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Sina Shaddel

Nutrient recovery from wastewater by crystallization – Improving the process efficiency, economics and product quality

NTNU
Norwegian University of Science and Technology
Thesis for the Degree of
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Preface

The present thesis is submitted to the Norwegian University of Science and Technology (NTNU) for partial fulfillment of the requirements for the degree of Philosophiae Doctor (Ph.D.).

The work was carried out at the Department of Civil and Environmental Engineering, NTNU, in Trondheim, under the supervision of Professor Stein Wold Østerhus, NTNU and cosupervision of Professor Jens-Petter Andreassen, NTNU.

The research in this thesis was financed as a 4-year Ph.D. position, including 25% teaching duties, at the Department of Civil and Environmental Engineering, NTNU, granted by the Research Council of Norway (RCN) as a part of RECOVER project (RCN grant no. 90040107) and the industrial partners. The RECOVER project was organized with the industrial partners: Cambi, Kemira, Krüger Kaldnes, Norconsult, Salsnes Filter and Doscon and the research partners: SINTEF and NMBU.

In accordance with the requirements of the Faculty of Engineering at NTNU, the present thesis comprises an introduction to the research that has resulted in five scientific papers.

Acknowledgements

This work was carried out at the Water and Wastewater group, in the Department of Civil and Environmental Engineering at the Faculty of Engineering, Norwegian University of Science and Technology, Trondheim.

I would like to express my sincere appreciation to my supervisor Stein Wold Østerhus. Thank you for all your supports. You believed in me and I have truly learnt a lot from you. I really appreciate it. I am very thankful to my co-supervisor Jens-Petter Andreassen, as well as Seniz Ucar. A great acknowledgement goes to you for your helpful comments and feedbacks. You have provided me with valuable advices and scientific insights.

Further, I also want to thank all the technical staff at IBM especially Trine Margerte Hårberg Ness, Thuat Trinh and Arne Grostad for supporting me in the lab. Many thanks to all administrative staff at IBM for their help. I would like to thank all IBM members and especially the fellow PhD students. I enjoyed all the small chats, complaining and laughing that made me smile and clear my head from work.

A big hug to my family, my mom and sister who supported me to do this Phd. I dedicate this effort to my late father. I am deeply thankful to thank my spouse, Neda for all love, support and help. Neda, I really appreciate the effort you put in supporting me throughout the difficulties of my PhD. Your value to me is beyond words!

Abstract

The long-term strategic design of wastewater treatment plants requires measures to address a range of sustainability challenges, including the rapid population growth, climate change, urbanization and stressful position for some natural resources. The resource recovery from wastewater have been extensively elaborated in scientific publications as well as rapid development of nutrient recovery technologies in the market. However, due to various technical and non-technical reasons (economic, environmental and societal) the implementation in municipal wastewater treatment plants is still poor. In this context, this work investigates the nutrient recovery from nutrient-rich wastewater streams. Based on the performed review of nutrient recovery technologies three main areas for improvement have been identified including recovery efficiency, product quality and financial sustainability. Further, an alternative process configuration for phosphorus recovery in the plants using enhanced biological phosphorus removal (EBPR) is presented to mitigate the operational challenges, enhance the recovery efficiency and reduce the recovery costs. The recovery efficiency and product properties of calcium phosphates were compared to struvite both by thermodynamic modeling and by experimental studies. The detailed investigation of the effect of supersaturation regulators on product properties and phosphorus recovery is presented, which can contribute in the integrated improvement of recovery efficiency and product quality. Application of seawater as a low-cost alternative magnesium source for struvite production was investigated and compared to a conventional magnesium source (i.e., $MgCl_2$). The challenges associated with using seawater and the mitigation measures for them were studied. Further, the reaction kinetics and crystal growth studies were presented for struvite crystallization by both seawater and $MgCl_2$. The impact of the important supersaturation regulators on struvite crystallization kinetics were studied.

The findings in this study may improve the understanding of the nutrient recovery from nutrient-rich streams at wastewater treatment plants. Further, it can contribute to reduce the operational costs and operational challenges as well as improving the recovery efficiency and producing product with improved properties. Products with higher quality and lower production costs will have a higher chance for market penetration and implementation in full-scale.

Sammendrag

En langsiktig og strategisk utforming av avløpsrenseanlegg krever løsninger for å møte en rekke bærekraftsutfordringer, slik som befolkningsvekst, klimaendringer, urbanisering og økt press på naturressurser. Forskning på ressursgjenvinning fra avløpsvann er allerede omtalt i utstrakt grad i vitenskapelige publikasjoner, og det skjer en rask utvikling innen teknologi for utvinning av næringsstoffer. Av ulike grunner (tekniske, økonomiske, miljømessige og samfunnsmessige) går implementeringen av nye løsninger i kommunale avløpsanlegg langsomt. I lys av dette er det i denne studien gjort undersøkelser av utvinning av næringsstoffer fra næringsrike avløpsstrømmer.

Basert på en gjennomgang av tilgjengelige løsninger for gjenvinning av næringsstoffer er det identifisert tre hovedområder for forbedring; gjenvinningsgrad, produktkvalitet og økonomisk bærekraft. Videre presenteres en alternativ prosesskonfigurasjon for fosforgjenvinning i renseanleggene som har biologisk fosforfjerning (EBPR). Dette har til hensikt å dempe de driftsmessige utfordringene, forbedre gjenvinningsgraden og redusere utvinningskostnadene for fosfor. Gjenvinningsgraden og produktegenskapene til kalsiumfosfater ble sammenlignet med struvitt både ved termodynamisk modellering og eksperimentelle studier. Det presenteres her en detaljert undersøkelse av effekten av overmetningsregulatorer på produktegenskaper og fosforgjenvinning, noe som kan bidra til forbedring av utvinningseffektivitet og produktkvalitet. Anvendelse av sjøvann som et rimelig alternativ til magnesiumkilde for struvittproduksjon ble undersøkt og sammenlignet med en konvensjonell magnesiumkilde (dvs. $MgCl_2$). Utfordringene knyttet til bruk av sjøvann og avbøtende tiltak med hensyn til disse ble studert. Videre er reaksjonskinetikken og krystallvekststudiene for struvittkrystallisering med både sjøvann og $MgCl_2$ presentert. Effekten av de viktige overmetningsregulatorene på reaksjonskinetikken ved struvittkrystallisering ble studert.

Funnene i denne studien kan forbedre forståelsen av ressursgjenvinning fra næringsrike strømmer ved renseanlegg. Videre kan det bidra til å redusere driftskostnader og driftsutfordringer, samt forbedre utvinningseffektiviteten og produktegenskapene. Produkter med høyere kvalitet og lavere produksjonskostnader vil øke sannsynligheten for markedsinntrengning og implementering i full skala.

