal matrix. However, the presence of iron and aluminium was less than 1%, as detected by EDX. The presence of iron and heavy metals will be further discussed in the section 4.1.4.5 Purity of the product.

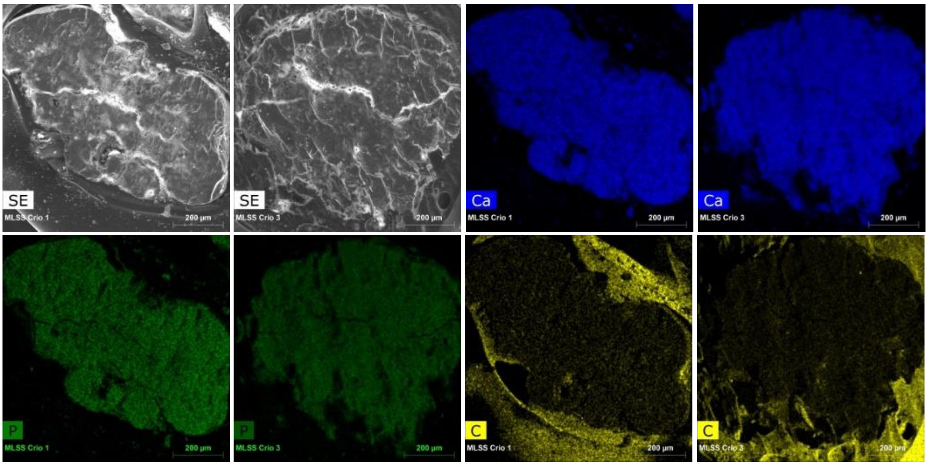


Figure 4.3 SEM images of two cryosected granules and elemental mapping using EDX of P, Ca and C

4.1.4.4 Identification of mineral species in PNA granules

Figure 4.4 shows the XRD diffractogram of a dried and ground sample from the MLSS. It suggests the presence of four types of crystalline calcium phosphates: hydroxyapatite ($Ca_5(PO_4)_3(OH)$), apatite ($(Ca_4Na_{0.01}Mg_{0.02})(Ca_6Na_{0.13}Mg_{0.03})(PO_4)_6$), chloroapatite ($Ca_5(PO_4)_3Cl$) and calcium sulphide phosphate ($Ca_{10}(PO_4)_3S$). A second XRD analysis of dried and ground granules from the bottom of the reactor (data not shown) showed a similar pattern, with the presence of crystalline hydroxyapatite and apatite, and two other crystalline calcium phosphates: oxyapatite ($Ca_{10}(PO_4)_6O$) and fluorapatite ($Ca_5(PO_4)_3F$). It should be noted that the granules sampled from the bottom of the reactor were dried at 105°C, while the MLSS sample was dried at room temperature. It is possible that the higher temperature caused the dehydration of hydroxyapatite to oxyapatite.

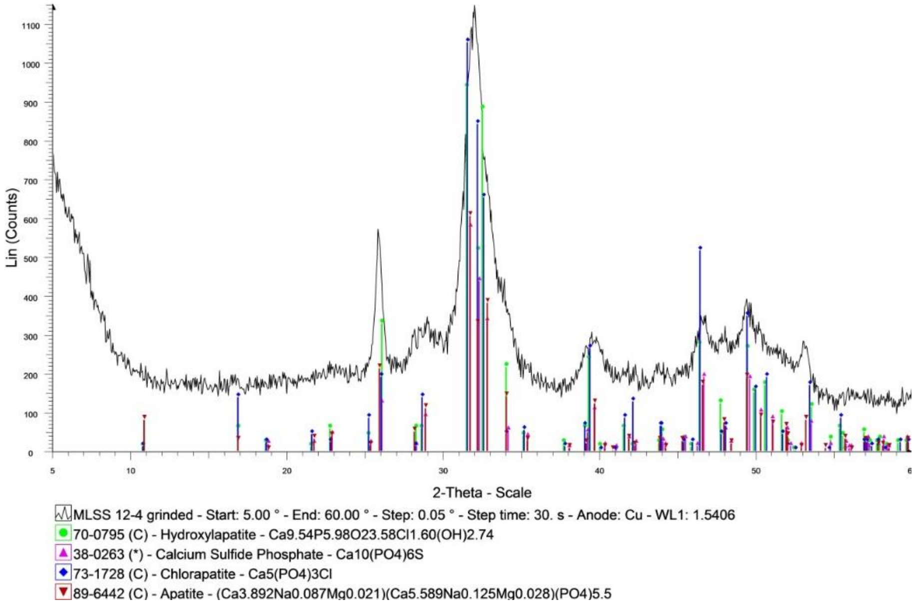


Figure 4.4 XRD diffractogram for dried granules from the MLSS

Na and Mg were only detected in minor amounts (< 1%) by both EDX and ICP, and S was not detected by any of the methods. Therefore, the presence of calcium phosphates containing these minerals can only be minor and is therefore disregarded. Chloride and fluoride are not measured by any of the methods used in this study, so their presence cannot be ruled out. Both chloro- and fluoroapatite are also common members of the apatite family and are naturally found in phosphate rock. However, as they were not coherently detected by XRD, hydroxyapatite is considered to be the main mineral.

The XRD only detects crystalline structures but the background noise suggests the presence of amorphous compounds. The hydroxyapatite precursors are more water soluble, indicating a lower degree of crystallinity compared to hydroxyapatite. Following the results of the ICP analysis, the Ca/P ratio of the granules (1.64) is close to but slightly lower than the theoretical ratio of hydroxyapatite (1.67). The presence of ACP or other amorphous precursor phases may explain the slightly lower Ca/P ratio but also contribute to the background noise detected by XRD.

4.1.4.5 Purity of the product

Table 4.5 shows the content of phosphate (expressed as P_2O_5) and metals in the granules from this study, calcium phosphate pellets recovered through chemical precipitation from wastewater (Crystalactor), and average values of phosphate rock reserves and P fertilizer used in Europe. The limits of heavy metals content proposed to be included in the EU Fertilizer Regulation, as well as the requirements of the elemental phosphorus industry, are listed together with the phosphorus products in Table 4.5 for comparison.

The granules recovered from the PNA reactor compared well with calcium phosphates pellets recovered through chemical precipitation from wastewater and average P fertilizers used in Europe. They had a higher phosphate content and comparable or lower content of metals. It is clear that cadmium is the metal of greatest concern for conventional P fertilizer, which does not comply with the strictest standards of the proposed revision of the legislation. Cadmium occurs naturally in phosphate rock reserves, although with geographical differences, and the cadmium present in mined phosphate rock end up in the resulting fertilizer product.

The amounts of heavy metals detected in the granules on the other hand, complied well with the proposed EU limits for P fertilizer. The only exception was chromium, where compliance could not be evaluated. This was due to the fact that only Cr VI, the highly toxic and carcinogenic oxidation state, is proposed to be regulated, while the ICP analysis done in this study reports chromium as the total amount without specifying the oxidation state. Therefore, the amount of the chromium present in the granule that is found in the form of Cr VI would need to be further examined. However, the total chromium content of the harvested granules was lower compared to average P fertilizer on the market.

The phosphorus industry is mainly concerned about a sufficiently high phosphate concentration and, in relation to metals, limited amounts of copper, zinc and iron. The recovered granules passed all of these requirements. Furthermore, phosphate products recovered in the form of calcium phosphate are welcomed by the industry, while the presence of magnesium and ammonium interfere with the process and has hindered struvite as a secondary phosphate rock candidate [67].

The organic content of the granules sequestered from the bottom of the reactor was less than 30 wt%, but the organic fraction might still have to be removed before the product can be accepted by the industry. The fact that the organics were mainly found on the exterior of the granules and not incorporated into the mineral structure (section Elemental composition and distribution in PNA granules) would facilitate the removal.

Table 4.5 Phosphate and metals content of phosphate products compared to the proposed EU limits for P fertilizer and requirements from the P industry

Parameter	Unit	Granules[a]	Crystalactor pellet[b]	P fertilizer[c]	Phosphate rock[d]	Requirements P industry[e]	Proposed EU limits[f]
P_2O_5	wt%	36	26	19	36	≥25	≥5
Cd	mg (kg P_2O_5)$^{-1}$	0.041	7.7	38	69	-	20-60[i]
As	mg (kg DW)$^{-1}$	4.7	2	7.6	11	-	60
Cr	mg (kg DW)$^{-1}$	37	8	90	188	-	2[ii]
Cu	mg (kg DW)$^{-1}$	10	-	-	-	500	-
Fe	mg (kg DW)$^{-1}$	878	1260	-	-	10 000	-
Hg	mg (kg DW)$^{-1}$	0.21	-	-	0.05	-	2
Ni	mg (kg DW)$^{-1}$	0.85	8	15	29	-	120
Pb	mg (kg DW)$^{-1}$	0.29	-	2.9	10	-	150
Zn	mg (kg DW)$^{-1}$	25	310	166	-	1000	-

-, not determined

[a] This study (ICP-OES and ICP-MS); [b] Driver et al. (1999); [c] Mortvedt (1996); [d] Nziguheba and Smolders (2008); [e] Schipper et al. (2001); [f] [97]

[i] 60 mg/kg P_2O_5 at the date of application of the regulation, 40 mg/kg P_2O_5 3 years after application and 20 mg/kg P_2O_5 12 years after application; [ii] Cr VI

4.1.4.6 Inorganic core of hydroxyapatite in PNA granules

The mean values of the centrate used during the operation of the reactor are shown in Table 4.6, alongside the calculated saturation indexes for hydroxyapatite, calcite and struvite. Hydroxyapatite clearly had the highest saturation index, meaning it is thermodynamically the most stable phase under the conditions defined. This corresponds well with the results of the ICP and XRD analyses, which both pointed to hydroxyapatite being the main constituent of the mineral core of the granules.

Calcite and struvite had much lower saturation indexes and, accordingly, neither of these compounds were detected by spectral analysis performed on the granules. The SI calculations were performed on the centrate and, as the PNA process consumes carbonate as well as ammonium, the saturation index for struvite and calcite is expected to be even lower inside the granules.

Table 4.6 Centrate composition and SI of hydroxyapatite, calcite and struvite

Parameter	Unit	Centrate
T	°C	25
pH		8.1 ± 0.2
Alkalinity	(mg $CaCO_3$) L^{-1}	4401 ± 479
N-NH_4^+	mg L^{-1}	966 ± 130
P-PO_4^{3-}	mg L^{-1}	57 ± 27
Ca^{2+}	mg L^{-1}	79 ± 33
Mg^{2+}	mg L^{-1}	14 ± 8
K^+	mg L^{-1}	279 ± 40
Na^+	mg L^{-1}	345 ± 47
Cl^-	mg L^{-1}	507 ± 77
S-SO_4^{2-}	mg L^{-1}	23 ± 8
N-NO_3^-	mg L^{-1}	0.38 ± 0.32
Mineral		**SI**
Hydroxyapatite		12.9
Calcite		1.66
Struvite		0.56

However, in addition to thermodynamics, kinetics also influence the formation and growth of crystals. Ostwald's rule for multi-phase precipitation of sparingly soluble inorganic salts states that it is not generally the most stable but rather the most soluble phase that crystallizes first.