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List of papers

The following publications are included in this thesis:

(I) **Sustainable sewage sludge management: From current practices to emerging nutrient recovery technologies**
Sina Shaddel, Hamidreza Bakhtiary-Davijany, Christian Kabbe, Farbod Dadgar and Stein W. Østerhus. (2019).
Sustainability Journal. 11 (12), DOI: 10.3390/su11123435.

Designed the study: SS. Wrote the paper: SS and HBD. All authors contributed in the discussion and revision of the paper.

(II) **Enhancing efficiency and economics of phosphorus recovery process by customizing the product based on sidestream characteristics – an alternative phosphorus recovery strategy.**
Sina Shaddel, Seniz Ucar, Jens-Petter Andreassen, Stein W. Østerhus (2019).
Water Science & Technology 79(9):1777-1789. DOI: 10.2166/wst.2019.178.

Designed the study: SS. Performed the experiments: SS. Analyzed the data: SS and SWO. Wrote the paper: SS. All authors contributed in the discussion and revision of the paper.

(III) **Engineering of struvite crystals by regulating supersaturation- Correlation with phosphorus recovery, crystal morphology and process efficiency.**
Sina Shaddel, Seniz Ucar, Jens-Petter Andreassen, Stein W. Østerhus (2019).
Journal of Environmental Chemical Engineering 7(1). DOI: 10.1016/j.jece.2019.102918.

Designed the study: SS. Performed the experiments: SS. Analyzed the data: SS. Wrote the paper: SS. All authors contributed in the discussion and revision of the paper.

(IV) **Struvite crystallization by using raw seawater: improving economics and environmental footprint while maintaining phosphorus recovery and product quality.**
Sina Shaddel**,** Tonje Grini**,** Seniz Ucar, Kamal Azrague, Jens-Petter Andreassen, Stein W. Østerhus (2019). *Water Research,* DOI: 10.1016/j.watres.2020.115572.

Designed the study: SS. Performed the experiments: SS and TG. LCA study: KA. Analyzed the data: SS. Wrote the paper: SS. All authors contributed in the discussion and revision of the paper.

(V) **Crystallization kinetics and growth of struvite crystals by seawater versus magnesium chloride as magnesium source: towards enhancing the economics of struvite crystallization.**
Sina Shaddel**,** Tonje Grini**,** Seniz Ucar, Jens-Petter Andreassen, Stein W. Østerhus (2020). *Chemosphere,* DOI: 10.1016/j.chemosphere.2020.126968.

Designed the study: SS. Performed the experiments: SS and TG. Analyzed the data: SS. Wrote the paper: SS. All authors contributed in the discussion and revision of the paper.

Conference papers/Posters/Related publications

Enhancement of efficiency and economy of phosphorus recovery process by customizing the product based on reject water characteristics.
Sina Shaddel, Stein W. Østerhus**.**
Conference proceeding, IWA Nutrient Removal and Recovery Conference 18-21 November 2018, Brisbane, Australia.

Struvite production by using raw seawater - How to improve the economics and keep the product quality?
Sina Shaddel, Stein W. Østerhus.
Conference proceeding, 3rd IWA Resource Recovery Conference 8-12 October 2019, Venice, Italy (ISBN: 9788894470000).

Nano-enhanced Adsorptive Media for Nutrient Recovery from Wastewater
Sina Shaddel, Ed Weinberg, Stein W. Østerhus.
Norwegian NanoSymposium 16-17 October 2019, Trondheim, Norway (Poster)

Sjøvann kan framskynde overgangen til sirkulærøkonomi og effektivisere fosforgjenvinning (title in English: seawater can accelerate the transition to circular economy and make phosphorus recovery more efficient)
Sina Shaddel, Tonje Grini.
Vann 2018; Volume 53. (2) s. 238-241 (written in Norwegian)

Sjøvann kan effektivisere fosforgjenvinning (title in English: seawater can make phosphorus recovery more efficient)
Sina Shaddel, Tonje Grini.
Vannspeilet, July 2018 (written in Norwegian)

Presentations/Popular science

Avløpsvann er penger rett i do (title in English: wastewater is money right in the toilet) Sina Shaddel, Adresseavisen Mandag 4. desember 2017 (written in Norwegian)

RECOVER – Resource recovery from wastewater, Sina Shaddel. 2017, Techzone.

Orientering om Recover prosjektet (title in English: orientation on the Recover project), Sina Shaddel, 2018, VA-Dagene Midt Norge.

Avløpsvann - penger rett i do. Forsker Grand Prix, 2018, NRK.

Kjemiske trinn i gjenvinning av fosfor fra avløpsvann (title in English: chemical processes in recovery of phosphorus from wastewater), Sina Shaddel, Tonje Grini Kursdagene 2019 - Tenka (Bærekraft i vannbransjen).

Ressursgjenvinning – Avløpsvann er penger rett i do (title in English: resource recovery- wastewater is money right in the toilet) Sina Shaddel. 2019, Midt-Norsk Ingeniørkonferanse.

Fosforfjenvinning fra avløpsvann (title in English: phosphorus recovery from wastewater), Sina Shaddel, 2019, Trondheim kommune.

Abbreviations

AD	Anaerobic digestion
BIA	Brukerstyrt innovasjonsarena (User-driven research-based innovation)
Bio-P	Biological phosphorus removal
BOD	Biological oxygen demand
C	Carbon
CaP	Calcium phosphate
COD	Chemical oxygen demand
EBPR	Enhanced biological phosphorus removal
HRT	Hydraulic retention time
IAP	Ion activity product
IC	Ion chromatography
LCA	Life cycle assessment
MBBR	Moving bed biofilm reactor
Mg	Magnesium
N	Nitrogen
P	Phosphorus
K	Potassium
PAH	Polycyclic aromatic hydrocarbons
PAO	Polyphosphate accumulating organism
PCB	Polychlorinated biphenyls
PHA	Poly-hydroxyalkanoates
SEM	Scanning electron microscopy
SI	Saturation index
SRT	Solid retention time
SS	Suspended solids
T	Temperature
TSS	Total suspended solids
VFA	Volatile fatty acid
VSS	Volatile suspended solids
WAS	Waste activated sludge
WRRF	Water resource recovery facilities
WWTP	Wastewater treatment plant
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Introduction

Wastewater treatment plants are essential facilities that have been meant to remove contaminants from wastewater before return to the water cycle to protect public health and the environment. Nowadays, the long-term strategic design of wastewater treatment plants is driven by a range of sustainability challenges, including the rapid population growth, climate change, urbanization, and stressful position for some natural resources. Today, around 380 billion cubic meters of wastewater are produced annually worldwide with a projected rise of 24% by 2030, 51% by 2050 (Qadir et al., 2020). The worldwide population is projected to rise by 40% from 7.7 billion individuals in 2019 to 8.5 billion in 2030, 9.7 billion in 2050, and 10.9 billion in 2100 (United Nations, 2019). This requires a more sustainable use of resources and revision of several of the current treatment practices due to resource inefficiency. In other words, there is a need for a transition from pollutant removal towards resource recovery by recognizing wastewater as a resource rather than waste stream.