Subsequently, thermodynamic driving forces act to transform the salts into more stable phases [98].

In the case of the formation of crystalline hydroxyapatite, the precursor phases are more water soluble and form first, and are then transformed into the stable form of hydroxyapatite. Granules are usually discussed in terms of retention of biomass, but it seems that they are also playing an important role in the retention of amorphous precursor phases and allow sufficient retention for the transformation into hydroxyapatite that, once formed, has poor water solubility. No crystals were detected in the bulk liquid or on the walls of the reactor, despite the high SI of hydroxyapatite. This indicates that any formation of calcium phosphates outside the granules are re-dissolved before they reach to transform into hydroxyapatite, while the granules allow for the growth and accumulation of an inorganic core of crystalline hydroxyapatite.

The findings are in line with other studies on biomineralization in different types of granular sludge, which have also confirmed hydroxyapatite as the prevalent mineral. Mañas et al. (2011) confirmed that biologically induced precipitation of hydroxyapatite accounted for 45% of overall P removal in aerobic granules, while Tervahauta et al. (2014) demonstrated that hydroxyapatite was present in the inorganic core of anaerobic granules treating black water.

4.1.4.7 Biologically induced precipitation of calcium phosphates in PNA granules

In this study, no precipitation or scaling was noted in the bulk liquid or on the walls of the reactor, but only in association with the granular sludge, indicating that the mineralization was biologically induced. The same was reported in a full-scale anammox reactor where apatite was observed [93].

The typical operational pH of a PNA reactor is close to neutral [37], which is lower than for phosphate crystallizers which are typically operated at pH 8.0–8.5 [46]. In this study, the 50-day mean value ranged between 7.2 and 7.7 (see Table 4.1). However, the physical and biochemical properties of granular PNA sludge makes it act as a biological crystallizer. In PNA granular sludge, the anammox biomass grows in the inner anoxic zone covered by a layer of aerobic ammonium oxidizing bacteria [35,36]. The granules thus provide stratification in terms of microflora, dissolved oxygen and substrate throughout the biofilm [35,36]. Anammox bacteria anaerobically oxidizes ammonia to nitrogen gas with nitrite as the electron acceptor ([31]. The reduction of carbonate consumes protons, with a subsequent increase in pH. The decrease in carbonate simultaneously decreases the alkalinity, which further facilitates changes in pH. Elevated internal pH has accordingly been measured inside PNA granules [100].

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \\ \rightarrow 1.02N_2 + 0.26NO_3^- + 2.03H_2O + 0.066CH_2O_{0.5}N_{0.15} \qquad \textbf{Eq. 4.4}$$

Although formation of calcium phosphate minerals in anammox and PNA sludge has been confirmed, the exact microbiological mechanisms are still unknown. It is, for example, not known if the precipitation is linked to a specific strain, or if it is a mere side effect of microbial activity. As pH is one main driver of precipitation, it can be assumed that bulk liquid pH, as well as the anammox activity, could be important factors. The cut-off pH for good nitrogen removal with maintained mineral growth should be further examined. The granule size could also have an impact due to mass transfer resistance, and granule size has been shown to impact the inorganic content in aerobic granules [101]. To elucidate the microbiology behind the biomineralization of PNA sludge would be an interesting topic for further research.

4.1.4.8 Recovery and utilization of biologically precipitated calcium phosphate

Anammox are slow-growing organisms and PNA sludge is in demand for inoculation of new installations. Therefore, there could be a potential conflict between granules for inoculation and harvest of a phosphorus product. However, the experience from both this study and a full-scale anammox installation [93] show that there is stratification inside the reactor, where granules with a high inorganic content settle at the bottom and the granules in the mixed liquor have a higher biomass content. Since the inorganic core is biologically inactive, harvest of these granules should not conflict with demand for sludge for inoculation purposes.

Harvested granules could either be incorporated as a secondary raw material into the current infrastructure where phosphate rock is processed into fertilizer or elemental phosphorus, or spread directly onto fields, as is done with sewage sludge. If used as a secondary raw material in the phosphorus industry, the organic fraction would have to be removed, but because the biomass is attached externally, it should be easier to remove compared to impurities that are incorporated into the mineral, such as the heavy metals present in raw phosphate rock or the magnesium in struvite.

If the harvested product is to be used directly as a fertilizer, it might not be a disadvantage should some biomass remain, as this adds organic material to the soil. The P content of the granules (158 g (kg DW)$^{-1}$) is higher than that of sewage sludge (typical P content around 30 g/kg DW [102]) and thus the granules represents a concentrated source of P which facilitates handling.

How much phosphorus a PNA system can remove still needs to be deduced. Once the production potential is known a cost-benefit analysis should be done in order to evaluate the feasibility of continuous calcium phosphate harvest. A 65.8% total phosphorus removal (with an incoming phosphorus concentration of 13 mg P/L) was reported from a lab-scale anammox reactor operated on synthetic wastewater simulating effluent from a partial nitritation reactor treating centrate [103]. In a study on biologically induced phosphorus precipitation in a UASB reactor treating black water, the recovery potential was estimated to 7 g P person^{-1} year $^{-1}$, representing 2% of the incoming phosphorus [99].

4.2 Understanding nutrient flows for augmented nutrient recovery

The two previous chapters have dealt with processes to recover nutrients from wastewater. However, in order to achieve an efficient recovery, it is important to understand the flows of nutrients within the wastewater treatment plant and locate hot-spots for recovery. Such studies have been done for phosphorus and nitrogen, but similar analysis are lacking for potassium.

This chapter aims to outline the faith of the three macronutrients (N-P-K) through the sludge line of a Bio-P WWTP, with special attention to potassium, in order to better understand potential nutrient mining opportunities. The three nutrients differ in terms of load to the plant, but, as shown in this chapter; also take different routes within the plant.

Results from this chapter has been accepted for publication in the following journal:

Johansson, S., Ruscalleda, Saerens, B., M., Colprim, J.. Potassium recovery from centrate: Taking advantage of autotrophic nitrogen removal for multi-nutrient recovery. *Journal of Chemical Technology and Biotechnology*, 2019, 94(3):819-828

4.2.1 Motivation

The importance of recovery and recycling of nutrients to achieve a resource efficient and sustainable economy has been recognized by the European Commission. However, the EU action plan for the Circular Economy is only mentioning phosphorus in relation to recycled nutrients [61]. At the same time, concerns have been raised over the global negative potassium balance in agricultural soils [104], threats to food security due to the dependence on imports of potash from the few countries that control its production [2,7,105] and a general lack of understanding of the anthropogenic impact on potassium fluxes on the macroecological scale [18].

Although potassium commonly is a limiting factor for plant growth in terrestrial ecosystems [18], it is generally abundant in surface waters and therefore not considered to contribute to eutrophication. Due to this, potassium, unlike nitrogen and phosphorus, is not regulated in the EU Waste Water Treatment directive, nor in national legislations, and consequently is neither targeted nor being monitored at wastewater treatment plants.

The lack of understanding of potassium flows through the food production and consumption system is limiting the optimal implementation of recovery strategies. Efforts to recover potassium has largely been targeted at the same streams as where phosphorus typically is recovered, such as manure [45,106] and fly ash from bioenergy production [107]. Within municipal wastewater treatment plants, centrate represent a nutrient rich stream typically targeted for phosphorus recovery, but has also been subjected to studies aiming at potassium recovery using electrodialysis [108] , powder reactive sorbents [109] or, as presented in this thesis, precipitation of potassium struvite, but actual monitoring of the potassium flows through municipal WWTPs is still lacking.

4.2.2 Objectives

The aim of this chapter is to analyze and understand the flow of nutrients through the sludge line of a Bio-P WWTP in order to explore potential nutrient mining opportunities. Special focus was placed on potassium due to the lack of studies on the fluxes of this nutrient. The analysis can help decide for where and how to most efficiently recover each nutrient.

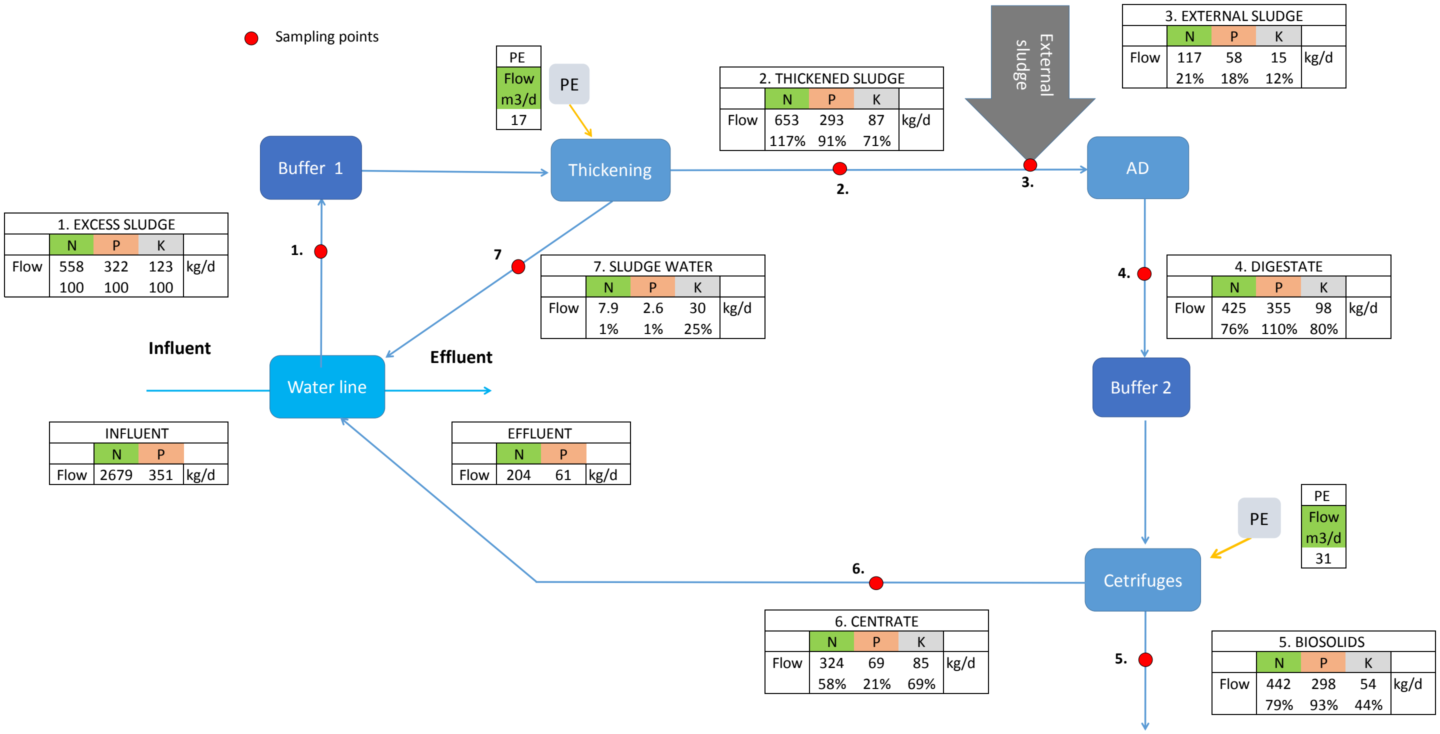
4.2.3 Experimental approach

4.2.3.1 Description of the sludge line of WWT Antwerp South

Excess sludge from the biological treatment is sent to three thickening tables for dewatering before the sludge is sent to digestion. The plant receives sludge from other WWTPs and the external sludge is fed to the anaerobic digester together with the thickened sludge from the plant. The external sludge accounts for 14 % and the thickened sludge for 86 % of the flow to the digester on a volumetric basis. The digestate passes two centrifuges in order to decrease the water content of the biosolids. After digestion the digestate is pumped into a buffer tank. The centrifuges are started once the buffer tank is full, typically three times per week. Sludge water from the thickening tables, and reject water (centrate) from the centrifuges is sent back to the inlet of the plant. The biosolids are collected daily (during weekdays) and sent to incineration. Polyelectrolyte (PE) is being dosed to the thickening tables and the centrifuges in order to promote coagulation and facilitate dewatering.

4.2.3.2 Sampling campaign and data collection

A sampling campaign was carried out over the sludge line during 6 weeks in spring time. Samples were taking at the following points: 1) Excess sludge, 2) Thickened sludge, 3) External sludge, 4) Digestate, 5) Biosolids, 6) Centrate, 7) Sludge water (Figure 4.5). Data on P and N concentrations in the influent and effluent of the plant was obtained from the company Aquafin that operates the plant. Due to that K is not regulated, it is not being monitored by the plant and no data on influent and effluent potassium concentrations was therefore available. The dry solids content of the excess sludge, the thickened sludge, the external sludge and the digestate is monitored continuously by the plant using on-line sensors.



PE
Flow m3/d
17

3. EXTERNAL SLUDGE				
	N	P	K	
Flow	117	58	15	kg/d
	21%	18%	12%	

2. THICKENED SLUDGE				
	N	P	K	
Flow	653	293	87	kg/d
	117%	91%	71%	

1. EXCESS SLUDGE				
	N	P	K	
Flow	558	322	123	kg/d
	100	100	100	

7. SLUDGE WATER				
	N	P	K	
Flow	7.9	2.6	30	kg/d
	1%	1%	25%	

4. DIGESTATE				
	N	P	K	
Flow	425	355	98	kg/d
	76%	110%	80%	

INFLUENT			
	N	P	
Flow	2679	351	kg/d

EFFLUENT			
	N	P	
Flow	204	61	kg/d

PE
Flow m3/d
31

6. CENTRATE				
	N	P	K	
Flow	324	69	85	kg/d
	58%	21%	69%	

5. BIOSOLIDS				
	N	P	K	
Flow	442	298	54	kg/d
	79%	93%	44%	

Figure 4.5 Mass flow of nutrients over the sludge line of WWTP Antwerp South

4.2.3.3 Solids mass balance

The volumetric flows of excess sludge, thickened sludge, external sludge and digestate are monitored by the WWTP by on-line flow meters. The flow of centrate and sludge water is not being monitored and had to be calculated. A solids and a water mass balance over the centrifuges and the thickening tables respectively was used for this purpose (Figure 4.6). For the calculations it was assumed that there were no solids in the PE and in the reject waters.

Solids mass balance:

$$Q_{sludge,out} = \frac{\%TS_{sludge,in}}{\%TS_{sludge,out}} \cdot Q_{sludge,in}$$

H_2O mass balance:

$$Q_{reject\ water} = \left(1 - \frac{\%TS_{sludge,in}}{100}\right) Q_{sludge,in} - \left(1 - \frac{\%TS_{sludge,out}}{100}\right) \cdot Q_{sludge,out} + Q_{PE}$$

where ‘sludge, in’ denotes excess sludge or digestate, ‘sludge, out’ denotes thickened sludge or biosolids. *Q* denotes the flow of biosolids, digestate, PE and centrate in tons/day. It is assumed that the density of digestate, PE and centrate is 1 ton m^{-1}.

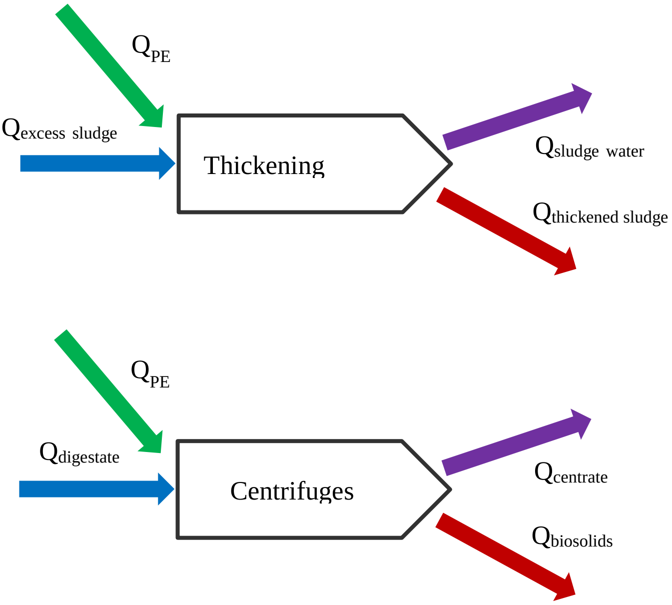


Figure 4.6 Flow diagram over the thickening tables and centrifuges

4.2.4 Results and Discussion

4.2.4.1 Nutrient load to the plant

The nutrient load to the plant was calculated to be 15.7 g N (p.e., d)$^{-1}$ and 2.25 g P (p.e., d)$^{-1}$. These values are similar to previous estimates of the load from households, 13.5 g N, 2.1 g P and 4.0 g K per person and day [110], although it should be kept in mind that the load to the plant is expressed on a p.e. basis and the load from households on a person basis. Just a small amount of the nutrients eaten as food are retained in the body, so the load from households is closely reflecting the amount of nutrients being consumed. In fact, nutrient content in wastewater can be a more accurate estimate on food consumption patterns as unfortunately not all bought food is consumed, but some is discharged of as food waste. A food basket study showed that 18 g N, 1.8 g P and 3.9 g K are bought by consumers per day [111]. Food basked surveys as well as wastewater analysis take into account food additives which can contribute to loads in the case of potassium and phosphorus [111].

The nutrient load from households depend on household consumption patterns and can therefore vary between regions or over time due to changes in behaviour. For example, it has been shown that higher meat consumption lead to higher nitrogen loads to WWTPs [16]. This could be a reason for the higher nitrogen load to the plant in this study as compared to the referenced value.

The ratio between the three macronutrients reflects the fact that nitrogen is the most abundant nutrient in plant photosynthetic tissue, followed by potassium and phosphorus [18]. The same relation between the nutrients can be seen in the amounts of each nutrient added as synthetic or mineral fertilizer to soils globally, with nitrogen being the most abundant (109 Mton N per year), followed by potassium (32 Mton K per year) and phosphorus (21 Mton P per year) [10].

4.2.4.2 Role of potassium in Bio-P plants

Potassium plays an important role in EBPR. Potassium and magnesium act as counter-ions in the poly-P chain and are co-transported together with phosphorus in and out of bacterial cells [112,113]. Consequently, phosphorus removal as well as poly-P content of biomass has been shown to be negatively affected due to potassium shortage [113].

Data on the amount of potassium that is taken up by biomass from the water phase is lacking, but various K:P and Mg:P ratios in poly-P have been proposed in the literature, ranging from 0.20-0.28 g Mg (g P)$^{-1}$ and 0.27-0.42 g K (g P)$^{-1}$ [24].

Although potassium is incorporated into the poly-P structure, it seems less hardly bound in the biomass than nitrogen and phosphorus. Almost a third of the potassium going into the thickening tables is released and returned to the water line with the sludge water, while the corresponding numbers for nitrogen and phosphorus are miniscule (Figure 4.5). This could be attributed to the potassium ion being small and can be easily leached, while P and N are bound in more complex biomass structures. A similar example can be taken from the plant world where, unlike nitrogen and phosphorus, potassium is not a constituent of plant biomolecules, but occurs in soluble K+ form and thus is more easily leached from leafs as well as from soils [18].

4.2.4.3 Nutrient flows through a Bio-P WWTP

Calculations based on data from the plant showed that 351 kg phosphorus and 2679 kg nitrogen enter the plant each day. 16% of incoming phosphorus and 7.6% of incoming nitrogen leave the plant with the effluent. The corresponding calculations could not be made for potassium as data on influent and effluent potassium concentrations were lacking. Around 85% of the incoming phosphorus ends up in the sludge and is removed from the plant with the biosolids (Figure 4.5). This is in line with the current understanding that typically 90% of incoming P ends up in the biosolids [21]. For nitrogen, the majority of the removal occurs in the biological treatment, where ammonia is oxidized and leaves the plant as nitrogen gas. Only 16% of incoming nitrogen is estimated to leave the plant with the biosolids.

The excess sludge contained 470 ± 164 mg TKN L^{-1}, 271 ± 51 mg P L^{-1} and 103 ± 12 mg K L^{-1}. This corresponds to a load of 3.26 g N (p.e., d)$^{-1}$, 1.88 g P (p.e., d)$^{-1}$ and 0.72 g K (p.e., d)$^{-1}$. These values reflects that around 80% of the incoming nitrogen is removed in the biological treatment of the wastewater, while the main part of the phosphorus is incorporated into and removed with the sludge. If it is assumed that the studied WWTP receives a similar amount of potassium as the estimated load from household, it is seen that the vast majority (around 80%) of the potassium leaves the plant with the effluent and just a small fraction ends up in the sludge line.

The soluble nature of potassium is also displayed at the dewatering units (Figure 4.5). While only minor fractions (1–2%) of the nitrogen and the phosphorus is found in the return flow from the thickening tables, some 25-30% of the potassium in the excess sludge is returned to the water line via this stream. The flow of centrate was calculated to be 198 m3/d while the sludge water flow was calculated to be 1056 m3/d. These two streams are returned to the inlet of the plant where they represent 0.3 and 1.4% of the incoming flow respectively. The centrate contributes 19.7% of the P load and 12.1% of the N load to the plant. The flow of centrate is the average daily flow. In reality the centrifuges are only operated a couple of days per week.

Before digestion, the combined stream of thickened and external sludge contained 117 ± 301 mg $N\text{-}NH_4^+$ L^{-1}, 81.2 ± 91 mg $P\text{-}PO_4^{3-}$ L^{-1} and 43.5 ± 20 mg K^+ L^{-1}. During anaerobic digestion nutrients are released due to the degradation of organic matter, and in the case of Bio P sludge, the lysis of poly-P. Consequently, the digestate had concentrations of ammonium, phosphate and potassium ion at values many times higher than prior to digestion, 1525 ± 205 mg $N\text{-}NH_4^+$ L^{-1}, 318 ± 46 mg $P\text{-}PO_4^{3-}$ L^{-1} and 485 ± 18 mg K^+ L^{-1} (Table 4.9 Nutrient release in the digester). As mentioned in chapter 4.2, there was a slight decrease in the nutrient concentrations from the digestate to the centrate that can be attributed to the storage of digestate in a buffer tank before centrifugation. There is also a dilution factor due to the addition of poly-electrolyte for dewatering.