Wastewater is a transport medium for several resources due to added material, chemicals and energy from households and businesses to water, while the abundance of a source and need for the treatment are determining factors that make it suitable for recovery. Therefore, the modern generations of wastewater treatment are important players towards a waste-based economic growth and paradigm-shift from waste treatment to resource recovery. The importance to consider wastewater as a resource is clear but the question is where to focus on while there is an array of technical options for the recovery of variety of alternatives. The water, energy and nutrient recovery (P, K, N) are known alternatives, while other emerging options are the recovery of volatile fatty acids (VFAs), polyhydroxyalkanoates (PHAs), carbon-chain elongation, extracellular polymeric substances (EPSs), single-cell protein (SCP), iron phosphate and cellulose (Kehrein et al., 2020). Although the on-site energy recovery at sewage treatment plants has received more attention, nutrient recovery from wastewater should not be overlooked (Van Loosdrecht and Brdjanovic, 2014). The availability of technology for nutrient recovery from wastewater is not the primary obstacle, although there is a lack of social-technological and business methodology to recognize the most sustainable solutions (Guest et al., 2009).

It is estimated that annually 16.6 million metric tons of nitrogen, 3 million metric tons of phosphorus and 6.3 million metric tons of potassium are released into wastewater produced worldwide while full recovery of these nutrients from wastewater could, theoretically, offset 14.4% of global demand for nitrogen as a fertilizer nutrient; phosphorus 6.8% and potassium 18.6% (Qadir et al., 2020). The management of P and N in wastewater has gained more importance due to the stringent N and P discharge standards in recent years and the fact that these nutrients are acting as key drivers for nutrient recovery from wastewater. The P recovery is much more urgent compared to N recovery because P is a finite resource with projected scarcity (Khiewwijit, 2016). Therefore, the current practices and status of handling nutrients in wastewater should be revised to develop conceptual models for a sustainable transition towards reuse of resources in wastewater. Although the uncertainties about which techniques are most useful and how to combine them stand in the way, the recovery of phosphorus from wastewater based on available infrastructure and business perspective could be of great interest. It shows that phosphorus management in wastewater streams is a global and growing challenge.

Fertilizers replace the consumed nutrients by crops from the soil while without the supplement of fertilizers, crop yields and agricultural productivity, and consequently food production would be significantly reduced. Phosphorus is an essential raw material of mineral fertilizers as well as high value adding industrial products, including electric vehicles, electronics, pharmaceutical, and high functional plastics. Phosphorus is a bioessential and irreplaceable element which is essential for food production. Fertile soils are essential for sustainable production of crops for food, although few soils are fertile without addition of plant-available nutrients (Dawson and Hilton, 2011). It is estimated that agroecosystems account for 80-90% of the world’s total P consumption (Heckenmüller et al., 2014). Nowadays, 50% of worldwide food production is estimated to be based on mineral fertilizers (Galloway et al., 2008), with the largest contribution from domestic sewage at 54 % owing to the crucial role of phosphorus in food production and livestock farming, followed by agriculture at 38 % and industry at 8 % (Mekonnen and Hoekstra, 2018). It was estimated that 1.47 million metric tons of phosphorus from human activities entered the earth's freshwater bodies each year between 2002 and 2010 (Mekonnen and Hoekstra, 2018). These phosphorus loads are higher than assimilation capacity of freshwater bodies in 38 % of the earth's land surface equivalent to an area housing 90 % of human population (Mekonnen and Hoekstra, 2018). Wastewater is one of the possible P sinks considering the cycle of phosphorus, although the recycling of phosphorus from wastewater is in early stage of development. This is because wastewater system decisions traditionally driven by considerations of function, safety and cost-benefit analysis, while the mining of phosphate rock is the only cost-effective production method to date (Guest et al., 2009).

Several recent studies suggest that the phosphate rock reserves could be depleted within 30–300 years (Cordell et al., 2009; Vaccari, 2009). This dramatic fluctuation in geological stock estimation has two reasons. First, new discoveries and improved information cause dramatic change in phosphate rock reserves, as before mid-1990s limited information was available on worldwide phosphorus reserves. Second, due to dynamic economic and technical factors as opposed to an absolute physical evaluation because at the time of determination they refer to that part of reserve that could be economically extracted. In other words, today's resources can be tomorrow's reserves with new mining and processing technologies or with increased market price. Therefore, the determination of phosphate rocks reserves is very difficult (Chen and Graedel, 2016). The phosphorus reserves are finite and non-renewable from the perspective of human timescale, although depletion timelines are uncertain. The rapid depletion of quality reserves implies higher costs for future extraction owing to relatively inaccessible location and high environmental and ecological vulnerability of deposits that need to be exploited (Chen and Graedel, 2016). The phosphorus mining has a huge environmental impact due to generation of by-products like gypsum. The byproducts are often not disposed of in an environmentally friendly manner, which are contaminated with radioactive elements and heavy metals (Verstraete et al., 2009).

Phosphorus is on the list of critical raw materials which means that it may reach or exceed thresholds for both supply risk and economic importance. Quality phosphate rocks are available in only a few countries and most of countries in the world are almost entirely dependent on phosphorus imports; therefore, the opportunity to recover phosphorus will greatly reduce the supply risk. However, regardless of exact timetable of global phosphate rocks depletion, phosphorus is a limited and irreplaceable resource. Therefore, the recovery of phosphorus from waste streams can be a promising approach to reduce the conventional mining and moderate the expected future shortage of phosphate rocks used to produce phosphorus fertilizers (Shaddel S et al., 2019).

Taking Europe as an example shows that phosphorus recovery is gaining momentum and there are currently more than 50 permanent phosphorus recovery plants in Europe, half of which have been commissioned in the last 4 years. However, this addresses a small proportion of as Europe has 30,000 wastewater treatment plants and around 2,000 of them are large enough to make phosphorus recovery economically feasible today. The phosphorus fertilizers sourced from secondary raw material than the phosphate rock-derived products have generally lower environmental and health life cycle impacts, especially in areas of high livestock and population density (Tonini et al., 2019). The societal costs of circular products derived from sludge is 81%, manure 50%, and meat and bone 10% lower than rock-derived superphosphate. Therefore, P recovery from non-conventional P-rich sources by efficient and economically viable solutions can accelerate a sustainable development.

It was concluded that even without considering depletion risks of phosphate rocks, short-term and local environmental and health co-benefits might underlie the societal cost effectiveness of advanced phosphorus recovery (Tonini et al., 2019). This shows the potential for further research to accelerate the phosphorus recycling from wastewater streams. The proposed actions in this way require considering both the environmental and business drivers. Further, innovative solutions are required like the past two decades that phosphorus recovery from wastewater has been subject to much innovation, and the trend looks set to continue. These processes could potentially open substantial new possibilities of recovery, although they are still in the early stages of development and testing. Therefore, the search for process solutions that improves the overall efficiency of the phosphorus recovery process along with product properties and economics are well motivated.

1.2 RECOVER project

RECOVER project was a user-driven Research-based Innovation (BIA) aimed to deliver innovative solutions to current technological gaps in comprehensive wastewater management systems applicable to Norway and globally through innovation in biological processes with focus on resource recovery. The project was 80% funded by research council of Norway (NFR) and 20% by industrial partners: Cambi, Kemira, Krüger Kaldnes, Norconsult, Salsnes Filter and Doscon. The research partners were: NTNU, NMBU and SINTEF. The associated partners in this project were two wastewater treatment plants: IVAR and HIAS. The presented study was performed as a part of the RECOVER project (2015-2020) at the Department of Civil and Environmental Engineering, NTNU. This study has focused on the nutrient recovery (P and N) from nutrient-rich streams at the wastewater treatment plants.

1.3 Aim of the research

In relevance with the current focus on phosphorus recovery from wastewater, this work is included within the RECOVER project as nutrient recovery from nutrient-rich wastewater streams. We seek to define the research gaps by comprehending the current practices and state-of-the-art technologies for nutrient recovery from wastewater. The identified general aims were to improve I) process efficiency, II) product properties and III) economics of the phosphorus recovery from nutrient-rich streams by crystallization. Theoretical studies and experimental work have been used to investigate new processes and to improve the performance of available techniques for recovery of nutrients (with focus on phosphorus and nitrogen), including production of value-added products via crystallization technique. The main objectives are as follows:

Objective 1: Comprehending the current practices and state-of-the-art technologies for nutrient recovery from sewage sludge.

Objective 2: Improving the performance of phosphorus recovery process from nutrient-rich wastewater streams.

Objective 3: Improving the overall process efficiency via coupling the recovery efficiency and product properties.

Objective 4: Improving the economics of phosphorus recovery process by using low-cost alternatives to chemicals.

1.4 Thesis structure

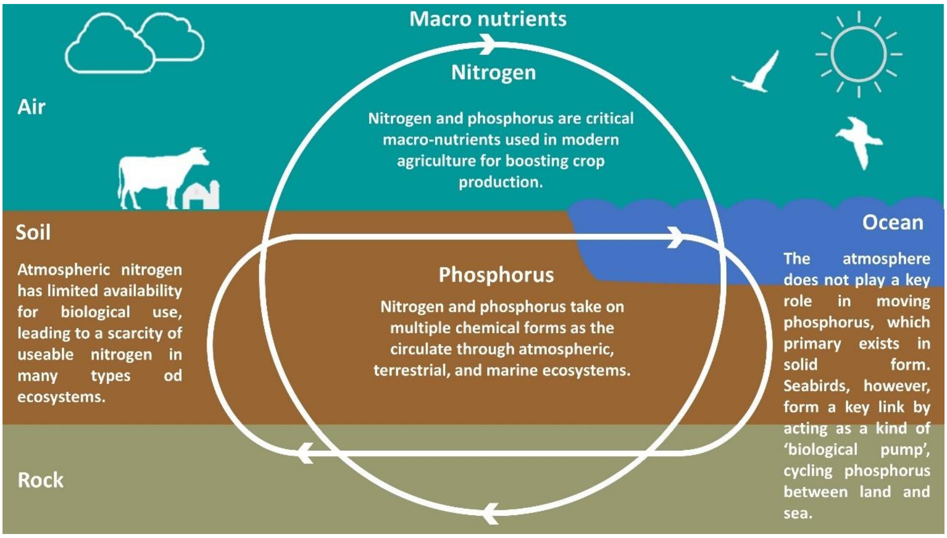
The theoretical background of this work is given in chapter 2. Following in chapter 3, findings are summarized and discussed. Chapter 4 presents the concluding remarks and outlook. Five publications included in this thesis are attached as well as supplementary attachments for the convenience of the reader.

CHAPTER 2

BACKGROUND

2.1 Phosphorus in wastewater

Phosphorus is billions of years old, while it has only been known to us as an element for 350 years. Figure 1 presents the cycle of nitrogen and phosphorus in biosphere. The production of domestic and industrial waste due to human activities have notably increased the P content in the hydrosphere which can cause eutrophication (Luo et al., 2018). Phosphorus can be found in different forms in the soil; soluble, mineral, adsorbed and organic. The soluble fraction is mainly used by plants and crops which is a small fraction of the total P, while insoluble P (organic and mineral) is the dominant form in the soil in chemical bond to aluminum/iron phosphates and calcium phosphate forms. The amount of P present in the atmosphere is very low at any time because gaseous forms of phosphorus are not stable. In the atmosphere it can be found adsorbed on particular matter that rapidly removed from the atmosphere by precipitating processes (Pasek et al., 2014).



Nitrogen and phosphorus are critical macro-nutrients used in modern agriculture for boosting crop production.

Atmospheric nitrogen has limited availability for biological use, leading to a scarcity of useable nitrogen in many types od ecosystems.

Nitrogen and phosphorus take on multiple chemical forms as the circulate through atmospheric, terrestrial, and marine ecosystems.

The atmosphere does not play a key role in moving phosphorus, which primary exists in solid form. Seabirds, however, form a key link by acting as a kind of ‘biological pump’, cycling phosphorus between land and sea.