Although the value of total nitrogen in the digestate (4.83% on a dry solids basis) is in line with other digestates within the Aquafin area, as well as corresponding to the literature [102], the calculated mass flow of nitrogen in the digestate (481 kg N d^{-1}) is much lower than the combined nitrogen flow to the digester (770 kg N d^{-1}) as well as the combined flow out from the centrifuges (766 kg N d^{-1}). It thus has to be considered to be an outlier.

Roughly 80% of the phosphorus in the digestate leaves the plant with the biosolids, while the remaining 20% goes to the centrate (Figure 4.5). In the case of nitrogen, a smaller fraction (60%) ends up in the biosolids while around 40% goes to the centrate. For potassium, the mass balance over the centrifuges does not close well, either the values of the centrate or the biosolids are overestimated, based on the digestate, 56% of the potassium ends up in the biosolids, while 69% ends up in the centrate. Yet, it indicates that similar to the case over the thickening tables, a larger fraction of the potassium goes to the water fraction than to the sludge.

4.2.4.4 Recovery strategies in the sludge line

As has been outlined earlier in this chapter, the fate of the macronutrients differ considerably from each other, both in the food production system, but also within the WWTP. Nitrogen is characterized by the many forms it can take and the fact that it can be removed from the water fraction by conversion into nitrogen gas. Under standard conditions, phosphorus does not form any gaseous compounds and is commonly immobilized as soluble phosphates are rapidly fixed into insoluble forms [6]. Potassium on the other hand is commonly present in the ionic K+ form and is therefore typically found in the water phase.

The majority of the phosphorus leaves the WWTP with the biosolids, yet, most phosphorus recovery installations are placed on the centrate. It has been argued that higher recovery potentials can be achieved when struvite precipitation is placed directly on the digestate due to the higher phosphate concentrations (there is a dilution factor to the centrate due to polymer addition at the centrifuges) and the fact that precipitation is determined by equilibrium concentrations [26].

Although a majority of the potassium is leaving the plant with the effluent, there are considerable amounts found in the centrate. Direct recovery of potassium in the form of potassium struvite from centrate is not possible due to the high content of ammonium, which is inhibitory to potassium struvite formation. As discussed in Chapter 4.2, a nitrogen removal step, such as autotrophic nitrogen removal, prior to struvite precipitation can allow for the formation and recovery of potassium struvite. Electrodialysis has been suggested as a strategy to concentrate nutrients from centrate and other waste streams, either for direct use as fertilizer of combined with struvite precipitation, but is still struggling with high concentrations of sodium [108].

Spreading of dewatered digested sludge is a straightforward way to return nutrients to soils. However, concerns over the presence of metals and other harmful substances have resulted in the prohibition of this practice in several regions and countries. As a results, incineration is the common route for sludge disposal in any countries, especially in the Netherlands and Belgium where it accounts for more than 80% (Table 1.1 in Introduction). The incinerated ash has a relatively high P-content, but with a limited plant availability [21]. Phosphorus can anyways be recovered through acid leaching from the sludge ash [21,46]. Nitrogen is driven off during combustion and is therefore lost for recovery purposes, potassium on the other hand remains in the incinerated ashes together with phosphorus. This has been taken advantage of in trials to precipitate potassium struvite from fly ashes dissolved in acidified water, which dissolves the phosphate and potassium present [107].

4.3 Combining anammox with struvite precipitation for multi-nutrient recovery

In the previous chapter, biologically induced precipitation by PNA granular sludge was proposed as a way to recover phosphorus without the addition of chemicals. In this chapter, the implication of placing PNA as a pre-treatment step before struvite precipitation is discussed. Much of the discussion on nutrient recovery has been focused on phosphorus, but in this chapter focus is placed on the recovery of another key macronutrient: potassium.

Results from this chapter has been accepted for publication in the following journal:

Johansson, S., Ruscalleda, Saerens, B., M., Colprim, J.. Potassium recovery from centrate: Taking advantage of autotrophic nitrogen removal for multi-nutrient recovery. *Journal of Chemical Technology and Biotechnology*, 2019, 94(3):819-828

4.3.1 Motivation

Recycling of nutrients from waste streams has been recognized by the European Union as an important step towards a sustainable and resource efficient economy [61]. However, recovery strategies have been overwhelmingly focused on phosphorus while recovery and reuse of potassium has received much less attention, in spite of potassium too being a key macronutrient and, just like phosphorus, derived from limited geological sources. Although estimates on remaining reserves of phosphate rock and potash are stained by uncertainties, it remains a fact that the European Union, as well as many large agricultural countries depend on imports of potash for fertilizer production [2,74], while the geographical distribution of potash mines is narrowly limited with five countries accounting for 80 % of the world´s potash production [104]. To develop local and sustainable sources of potassium is a step towards national self-sufficiency of nutrients and goes in line with the European Union’s aim to protect businesses again scarcity of resources and volatile prices.

On a global basis, 21 Mton P and 32 Mton K are added to soils on annually [10], a ratio reflected in the nutrient load from households, which have been estimated to 2.1 g P, 13.5 g N and 4.0 g K per person and day based on Swedish conditions [110]. This provide an order of magnitude of the recovery potential of potassium from municipal wastewater. Recovering and returning these nutrients to soils would decrease dependence on mineral fertilizers, which depend on imports of limited geological resources associated with negative environmental impact due to mining.

Within municipal wastewater treatment plants, nutrients bound in the organic matter are released during anaerobic digestion of sludge, and found in the digested sludge liquors after centrifugation. This reject water, the centrate, is rich in phosphate and potassium and represents an opportunity for potassium mining in the form of potassium struvite, especially at EBPR plants. However, the centrate also have a high ammonium concentration, which is inhibitory to potassium struvite formation [80]. A nitrogen removal step is therefore required if potassium struvite recovery is targeted. Technologies such as nitrification/denitrification and ammonia stripping have been applied to remove nitrogen from manure and urine for subsequent potassium struvite precipitation [45,114,115]. However, both of these strategies have drawbacks; nitrification/denitrification requires extensive aeration and the presence and possible addition of an organic carbon source, while ammonia stripping efficiency relies on a high operational pH, typically achieved by NaOH addition. Presence of Na can lead to formation of sodium struvite (MSP, $MgNaPO_4 \cdot 7H_2O$), which is competing with MPP formation [81]. Application of PNA for nitrogen removal represents a drastically lower energy demand compared to conventional nitrification-denitrification and no need for chemical or organic carbon addition.

Furthermore, centrate is characterized by a high bicarbonate alkalinity, equivalent to a high buffer capacity. Dosing of chemicals to adjust the pH is a major cost if struvite production is targeted directly on the centrate [116]. CO_2 stripping through aeration has been applied to decrease the alkali dosing [117,118], but this is in turn a rather energy demanding process. PNA biomass is autotrophic and relies on bicarbonate as sole carbon source. Thus, PNA could be an energy-efficient way to reduce the alkalinity before struvite precipitation.

4.3.2 Objectives

This works aims to demonstrate the feasibility of combining PNA and struvite precipitation for the simultaneous recovery of potassium and phosphorus in the form of MPP from municipal wastewater, and to assess PNA as an alternative to conventional CO2 stripping.

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Table 4.7 Composition of centrate and PNA effluent used for the different experiments

		Chem-P				Bio-P		
Species	Unit	Centrate	Mg:P essay	pH essay	Temp. essay	Centrate	pH essay	Temp essay
pH		8.0±0.02	7.6	7.7	7.7	7.8	7.5	7.6
Alkalinity	mg $CaCO_3$ L^{-1}	3276±174	327±0.71	371±34	399±4.9	3407[a]	701[a]	752[a]
$P\text{-}PO_4^{3-}$	mg L^{-1}	59±6.0	53±0.14	60±0.57	53±0.21	222	233±1.0	233±0.5
$N\text{-}NH_4^+$	mg L^{-1}	949±80	109±1.4	143±13	138±0.0	963	228±2.0	225±5.0
K^+	mg L^{-1}	251±2.1	261±0.71	273±2.8	276±1.4	327	367	363
Mg^{2+}	mg L^{-1}	12±0.3	4.5±1.1	13.9±0.21	8.29	-	4.36	4.27
Ca^{2+}	mg L^{-1}	54±0.55	33±0.55	35±0.78	38.8	-	21.6	21.3
Na^+	mg L^{-1}	-	319±0.5	368±3.5	387±2.0	-	-	-
Cl^-	mg L^{-1}	-	618±5.0	435±0.0	656±2.0	-	-	-

-, not determined

a) converted from meq L^{-1}

4.3.3 Experimental approach

4.3.3.1 Experimental procedure

Experiments using Chem-P PNA effluent were conducted in 1 L glass beakers, with 500 ml working volume. 1 M NaOH solution and magnesium chloride in powder form ($MgCl_2 \cdot 6H_2O$) were used to adjust pH and Mg:P ratio. The solids were captured using 0.2 µm filters and dried at 46 °C for 48 hours for analysis by X-ray diffraction (XRD).

To assess the effect of pH and temperature on the removal of ammonium through stripping, separate tests were made using Chem-P PNA effluent where no magnesium source was added. The experimental outline is presented in Table 4.8. The ammonium concentration was measured before and after stirring for one hour.

Table 4.8 Experimental conditions for batch experiments assessing the influence of pH, and temperature on ammonia stripping conducted on Chem-P PNA effluent

Serial	pH	Temp. (°C)
1	10	20
2	10	25
3	10	30
4	10	35
5	10	40
6	8	25
7	9	25
8	10	25
9	11	25
10	12	25

The second set of batch experiments, using Bio-P PNA effluent, was carried out in 4 L glass reactors, with 3000 ml working volume. 32 % magnesium chloride solution and 29 % sodium hydroxide solution were used to correct the pH and Mg:P ratio. Wet samples of the precipitates were taken for particle size analysis and microscopic imaging. The solids were captured using 0.60 µm filters and dried at room temperature for 36 hours for analysis by XRD and of chemical composition.

Table 4.7 shows the composition of the centrate fed to each reactor and the PNA effluents used for each set of experiments

4.3.3.2 Sampling campaign over the sludge line

A sampling campaign was conducted over the sludge line of WWTP Antwerp South in order to assess the scope of potassium recovery in side-stream. The WWTP receives external sludge from other WWTPs, which is fed to the digester together with the thickened sludge from the plant. The external sludge accounts for 14 % and the thickened sludge for 86 % of the flow to the digester on a volumetric basis. Samples were taken twice per week during six weeks' time. Data on flows of thickened sludge, external sludge, and digestate were obtained from Aquafin, except the flow of centrate and sludge water (return flow from thickening tables), which were calculated using solids and water mass balances over the centrifuges and thickening tables respectively

4.3.4 Results and Discussion

4.3.4.1 PNA reactor: Ammonium and alkalinity removal prior to struvite precipitation

During the experimental period, the Chem-P PNA reactor was operated at 25 °C, a hydraulic retention time of 3.6 days, and nitrogen loading rate of 266±22 mg $N\text{-}NH_4^+$ L^{-1} d^{-1}.