Figure 1: The cycle of nitrogen and phosphorus in biosphere, adopted after (Wendell and Bryan, 2019)

Phosphorus is the fifth most prevalent element in wastewater with very low input concentrations and discharge limits (Batstone et al., 2018). Protein-rich foods are the main source of phosphorus in human food and almost 100% of phosphorus eaten is excreted which is approximately 1.8-1.9 g/d P, 67% of which is excreted via the urine and 33% via the feces (Kroiss et al., 2011). The excreted P; by the human body is equivalent to 17% of all mined mineral P on a global scale, which make cities the P hotspots (Kehrein et al., 2020). Moreover, wastewater treatment plants are linked to the global nutrient cycle since a part of the nitrogen and phosphorus applied as fertilizer ends up in the wastewater streams. Phosphorus (P) and nitrogen (N) both originate from point sources (municipal landfill leachates, anaerobic digested sewage sludge, human urine, swine wastewater) and non-point sources (run-off from agriculture and pasture, aquaculture and atmospheric deposition) (Kumar and Pal, 2015). Therefore, the sewer system and wastewater treatment can contribute to collect and concentrate the phosphorus in a manageable mass flow providing potential for recovery.

The mechanical, chemical and biological processes are applied to capture nutrients from aqueous phase to a solid and separable phase (i.e., sewage sludge). In most cases, nutrients such as nitrogen and phosphorus, heavy metals and non-polar organics compound are concentrated in the sewage sludge. A well-functioning phosphorus removal process may capture 90% of the P entering the WWTP by transferring it into the sludge. (Cornel and Schaum, 2009). Figure 2 illustrates the mass balance of phosphorus in a typical wastewater treatment plant. Therefore, the valorization of phosphorus in the wastewater is possible via dewatered sludge (biosolid), dewatering liquor of waste sludge and recovery from incinerated sludge (sludge ash). The traditional route for nutrient recovery has been the application of biosolids, while due to the associated environmental risks there is a need for advanced nutrient recovery techniques with predictable product composition and properties. Phosphorus speciation is another important process consideration as phosphorus in aqueous phase can be grouped to organically bound phosphorus, polyphosphate and orthophosphate. Organically bound phosphorus can be captured in primary clarifiers or transformed to orthophosphates during anaerobic digestion. Biological conversion of polyphosphate to orthophosphates is possible as polyphosphates are soluble. Orthophosphate is inorganic soluble phosphorus and can form floc or precipitate out. However, inorganic phosphorus can be bound in Ca-P compounds with low solubility (Li et al., 2019a).

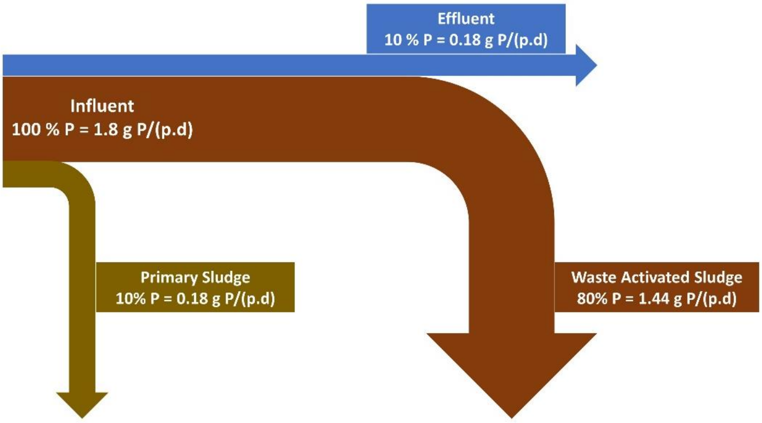


Figure 2: Schematic representation of P removal and distribution in WWTP (Christian Kabbe, 2019)

2.2 Drivers of phosphorus recycling

The recycling and reuse of nutrients in wastewater at a very early stage was performed by sprinkle irrigation of wastewater. In the beginning of 19th century and construction of new generation of sewer systems feces were carried away to be used as agricultural fertilizer and the treatment plants were upgraded by advance sewage sludge treatment and application of stabilized sewage sludge for nutrient reuse. The increase of society’s ecological awareness showed that sewage sludge is the sink for both nutrients and pollutants. Thereby, it is desirable to recover and recycle phosphorus in the wastewater in a cleaner form.

Although physical scarcity of phosphate rocks in near future is very unlikely, the recycling of phosphorus is of interest due to some ‘general aims’ (Udert, 2018). First, recycling would increase supply security and avoid economic scarcity due to financial market bubbles, supply and demand imbalance or geopolitical risks due to uneven distribution of phosphate reserves. A second reason is linked to the principle of intergenerational justice which aims to reduce opportunity costs for future generations and provide long-term access to sufficient amount of high-grade deposits (United Nations Rio Convention, 1992). Third, the key ideas of a circular economy, which are less than 30 years old, increasingly acknowledge that recycling and closing loops in the supply-demand chain are the competitive edge of economic development (Ohtake and Tsuneda, 2018). Finally, the loss of substantial amounts of phosphorus along the whole supply-demand chain, from mine to fork. In the end, this can cause the environmental pollution, especially the eutrophication of lakes and coastal waters which is a pressing problem as a result of today's global phosphorus flows (Udert, 2018).

Further, there are some 'specific objective and drivers' for phosphorus recovery from wastewater: 1) the potential for production of commercial fertilizers which consequently can reduce the greenhouse gas emission and energy consumption as well as partly off-set depletion of commercially-recoverable phosphate rocks, 2) appeal for reduction of cost, chemical use and sludge production in phosphorus removal to improve the sustainability in nutrient management, 3) the capacity to reduce the operational and maintenance issues and equipment issues due to uncontrolled precipitation, 4) reduction of sidestream loads from sludge operations to stabilize enhanced biological phosphorus removal, 5) potential to achieve a biosolid with lower P content and higher land application rates, 6) improving the dewaterability of biosolids and reduction of biosolid volume for disposal, 7) a revenue stream from sale of a market-ready product and 8) align with expected regulatory visions in the future (Jeyanayagam, 2018).

2.3 Phosphorus recovery

The composition of wastewater varies by source, which can significantly affect P recovery process design and performance. Different types of wastewater have been studied for the P recovery such as fertilizer industry wastewater (Hutnik et al., 2013), municipal landfill leachate (Siciliano, 2016), membrane concentrate (Bradford-Hartke et al., 2012), reject water generated from sludge digestion and dewatering processes (Lahav et al., 2013), poultry manure wastewater (Shih et al., 2017), swine wastewater (Ye et al., 2016), saline industrial wastewater (Crutchik and Garrido, 2011), urine (Tian et al., 2016), aquaculture wastewater (Zhang et al., 2016) and other concentrated streams. While it is possible to recover phosphorus in various forms, it is important to match suitable waste streams for recovery of intended products to ease constraints on recovery technology.

The desired outcome of nutrient management in wastewater utilities is the removal of nutrients to a certain degree followed by making the extracted nutrients available for various uses (i.e. in agriculture or other industries). Generally, as the efficiency of nutrient recovery techniques typically decrease with lower concentrations and the concertation of nitrogen and phosphorus in municipal wastewater is too low for efficient extraction directly from the influent, a three-step framework has been recommended. The three-step approach would include: 1) nutrient accumulation to high concentrations, 2) release of nutrients to smaller volumes and lower organic content, and 3) recovery of nutrients (Jeyanayagam, 2018). The candidate technologies for achieving each of the three steps are presented in Figure 3. Phosphorus removal and recovery are generally regarded as separate process steps. There are the well-established phosphorus removal processes which are well integrated into the wastewater purification process chain. The applied technique for phosphorus recovery depends on the technique used for the removal of phosphorus and the available form of phosphorus for recovery. Several physical, biological and chemical approaches have been developed for the recovery of phosphorus such as crystallization, adsorption and ion exchange processes, membrane-based processes, electrochemical and biological processes (Hutnik et al., 2013; Ichihashi and Hirooka, 2012; Loganathan et al., 2014; Luo et al., 2016; Tarayre et al., 2016). The success of final product of a P recovery technology depends mainly on process performance and product properties. The low purity products, high costs and complex operation is the drawback of several techniques, while crystallization has relatively high recovery rate, considerable economic efficiency, marketable product with few environmental risks (Peng et al., 2018; Tarayre et al., 2016).

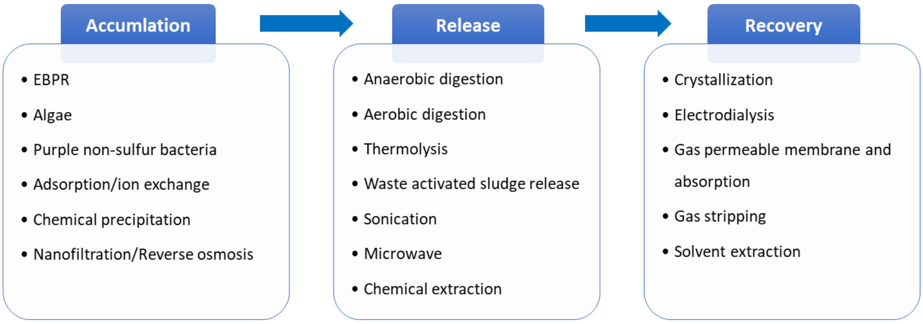


Figure 3: The main steps for extractive nutrient recovery from municipal wastewater (Water environment and reuse foundation, 2015).

The key challenge of P recovery is separation and capture of phosphorus from wastewater. While increasing stringent phosphorus regulations are expected to mitigate eutrophication in the future, the phosphorus recovery form wastewater complements the P removal by reducing the recycle loads. In addition, the potential for energy and chemical saving promotes the overall sustainability. The processes for recovery of phosphorus from the aqueous phase, sewage sludge or sludge ash are additional downstream process steps into the existing process chain. The separation of P in particulate form along with organic and inorganic material is possible by chemical P removal, while creation of strong chemical bonds makes the P release from the separated solid phase challenging. However, higher fraction of the removed P by enhanced biological phosphorus removal (EBPR) is available for P recovery. The recovery of phosphorus from sidestreams after sludge dewatering in EBPR improves the dewaterability of the sludge which further reduces the sludge disposal volume. Nuisance deposition of phosphate scales (i.e., struvite) reduces the wastewater treatment efficiency, while controlled and intentional precipitation of phosphorus is an effective mitigation strategy which produces high value product. The recovery limits and expenses are associated challenges with integrated phosphorus recovery units, although based on the available infrastructure and process benefits these processes have received attention. In general, recovery of the captured phosphorus in sludge is possible during several process steps of wastewater treatment, as shown in Figure 4. Generally, implementing P recovery can help to 1) reduce operating costs by offsetting aeration, supplemental carbon and chemicals (where applicable), 2) improve the sludge dewaterability and reduce the volume of sludge and biosolids, 3) reduce the nuisance precipitate scaling, 4) increase the reliability of biological processes by reducing the sidestream nutrient load on mainstream, 5) offset operating costs by selling the recovered product and 6) production of more favorable biosolid by alteration of P and N content with less limitation for land application due to P-indexing.

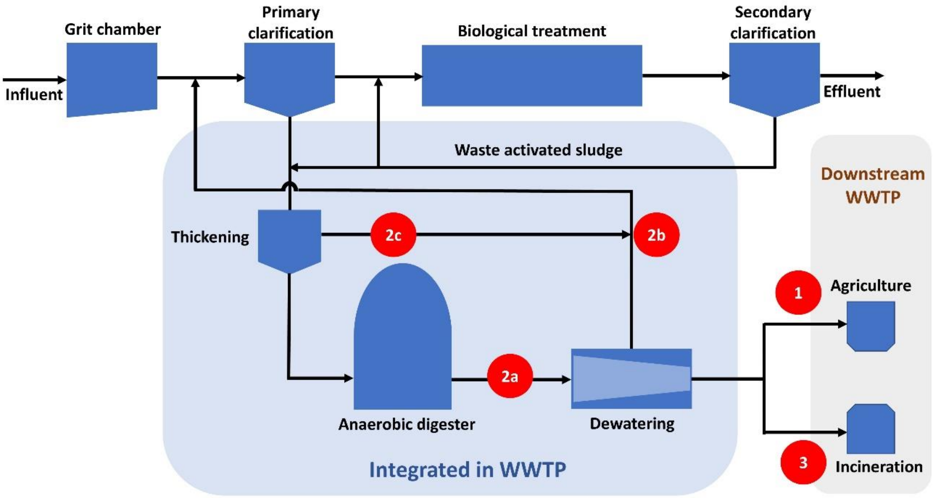


Figure 4: Hotspots for P recovery from the wastewater stream (simplified for centralized sanitation systems), Legend: 1 = direct sludge (biosolids) application in agriculture; 2a = P recovery within digested sludge prior to dewatering; 2b = P recovery from sludge liquor after dewatering; 2c = P recovery from liquor of pre-treated WAS; 3 = P recovery from mono-incineration ash, adapted after (Schoumans et al., 2015)

2.4 Selection of P recovery route

In principle, selection of a proper P recovery technique depends on several complicated factors such as the process requirements, local regulations and available infrastructure. However, from an application point of view, the candidate technology must be proven to be capable and feasible. Otherwise, ideas and developments end up as fancy high-tech, but fail to mature into innovation. In addition, in the selection of the candidate phosphorus recovery technique the following criteria should be considered: 1) production of the recovered material in such a chemical compound for further use as fertilizer or for production of balanced fertilizers, 2) the product should have better plant availability and dosing control compared to sewage sludge and conventional fertilizers, 3) avoid producing new harmful substances and waste streams, 4) provide storage possibilities of product by considering the expected future increase in phosphate price and 5) a perspective to minimize operational expenses and mitigate operational problems. From an economical point of view, due to several reasons a comparative analysis is only possible with a certain degree of uncertainty. The reactor volumes simultaneously are used for removal of organic compounds, nitrogen and phosphorus. Therefore, it is difficult to calculate the costs and economic efficiency of various processes because it is problematic to distinctly determine the investment and operational costs. Further, the calculation of sludge volumes from chemical and biological processes is mainly possible based on theoretical calculations (i.e., not through measurement). The local cost structures are also of considerable importance (Baumann, 2018).