The lab-scale Chem-P PNA reactor decreased the ammonium concentration by more than 85 % (Table 4.7). This is comparable to the performance of full-scale PNA reactors [37]. Ammonium has been shown to negatively impact the formation of MPP, due to the formation of MAP (Xu et al., 2011). The reason for this is that the solubility product for MAP is slightly smaller than the one for MPP. Reported values of the negative logarithm of the solubility product (pKsp) for MPP range between 10.6–12.2 [81–83], while the most commonly used value for MAP is 13.26 [25]. Consequently, when struvite precipitation is applied on streams with high ammonium concentrations, such as centrate, only traces of K are detected in the recovered product [84].

Potassium and phosphate are not consumed in any significant amounts by PNA biomass and the concentrations of these ions remained virtually unchanged after the PNA step (Table 4.7). The Chem-P PNA effluent had a N:P:K molar ratio of 5.2:1.0:3.9 with both potassium and ammonium in excess over phosphorus for MPP or MAP formation, leaving magnesium as the limiting ion.

Alkalinity represents the acid-neutralizing capacity of a system, and is mainly composed of carbonate species, while phosphate and ammonium can contribute in concentrated waters such as centrate. Stripping of CO_2 by aeration has been applied as a strategy to raise the pH for struvite crystallization. It also reduces the risk for calcium carbonate formation. PNA biomass is autotrophic and uses bicarbonate as the only carbon source and virtually functions as a biological CO_2-stripper.

The Chem-P PNA reactor reduced the alkalinity by 2910 mg $CaCO_3$ L^{-1}, which accounts for 90% removal (Table 4.7). This is more efficient compared to results from previous studies on CO_2 removal using air stripping. A pilot-scale CO_2 stripper removed up to 20 mg $CaCO_3$ L^{-1} from centrate [119], while a pilot-scale cascade stripper, also operating on centrate, was reported to reach a CO_2 reduction of 20 % (measured as dissolved CO_2), which resulted in caustic use savings of 32 % [118]. In a study on a mix of centrate and urine, the implementation of a CO_2 stripper decreased the NaOH consumption by 57 % as compared to operation without the stripper in place (the CO_2 removal efficiency was not reported) [120]. Thus, even a small reduction of the alkalinity results in important savings in terms of alkali dosing. This implies that the high alkalinity removal by PNA would strongly reduce the need for chemical and energy input to control the pH in struvite precipitation.

4.3.4.2 Establishing optimal parameters for maximum potassium recovery from Chem-P PNA effluent

Assessment of optimal Mg:P ratio

Precipitation experiments were conducted at pH 10 to determine the effect of molar Mg:P ratio on the removal of P, K and N. Phosphate and ammonium removal increased with the Mg:P ratio, while the potassium removal remained rather constant at 4.9 ± 0.7 % (Figure 4.7a). The phosphate removal increased to a maximum of 96 % at Mg:P ratio 1.75, but a ratio of 1.25 was sufficient to reach a phosphate removal above 90 %, with residual $P\text{-}PO_4^{3-}$ concentration of 4.0 ± 0.14 mg L^{-1}. Remaining experiments were conducted at Mg:P 1.25 ratio in order to minimize magnesium chloride dosing.

As the PNA effluent had an excess of potassium and ammonium over phosphate, only a fraction of these ions were removed through struvite precipitation, even when a good phosphate removal was achieved. The ammonium removal was slightly higher than the phosphate removal on a molar basis, indicating that some ammonium was stripped as ammonia.

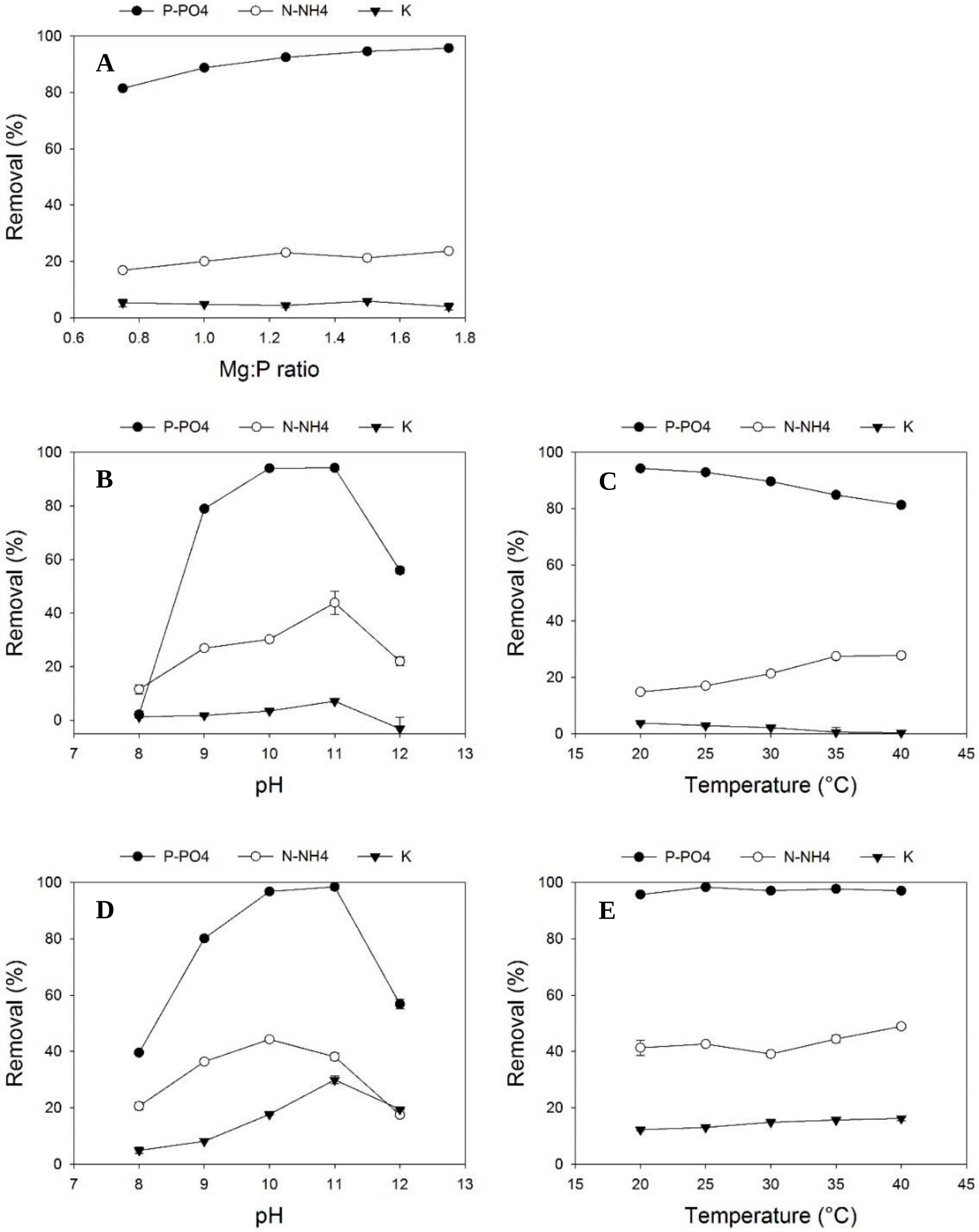

Figure 4.7 Nutrient removal from liquid phase during batch experiments using Chem-P PNA effluent (a-c) and Bio-P PNA effluent (d-e)

Influence of pH

The pH affects the solubility as well as the supersaturation and is therefore strongly influencing precipitation and nutrient recovery. The phosphate removal showed a peak between pH 10 and 11, while the potassium and ammonium removal increased up to pH 11 (Figure 4.7b). A sharp drop in nutrient removal was observed at pH 12. Simulation results showed that alkaline conditions favor the formation of magnesium hydroxides such as brucite ($Mg(OH)_2$) and magnesium phosphate ($Mg_3(PO_4)_2$), which both compete with struvite for magnesium ions.

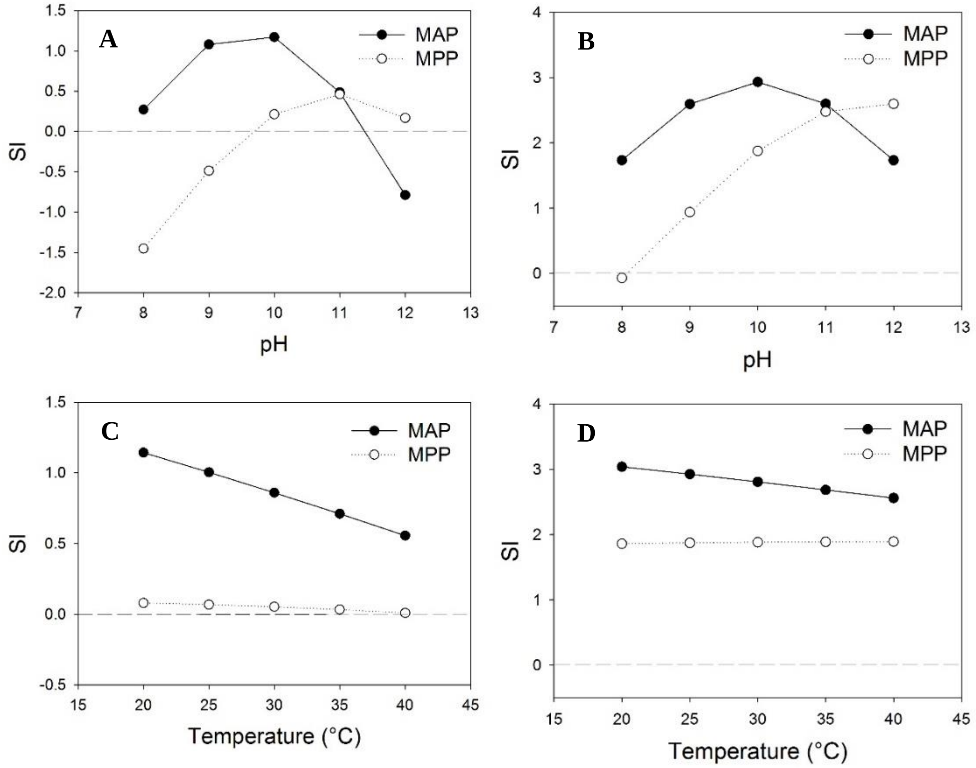

Figure 4.8 Saturation indices for MAP and MPP as a function of pH and temperature for Chem-P PNA (a and c) effluent and Bio-P PNA effluent (b and d), simulated with Visual Minteq

A maximum nutrient removal of 94 %, 7.1 % and 44 % of phosphate, potassium and ammonium respectively was observed at pH 11. The experimental results were confirmed with simulations that showed that the SI for MAP peaks at pH 10, while for MPP the SI peaks at pH 11 (Figure 4.8a). The results are in line with Xu et al. (2011), who found that the optimum pH for P and K removal from urine was at 11. A mix of MPP together with MAP was detected by XRD at pH 11

(Figure 4.9) confirming the presence of a multi-nutrient product containing all three macro-nutrients N, P and K.

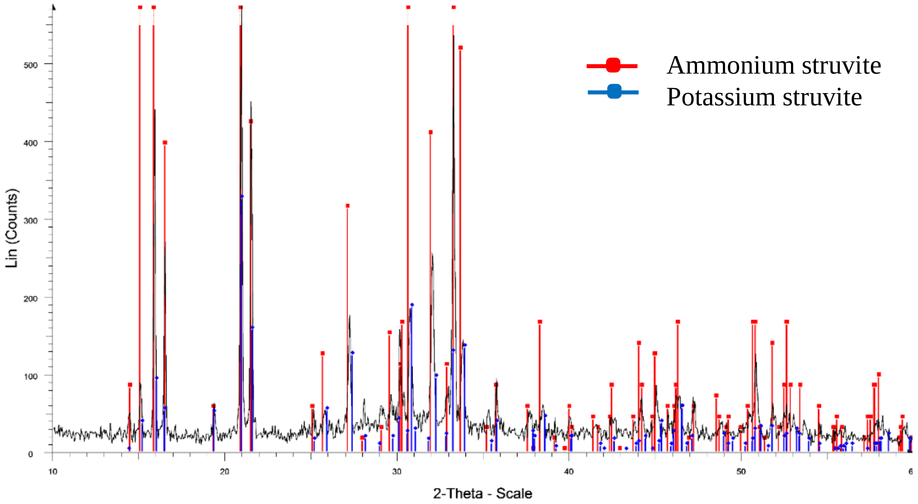

Figure 4.9 XRD diffractogram obtained from precipitate recovered from Chem-P PNA effluent at pH 11, Mg:P ratio 1.25, and 25 °C.

There was no difference in phosphate removal at pH 10 and 11 and remaining experiments were conducted at pH 10 in order to minimize sodium hydroxide dosing.

The molar removal of ammonium was higher than that of phosphate throughout the range of pH tested, indicating that removal of ammonia through stripping plays a role. Separate ammonia stripping experiments showed that the ammonium removal due to stripping becomes important at pH > 9 and can amount up to 25 % at pH 10 and 25 °C (Figure 4.10a).

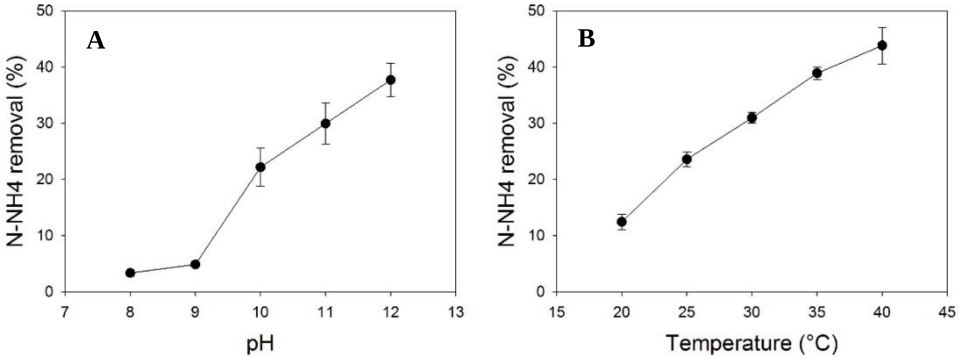

Figure 4.10 Ammonia removal through stripping from Chem-P PNA effluent as effect of pH a) and temperature b)

Effect of temperature

Temperature affects the solubility and thus the supersaturation, as decreasing solubility leads to a higher supersaturation. Phosphate and potassium removal decreased with temperature while ammonium removal increased (Figure 4.7c). The phosphate removal decreased steadily from 94 % down to 81 % as the temperature was increased from 20 to 40 °C. Potassium removal also decreased with temperature, from 3.8 % down to 0.4 %. Already at 35 °C there was virtually no removal of potassium. Ammonium removal on the other hand increased from 15 % up to 28 % in the temperature range of 20 to 40 °C.

The removal of ammonium is caused both by precipitation and ammonia stripping. The amount of free ammonia increases with temperature, which allows for more ammonium to be removed through stripping. The molar removal of ammonium surpassed that of phosphate at 25 °C, meaning that above this temperature ammonium is also removed by stripping. Results from stripping experiments (with no magnesium addition) showed that ammonium removal increased from 12 to 44 % along the temperature range of 20 to 40 °C (Figure 4.10b).

It has been reported that the solubility of MAP reaches its minimum at around 20 °C [43]. However, a more recent study reports that the solubility decreases with lower temperature (in the range 5–30 °C) [85]. In this study no temperatures below 20 °C were investigated as PNA applied in side-stream typically operates above 20 °C. Chemical equilibrium simulations confirmed that the SI for MAP decreases with increasing temperature, while the SI for MPP showed just a slight decrease (Figure 4.8c).

4.3.4.3 Validation of results using Bio-P PNA effluent

The experiments to assess the influence of pH and temperature on nutrient removal were repeated using effluent from a pilot-scale Bio-P PNA unit. Potassium and magnesium play important roles in biological P-removal and are co-transported together with phosphorus into bacterial cells where they are incorporated into the poly-P structure (general formula $(K_aMg_bPO_3)_n$) [121]. During anaerobic digestion, the poly-P is hydrolysed with subsequent nutrient release. Thus, centrate from Bio-P WWTPs is characterized by higher concentrations of phosphate and potassium compared to centrate from conventional activated sludge WWTPs.

Consequently, the phosphate concentration of the Bio-P PNA effluent was considerably higher (around 230 mg $P\text{-}PO_4$ L^{-1}) compared to the Chem-P PNA effluent (50–60 mg $P\text{-}PO_4$ L^{-1}) (Table 4.7). However, the pilot-scale PNA reactor didn't reach the same nitrogen removal efficiency as the lab-scale reactor, resulting in higher ammonium concentrations (close to 230 mg $N\text{-}NH_4$ L^{-1} as compared to 130 mg $N\text{-}NH_4$ L^{-1}) (Table 4.7). The resulting molar N:P:K ratio in the Bio-P PNA effluent was 2.1 : 1.0 : 1.2.

The higher nutrient concentration in the Bio-P PNA effluent led to generally higher removals compared to the Chem-P PNA effluent, due to that the endpoint of precipitation is defined by equilibrium concentrations. This is also reflected in the SI which is higher for MAP and MPP in the Bio-P PNA effluent (Figure 4.8b) as compared to the Chem-P PNA effluent (Figure 4.8a).

Removal of phosphate and ammonium showed peaks at pH 11 and 10 respectively, while the removal of potassium increased up to pH 11 (Figure 4.7d). Above pH 11, there was a sharp drop in the removal of all three nutrients. This confirms the results obtained with Chem-P PNA effluent that increasing pH up to 11 favor the formation of MPP. The same trend is observed in the results from SI calculation where the curves of MPP lies above the one for MAP at pH 11 and higher (Figure 4.8a and b).

Maximum potassium removal was observed at pH 11 with removals of phosphate, potassium and ammonium being 98 %, 30 % and 38 % respectively.

Temperature had less of an influence on the nutrient removal from the Bio-P PNA as compared to the Chem-P PNA effluent (Figure 4.7e). Phosphate and potassium removals remained virtually unaffected while an increase in the ammonium removal from 39 % to 46 % was noted when the temperature was increased from 30 to 40 °C. Again, pH has a stronger influence than temperature on struvite formation and because the experiment was conducted on constant pH the nutrient removal due to precipitation remained close to constant. Ammonium removal on the other hand increased with temperature due to ammonia stripping.

4.3.4.4 Quality of the product: Multi-nutrient recovery through co-precipitation of MPP and MAP

Table 4.9 shows the composition of precipitates recovered from experiments using Bio-P PNA effluent at pH 8–12. The experimental results are listed together with the theoretical composition of MAP and MPP for comparison. The experimental results reflect the recorded values on nutrient removal from the liquid phase (Figure 4.7d); the nitrogen content of the precipitates decrease with increasing pH, while the potassium concentration increase up to pH 11. At pH 8 the molar ratio of Mg:K:N:P was 1.0:0.03:0.94:0.96 which is close to the theoretical ratio of MAP. At pH 11 the Mg:K:N:P ratio was 1.0:0.29:0.66:0.97 indicating that it was composed of one third MPP and two-thirds MAP.

Table 4.9 Theoretical composition of pure MAP and MPP as compared to the composition of the product obtained at different pH from Bio-P PNA effluent

	Theoretical		This study				
	MAP	MPP	pH 8	pH 9	pH 10	pH 11	pH 12
Element	(%)	(%)	(%)	(%)	(%)	(%)	(%)
P	12.6	11.6	12.0	12.0	11.7	11.4	8.22
N	5.7	-	5.31	5.20	4.65	3.51	0.35
K	-	14.7	0.53	0.75	1.63	4.34	2.99
Mg	9.9	9.13	9.78	9.76	9.73	9.20	> 10.0
Ca	-	-	< 0.08	< 0.07	0.37	0.91	1.20

Not only the chemical composition but also the morphology of the crystals changed with pH (Figure 4.11). When the pH was increased from 8 to 12, the crystals became thinner and more elongated. If this was due to a higher fraction of MPP, or if it was merely an effect of the pH needs to be further examined. In a study by Wilsenach et al. (2007) it could not be concluded that MPP have different particle shape and size than MAP.