The potential for and favored method of phosphorus recovery depends on existing infrastructure for wastewater treatment. Chemical phosphorus removal (typically dosing of iron or aluminium salts) and enhanced biological phosphorus removal (EBPR) are the most applied technologies. In both cases, the phosphorus is diverted into the sludge; however, the bioavailability of chemically bound phosphorus in sludge is often debated and it is typically not readily available for recovery without first pretreatment processes such as acid leaching. On the other hand, phosphorus in soluble will naturally be release from the bacteria in EBPR sludge under anaerobic conditions – such as an anaerobic digestion that is the most applied treatment method for wastewater sludges in Europe. The combination of EBPR and anaerobic digestion at wastewater treatment plants provides the possibility for phosphorus recovery.

Phosphorus recovery by land application of sewage sludge is going to be banned due to incorporation of impurities and less control on the compositions of the sludge (Kennedy et al., 2007). Therefore, the recovery of phosphorus from liquid phase and sludge ash are the more relevant options. The comparison of all recovered materials from wastewater was performed against sewage sludge and commercial fertilizers (Brans, 2008). The damage unit and reference soil method were used to assess the purity and compatibility of the recovered materials. The lowest damage values correspond to lowest heavy metal content was recognized for recovered materials from the liquid phase, owing to good decontamination rates. The relatively low damage unit values theoretically make it possible to apply the recovered material more often or for longer period of time than single superphosphate commercial fertilizer before reaching the limit of heavy metal concentrations in the soil (Egle et al., 2016). Further, The economic assessment shows that the associated costs (not accounting for revenues and savings) for P recovery from the liquid phase are in the range of 6-10 € kg P^{-1}, while processes for P recovery from sludge are usually more expensive with wet-chemical and metallurgical processes in the range of 9-16 € kg P^{-1} and wet-oxidation processes 23-27 € kg P^{-1} (Egle et al., 2018). However, the combination of revenues and potential savings result in significantly different results.

The P recovery from sludge ash results in higher recovery rates and possibility to include the P-rich materials (e.g. meat and bone) and easy marketable products such as phosphoric acid, although the high amount and variety of waste streams and lack or high cost of removal of heavy metals are associated challenges with this technique (Egle et al., 2016). Therefore, in this study the nutrient-rich sidestreams at wastewater treatment plants are selected as the target stream for the recovery of the nutrients due to the presented discussion as well as smaller volumes and higher concentration of nutrients which makes them feasible candidates for recovery purposes.

There are multiple available options for P recovery from nutrient-rich streams such as membrane-based techniques, adsorption-based techniques, electrodialysis and crystallization. These techniques vary in principle behind each of them as well as efficiency, reactor type and product formed. Crystallization has less challenges for implementation in wastewater sector compared to membrane- and adsorption-based techniques. Fouling, concentration polarization and lack of draw solution are associated challenges with membrane-based techniques. Competition of different ions for adsorption, scaling and high costs are associated challenges with adsorption-based techniques. However, crystallization is a well-studied and mature technique for application in a variety of scales. Crystallization has also some limitations including the limited total P recovery of the total sewage plant P influx as it can be 5 % for direct precipitation and 65 % in the case of sludge dissolution and precipitation (Wollmann and Möller, 2015).

Based on the decision matrix mentioned above, crystallization was chosen as the targeted technique for the recovery of phosphors from wastewater. This is because crystallization is often more energy efficient and the growing crystal surface can be extremely selective in a way that it produces a product with few environmental risks (Peng et al., 2018). Impurities during the crystallization may remain in solution, crystallize separately, or incorporate in some way into the product crystal. However, crystallization is generally a technique that can be used in challenging separations such as nutrient recovery from wastewater as the separation (i.e., particle formation) and purification are combined in single stage as the regular order of crystal lattice allows purification to take place during crystal growth. Crystal surface plays an important role in purification stage as it provides a boundary between the ordered lattice and the crystalline solid state and the disordered liquid. The precursors must find a site where they can incorporate into the growing lattice. Simply, if the ‘guest’ precursor differs from the ‘host’ material it will not fit into the growth site. Further, the crystallized solid phase may be suitable for direct packing and sale, the construction and maintenance of the plant has lower costs and complexities. However, the yield of crystallization technique is limited by phase equilibria and process kinetics are more complex and less well-understood which results in complex experimental procedure to obtain detailed kinetic parameters.

Precipitation and crystallization products could be obtained from the nutrient-rich sidestreams during different steps of sewage sludge treatment (i.e., after solid-liquid separation of the influx sewage at the beginning of the treatment process, or after anaerobic digestion of the sludge). After sludge stabilization, the precipitation of P is possible from stabilized sludge or after dewatering of sludge which mainly leading to the production of calcium phosphates and struvite. The struvite crystallization is possible on non-dewatered sludge, after transformation of phosphates to orthophosphates by chemical redissolution and after solid-liquid separation and incineration of solid phase.