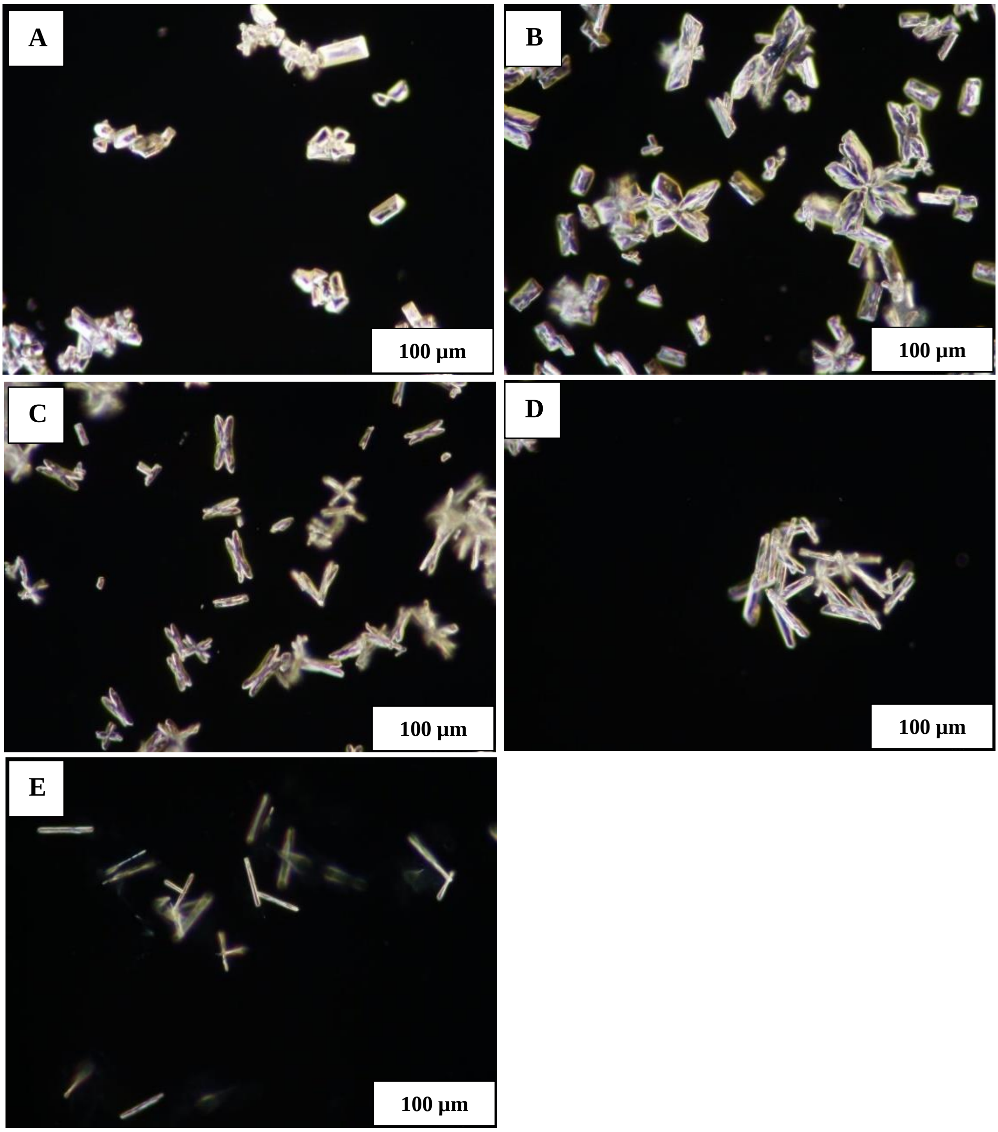

Figure 4.11 Microscopic images of crystals obtained from precipitation experiments using Bio-P PNA effluent at pH 8 a), 9 b), 10 c), 11 d), and 12 e) respectively.

4.3.4.5 Augmenting MPP recovery

The experimental results show that pH strongly influences the ratio between MAP and MPP formed (Figure 4.7b and d). The highest potassium removal was recorded at pH 11, which represents the highest supersaturation but not necessarily the optimal operational pH. High supersaturation promote nucleation and the formation of small crystals that are easily washed out. Although the higher phosphate removal was recorded between pH 10 and 11, full-scale MAP crystallizers operate at pH that represent a lower degree of supersaturation, typically in the range of 8.0–8.5 [46], in order to promote growth over nucleation. The optimal operational pH for MPP recovery needs to be assessed further in continuous experiments, but the results from this study suggest athat a slightly higher pH than for MAP recovery from centrate would be beneficial. The drastically lower alkalinity of PNA effluent compared to centrate could counteract the need for additional alkali dosing to reach this higher pH.

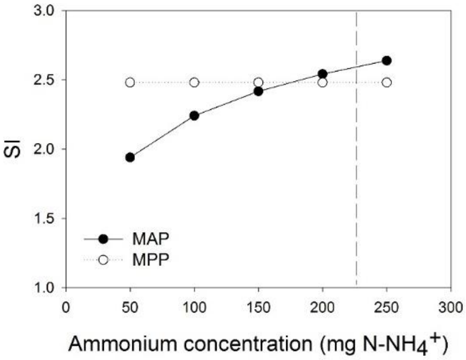

Figure 4.12 Influence of ammonium concentration on the saturation indices of MAP and MPP in Bio-P PNA effluent at pH 11, 25 °C and Mg:P ratio 1.25. Dashed line represent ammonium concentration of batch experiments.

The second factor influencing the MAP:MPP ratio is the residual ammonium in the PNA effluent, which has a negative impact on MPP formation. Traces of ammonium will always be present after autotrophic N removal, but the amount depends on the ammonium concentration of the centrate and the performance of the PNA reactor. Simulations based on the composition of the Bio-P PNA effluent showed that at pH 11, the SI for MPP is above the one for MAP up to ammonium concentration 175 mg $N\text{-}NH_4^+$ L^{-1} (Figure 4.12). This represents a N:P:K molar ratio of 1.7:1.0:1.2. At the time of the experiments the Bio-P PNA reactor reached an ammonium removal of only 76%, which resulted in an effluent ammonium concentration of 227 ± 1.5 mg $N\text{-}NH_4^+$ L^{-1} and corresponding N:P:K ratio 2.2:1.0:1.2. However, full-scale PNA reactors fed with centrate of a similar ammonium concentration can reach effluent ammonium concentrations of as low as 100 mg $N\text{-}NH_4^+$ L^{-1} or less [37]. This residual ammonium concentration would represent a N:P:K ratio of 0.9:1.0:1.2. In this case, the molar ammonium nitrogen concentration is less than half compared to the PNA effluent used for the experiments, and also less than the molar concentration of potassium. Consequently, at this ammonium concentration the SI for MPP is above the one for MAP (Figure 4.12) and a higher fraction of MPP in the precipitate would be to be expected. Correct operation of the PNA reactor to reach low effluent ammonium concentration is therefore crucial if MPP recovery is targeted.

A third factor influencing MPP recovery is the phosphate concentration. A higher phosphate concentration can polish residual ammonium and still allow for MPP formation. Augmented phosphate concentrations can be achieved by fermentation of waste activated sludge prior to anaerobic digestion [122]. The anaerobic conditions hydrolyses the poly-P and releases phosphate and magnesium in a stream that is fed to the crystallizer [123]. Potassium is a counter-ion in the poly-P structure and is released together with phosphate and magnesium under anaerobic conditions. Thus, the fermented stream to the crystallizer would have higher phosphorus, magnesium and potassium concentrations all which promote MPP formation. **Add Ito 2017**

Table 4.10 Nutrient concentrations through the sludge line at WWTP Antwerp South

	Before digester			After digester			Centrate		
Ion	PO_4^{3-}	NH_4^+	K^+	PO_4^{3-}	NH_4^+	K^+	PO_4^{3-}	NH_4^+	K^+
Unit	mg P L^{-1}	mg N L^{-1}	mg K L^{-1}	mg P L^{-1}	mg N L^{-1}	mg L^{-1}	mg P L^{-1}	mg N L^{-1}	mg L^{-1}
Conc.	15.5 ± 17	22.2 ± 57	29.9 ± 14	318 ± 46	1525 ± 205	485 ± 18	246 ± 16	1218 ± 115	429 ± 16

4.3.4.6 Potential for potassium recovery from PNA effluent

The number of PNA installations is growing with more than 100 already in place, most of them treating centrate at municipal WWTPs [37]. This implies a large and expanding market for the implementation of struvite recovery from PNA effluent. The amount of potassium, phosphate and ammonium available for recovery in side-stream was assessed by a sampling campaign over the sludge line at Antwerp South WWTP (Table 4.10). In the stream fed to the digester the concentrations of phosphate, potassium and ammonium were less than 30 mg L^{-1} due to the nutrients being bound in the sludge, while after anaerobic digestion the concentrations increased manifold to 318, 1527 and 485 mg L^{-1} of P-PO_4^{3-}, N-NH_4^+ and K^+ respectively. There was a slight decrease in nutrient concentration from the digestate to the centrate that could be due to a buffer tank between the anaerobic digester and the centrifuges where some precipitation can have occurred. The flow of centrate was calculated as 198 m^3/d, corresponding to a flow of 49, 241 and 85 kg d^{-1} of P-PO_4^{3-}, N-NH_4^+ and K^+ respectively. Expressed on a population equivalent basis this represents 0.28 g P-PO_4^{3-} p.e. $^{-1}$ d^{-1}, 1.41 g N-NH_4^+ p.e. $^{-1}$ d^{-1} and 0.50 g K^+ p.e. $^{-1}$ d^{-1}.

Full-scale (ammonium) struvite installations operating on centrate typically reach a recovery efficiency of 80-90% [44,46]. If an efficiency of 90% is assumed, together with the composition representing the maximum MPP/MAP ratio achieved in the batch experiences (Table 4.8), this would represent a recovery potential of 11 kg P, 4.3 kg N and 3.5 kg K per day. Based on incoming loads, this would represent 3% of the incoming phosphorus, 0.16% of incoming nitrogen and 0.5% of incoming potassium (the incoming potassium load is based on literature data). Although the recovery is modest compared to incoming loads, the main incitement for WWTPs to invest in an anammox and/or a struvite unit is to decrease the nutrient load to the main line, and, in the case of struvite, to reduce scaling, in a cost-efficient way. A combination of the two technologies allows for the reduction of both nitrogen and phosphorus to the main line. To place the anammox unit before the struvite step, as proposed in this thesis, would allow for potassium recovery, but also drastically reduce the alkalinity of the centrate, which would decrease the need for alkali dosing in the subsequent struvite precipitation step. It could thus represent an interesting nutrient mining opportunity in accordance with the circular economy framework**.**

5 DISCUSSION

5.1 Main contributions

5.1.1 Biologically induced mineralization

Biologically induced mineralization is no uncommon phenomena, in fact, our bones and teeth are composed of calcium phosphates that have been mineralized biologically. Similarly, mineralization is commonly found more specifically in wastewater sludges. Mineralization of sludge is associated with high sludge ages, typical for systems with high biomass retention such as membrane bioreactors and granular systems, and a subsequent reduced biomass yield during digestion [124]. One of the great assets of biotechnology is to take advantage of biological processes for the production of valuable products. In the framework of this thesis, the naturally occurring mineralization induced by PNA granules was evaluated as a possible phosphorus recovery product from wastewater. First of all, the precipitated mineral was identified as a high purity hydroxyapatite. Hydroxyapatite belongs to the same group of mineral as phosphate rock (apatite) and can therefore be incorporated directly into the existing infrastructure for the processing of phosphate rock into either fertilizer or high-grade phosphorus products. Secondly, the precipitated mineral was analyzed for the presence of metals and the compliance with requirements from the phosphate industry as well as the limits that are proposed to be included in the EU fertilizer legislation. The biologically induced hydroxyapatite complied well with these limits. In fact, the recovered pellets from the PNA reactor had a metals content well below the one of commonly used P fertilizer. Products recovered from waste streams are often regarded with suspicion as they can contain both biological and inorganic contaminants. It is however important to keep in mind the contaminants occurring in conventional products, something that is often neglected by the public. As this study shows, a product recovered from wastewater can in fact have a higher purity than a conventional product on the market. This means a double positive effect, the environmental benefit of recycling nutrients together with the safety aspect of a cleaner product.

5.1.2 Potassium recovery in the form of potassium struvite

Chapter 4.2 and 4.3 deal with the recovery of potassium from municipal wastewater. This is a field that has received very little attention, especially compared to the focus on phosphorus recovery in the past decade. The first outcome of this work is therefore to highlight the reasons and the need to recover and recycle potassium to fields. Although data on remaining reserves of both potash and phosphorus rock contain uncertainties due to it being provided by governments and production companies and is not independently verified, current estimates point to potash reserves being depleted even sooner than phosphate rock reserves. Due to the narrow geological distribution of potash mines many countries are depending on imports for the production of potassium fertilizer. Recovery and recycling of potassium would decrease this dependency and provide a sustainable and secure source of this macro-nutrient.

Wastewater concentrates the nutrients consumed by a society and the wastewater treatment plant is a point source for nutrient discharge to water bodies, but also represent an attractive nutrient mining opportunity. Chapter 4.2 suggested the recovery of potassium by precipitation of potassium struvite, an analogue to the more commonly known ammonium struvite. The recovery of potassium struvite is however depending on a low ammonium concentration in order to prevent competition from ammonium struvite formation. In Chapter 4.2, nitrogen removal by PNA biomass was demonstrated to remove sufficient ammonium for potassium struvite to form, although together with co-precipitation of ammonium struvite. The recovered product thus contained all three macronutrients (NPK). The pilot-scale PNA reactor where effluent was collected was not operating optimally and it is believed that the potassium struvite content could be higher if struvite precipitation would be placed after a properly functioning reactor.

Chapter 4.3 aimed to map the flow of potassium through the sludge line of the wastewater treatment plant. To the best of the author's knowledge, this would be the first study to attempt such a mapping. Even though the results are limited due to a limited sampling period it gives an idea of the different faith of potassium as opposed to phosphorus through the WWTP. Potassium is characterized by a high solubility, and while phosphate mainly end up in the sludge fraction, potassium tends to solubilize and be present in the water fractions, such as the effluent, and the reject water from dewatering tables and centrifuges. These data supports the idea of recovering potassium from the centrate as suggested in Chapter 4.2.

5.2 Future outlook

The outcomes of this thesis suggest two novel strategies for nutrient recovery from wastewater: biologically induced precipitation of calcium phosphate and recovery of potassium in the form of potassium struvite. Both strategies are taking advantage of autotrophic PNA biomass for nutrient recovery. Although the outcomes are promising, the technologies are still in the emerging phase and further work is needed to lead to the implementation in the full-scale.

Controlled biomineralization with the aim to recover phosphorus is a young field of research. In the scope of this work, the suitability of calcium phosphate precipitated within granular PNA sludge as a phosphorus recovery product from wastewater was demonstrated, but there are many steps to implementation in the full-scale. A main topic to investigate is the optimization of the process to reach a maximum phosphorus recovery while maintaining efficient nitrogen removal. As discussed in Chapter 4.1 the operational pH, the anammox activity and granule size are thought to be important factors as they influence the pH in the interior of the granules. The composition of the feed, and especially the calcium and phosphorus concentrations and the resulting Ca:P ratio, are also important parameters as they determine the saturation index of calcium phosphate. Recent work by Ma et al. (2018) showed that operation of an anammox expanded bed reactor operated on synthetic wastewater at pH 8.5 and a relatively high Ca:P ratio of 4.87 resulted in a phosphorus removal rate of 0.14 ± kg-P $(m^3, d)^{-1}$ while a nitrogen removal of 87.4 ± 2.9% was maintained. Once the operating parameters for maximum phosphorus recovery rate has been established in operation on real centrate, a cost-benefit analysis should be done in order to evaluate if the technology would be economically feasible to scale up. Although the inorganic granules settle by gravity, it should be assessed if it is more suitable to add them to the existing infrastructure for P fertilizer production or add them directly to field as fertilizer.

The discussion on potassium recovery and recycling is dwarfed by the focus on phosphorus recovery. Scholars seem to be more concerned about the potash supply for emerging economies [2,80], even though the EU too is depend on imports and import the majority of the potash used for fertilizer production. With the implementation of the EU Action Plan on the Circular Economy and a wider focus on recovery and reuse of nutrients, the debate might come to include potassium in the future. Although the experience from Putten in the Netherlands, the only full-scale implementation for potassium struvite recovery so far, has been successful, other implementations have no followed. From the site itself it has been suggested that hesitation from the industry to switch to new technologies can be the reason [45].

The concept to recover potassium struvite from centrate by using PNA for nitrogen removal has been proved in this work, but as discussed in Chapter 4.2 the technology still needs to be optimized. A main interest would be to find the cut-off ammonium nitrogen to potassium ratio that inhibit potassium struvite formation by formation of ammonium struvite. The process configuration would also need to be evaluated in continuous mode in pilot-scale in order to evaluate the stability. Because PNA is a biological process, the residual ammonium concentration will vary and the impact on the composition of the recovered product needs to be evaluated.

There is awareness among researchers, policy makers as well as the industry on the pressing need to move from a linear to a circular economy and from removal to recovery of nutrients from waste streams. Some examples from the policy side are the European Commission's Action Plan for the Circular Economy and the creation of the Critical Raw materials list to which phosphate rock has been added. The EU fertilizer legislation is under revision and is suggested to include recycled nutrients as well as limits to metals contents. This is expected to facilitate the introduction of recycled nutrients to the market.

5.3 Reducing human impact

Nutrients removed from soils during harvest (off-take) need to be replenished by farmers in order to sustain yields. This can be done either through return of crop residues, animal manure, organic solid waste, or wastewater or human excreta to fields, or by the input of synthetic or mineral fertilizer. Today, the human contribution of nutrients to soils is substantial. It has been estimated that globally close to 60% of phosphorus added to fields are from mined phosphate rock [3], while the natural gas-fueled Haber-Bosch process is fixing almost half the amount of nitrogen as is done biologically [9]. Corresponding estimates on the ratio between organic and mineral potassium fertilizer added to fields are lacking.

At the same time, the nutrient flows in the global food production and consumption system follow a mainly one-way trajectory; geological resources are extracted for the production of fertilizers, of which a large fraction are lost to the natural environment, either as run-off from crop fields and pastures (diffuse sources) or as discharge from inadequately treated wastewater from industries and households (point sources). This results in negative environmental impact such as eutrophication and nitrogen pollution of ground water, but the inefficiency also leads to a need for larger application of mineral fertilizer than needed. In other words, the inefficiencies of the current system has led to a dependency of imported mineral fertilizer of geological origin.

As discussed throughout this thesis, just a fraction of the nutrients applied to fields makes its way to the plate and further to the sewers where it can be recovered through the methods proposed in this thesis. The majority of nutrients are lost already in the food production step, i.e. from fields or through manure. Better agricultural management practices, including timing of application, actions to limit erosion, buffer zones of trees between fields and water bodies [6] are crucial in order to mitigate nutrient losses from the food production system and reduce the dependency on imported fertilizers.

Furthermore, current approaches to limit discharge of nutrients to the environment are largely focused on targeting and regulating point sources, such as wastewater treatment plants, manure or fields. A more efficient option however, would be to decrease the initial inputs. Even though technologies such as anammox and EBPR remove nutrients at lower energy and chemical costs than conventional treatment, targeting the discharge rather than the input can be compared to wiping a puddle rather than to close the dripping tap. Nutrient recovery such as struvite precipitation also has environmental costs such as input of chemicals and energy. A successful example on the strategy to limit inputs is national bans on phosphates use in detergents, which has led to decreased phosphorus loads to wastewater treatment plants [6,16].

Due to that nearly all nutrients consumed passes the body and end up in the sewers, wastewater is a fingerprint of societies and their consumption patterns. It has been calculated that the phosphorus content in human excreta is 0.3 kg P year $^{-1}$ for a vegetarian diet, while it is 0.6 3 kg P year $^{-1}$ for a meat-based diet [3]. Today, meat and meat products constitute the largest share of protein intake of adults in European countries (followed by grains and grain-based products, and milk and dairy products) [125]. Protein contain around 16% of nitrogen and a study from Sweden could show that the nitrogen load from households increased from 12 to 14 g N (p, d)$^{-1}$ between 1988 and 2006, an increase that could be attributed to increased meat consumption [16]. Increased loads of nitrogen and phosphorus are directly associated with higher costs for wastewater treatment.

The general requirements for protein intake is 0.83 g protein (kg bodyweight, day)$^{-1}$ [126]. This corresponds to 62 g protein per day for a person of 75 kg. The consumption of meat in Europe has increased from 130 g (capita, day)$^{-1}$ in 1961 to 208 g (capita, day)$^{-1}$ in 2011 [127]. The total protein intake in the same period has increased from 90 to 102 g (capita, day)$^{-1}$ between 1961 to 2011 [127]. Protein deficiency in affluent countries is extremely rare and concentrated to people who are hospitalized or by other means not able to eat. The vast majority is consuming well above the necessary protein requirements. The surplus of meat consumed therefore has to be viewed as unnecessary, especially taking into account the negative environmental and health impact of meat production. As an example, the livestock sector is responsible for 18 percent of greenhouse gas emissions (a higher share than transport), and might be the largest source of water pollution, as well as health concerns such as the emergence of antibiotic resistance [128].

Thus, the main approach to a sustainable nutrient scheme should be to use less and recycle more.

6 CONCLUSIONS

Digested sludge liquors represent a mining opportunity for nutrient recovery. All three macronutrients (N, P and K) can be recovered from this waste stream and returned to soil as fertilizer, either as is, or fed as a secondary raw material to the existing phosphate rock infrastructure.

The objectives of the thesis were fulfilled, the main contributions being: i) the characterization of the mineral core of PNA granules and the evaluation of the precipitate as a recovered phosphorus product, ii) the demonstration of PNA as a nitrogen removal step for sub-sequent potassium struvite recovery, iii) evaluation of autotrophic PNA biomass as a biological CO_2 stripper, iv) an understanding of the flow of potassium in the wastewater treatment plant.

From the first contribution, the following conclusions can be drawn:

- Biologically induced precipitation of calcium phosphate was confirmed in PNA granular sludge.
- Granules with a high inorganic content settled due to gravity, which allowed for easy recovery.
- Harvested granules showed a high phosphate content (16 wt%), with a Ca/P ratio close to that of hydroxyapatite, the presence of which was confirmed by XRD, although probably coexisting with amorphous calcium phosphates.
- The metals content complied with proposed EU limits for phosphorus fertilizer as well as with requirements from the phosphorus industry.
- The calcium phosphate formed without the addition of chemicals and is proposed as a novel phosphorus recovery product from wastewater.

From the second contribution, the following conclusions can be drawn:

- Ammonium removal by PNA makes possible potassium recovery through MPP from centrate.
- Coupling of PNA with struvite precipitation allows for the recovery of a multi-nutrient product containing all three macronutrients (N-P-K).
- Formation of potassium struvite is promoted by increasing pH and low ammonium concentrations.

From the third contribution, the following conclusions can be drawn:

- PNA biomass reduced the alkalinity of centrate by 90 %, which surpasses the performance of CO_2 strippers using aeration.
- PNA could substitute conventional CO_2 stripping as a pre-treatment of centrate before struvite precipitation with subsequent savings of energy and NaOH dosing for pH control.

From the forth contribution, the following conclusions can be drawn:

- As expected, the main part of the incoming phosphorus end up in the sludge fraction.
- Potassium is mainly present in the soluble K^+ form.
- Due to the soluble nature of potassium, the main part of the potassium is present in the water fractions (effluent, sludge water and centrate).

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