2.5 Crystallization

Crystallization is a phase transition process during which matter is transformed from a high free energy, disordered, solvated state to a crystal phase characterized by the regular arrangement of its building units at a low free energy state (Mullin, 2001). The applied technique for production of 70% of all solid materials by chemical industry is crystallization and precipitation from solutions (Giulietti et al., 2001). While there is a wide variety of equipment used to perform crystallization process, they have aspects in common as they include a step for generation of supersaturation to drive crystallization and a step that crystals are in contact with the supersaturated solution to consume the generated supersaturation for crystal growth. The selection or design of a proper crystallizer depends upon the feed material, the properties of the system and the product requirements. Crystallization from solution proceeds via establishment of supersaturation in the system, followed by spontaneous formation of the nuclei of the new phase, and the subsequent growth. The induction time is the time between a supersaturated solution reaching to the onset of nucleation, which can be measured by visual method, electroconductivity method, turbidimetric method, and light scattering method (Guo et al., 2006). Supersaturation is defined as the fundamental thermodynamic driving force for the crystallization to occur. The central driving force for crystallization is the difference between the chemical potential of a given substance in the solution and in the solid phase (Mullin, 2001). Nucleation events can be classified as primary and secondary nucleation where primary nucleation processes represent all cases of nucleation in systems that do not contain the forming crystalline matter; and secondary nucleation occurs when parent crystals catalyze the formation of a new crystalline phase of the same substance. Primary nucleation can further be divided into homogenous and heterogeneous nucleation. Homogenous nucleation occurs spontaneously in the system whereas heterogeneous nucleation is induced by the presence of a solid surface that can be the surface wall of the vessel, a foreign particle or an impurity in the medium (Bandyopadhyay, 2019). Most of the primary nucleation events happen via heterogeneous pathway because it is difficult to achieve the energy barrier for homogeneous nucleation and to completely eliminate surfaces aiding for nucleation in a precipitating system (Myerson, 2015). Therefore, primary heterogenous nucleation and secondary nucleation are the predominant nucleation mechanism in wastewater treatment. To optimize purification, in wastewater applications, the rate-limiting step for the growth of the crystal should be incorporation of the desired precursor into the crystal surface. Therefore, the supersaturation should be maintained at a level that provides enough mass transfer from the bulk solution to the growing crystal surface while limits the probability of impurity incorporation into the crystal. Generally, high supersaturation values increase the risk of impurity incorporation into the crystal which further lower the value of obtained product.

2.6 Selection of target product

The market entry of the recycled phosphorus compound depends on quality, price and public acceptance (Hukari et al., 2016). The advantage over conventional products (i.e. fossil-based products) needs to create a consistent and sustainable supply of products that comply with the demand in the market and with the desired quality and quantity for the market. This is what is called ‘demand driven’ supplying. However, when it comes to phosphorus recovery from wastewater there is complicating factors towards meeting demand specifications, or in the other words the product comes with highly variable properties. It should be noticed that the chemical or physical properties of the recycled phosphorus from wastewater are a function of other processes, those processes that are most probably more important for the treatment plants than the recovery of the phosphorus. In addition to local legislations, this is the main reason why it has proven to be so difficult over recent decades, despite all the efforts made, to find the durable application for the recovered phosphorus from wastewater. Prices, volume and (bio)chemical properties are among the important factors for the selection of targeted product. Based on the current supply chain the market penetration of available products are efficient strategies for short- and midterm than diversification and introduction of the new products require market development which is a long-term strategy.

The final product of phosphorus recovery mainly depends on the type of process used for the removal of phosphorus. Further, since introduction of impurities from wastewater in the final product is inevitable, the final product needs to indirectly be used for food production. This means that the most relevant application of the recovered phosphorus from wastewater is to be used as fertilizer or raw material for fertilizer production. The main criteria for the fertilizer industry are concentration of nutrients, solubility (i.e., plant availability) and level of contaminants (Hukari et al., 2016). Currently two separate markets for the application of phosphorus in agriculture is identified as conventional fertilizer or as fertilizer for organic farming (Georgi Dikov, Stefan Dörig et al., 2014). Considering the technical uncertainties associated with many emerging phosphorus recovery technologies as well as nontechnological hinders, the target product should have market potential of and competition potential against conventional fertilizers. In most cases, the recovered phosphorus product replaces a source that the processors are already using (manufacturer, traditional fertilizer supplier and resource recovery companies), so proving the quality, security of supply and functionality are important factors. Meeting the general requirements and demand means known chemical properties, known biochemical properties and known physical properties. Among the chemical properties I) the level of impurities such as organic (PAHs, PCBs) and inorganic contaminates (heavy metals), II) the presented elements (N-P-K-Mg) and the III) P-solubility in mineral acid, water and/or neutral ammonium citrate are important (Rabaey et al., 2018). Among the biochemical properties, the level of pathogens and pharmaceuticals, and among the physical properties the storage possibility, water content and size are important parameters. Further, considering the current economic situation and the low prices of fertilizers obtained from phosphate rock, the targeted phosphorus recovery technique should produce relevant volumes of product for a mature market such as fertilizer market. Moreover, the marketability of the final product is a crucial requirement for an industry-wide adoption of nutrient recovery from wastewater. The solid content should be high enough (>95%) with no odor or minimal odor as well as relatively uniform size distribution (e.g. 1, 2, 2.5 3 or 3 mm), low dust content (<1 % by weight) and minimum bulk density of 720 kg/m^3 are among the important determining characteristics that enhance the marketability of the final product (Jeyanayagam, 2018). In many cases the legal aspects, beside all considerations, could be even more important as in Europe, recovered phosphorus products that comply with the criteria in the REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) can obtain the status of product or fertilizer.

The relatively more attention to the challenges of linear economy along with recognition of the value of resources in wastewater has led to development of a multitude new recovery technologies. However, there are still several relevant technical and operational challenges that should be solved to provide higher benefits for wastewater treatment plants. The lack of full-scale references for several technologies and great variety of existing technical processes makes a thorough comparative assessment compelling. In general, the new products face many hurdles to break into the market. Further, the satisfaction of customer demand with a new product is important in the product development strategy by knowing the customer needs as well as well-designed marketing roadmap (Rabaey et al., 2018). However, the potential of recovered material as fertilizer improves the potential for market penetration. The decisive characteristic for the direct use of recovered material as fertilizer depends on plant available P in addition to total P content.

In the selection of the target product the discussed criteria were considered as well as the aim of this study to recover phosphorus as a product and not as waste or a product mixed with the waste materials. Therefore, a matrix of phosphate compounds including ammonium struvite-family compounds ($MgXPO_4 \cdot 6H_2O$; $X=NH_4^+$, K^+), calcium phosphates and phosphoric acid (H_3PO_4) are listed as the relevant products for P recovery.

2.7 Struvite and calcium phosphates

The calcium and magnesium are the chemicals most widely used for crystallization of phosphorus as the calcium phosphates and magnesium ammonium phosphate (struvite). Struvite and calcium phosphates are potential fertilizers or raw material for the fertilizer industry. The recovered phosphorus material may need further transfer and process in fertilizer factories (offsite), while struvite provides the opportunity for production of a final product at the wastewater treatment plant (onsite) such as Crystal green® technology. The phosphorus recovery by struvite has been developed based on the direct involvement of the potential users and based on the operational needs, while complicated technologies without operational benefits may have lower chance to enter the market. The limited market for the recovered product can be due to uncertainty in the viability of end-product. The low market prices for the raw materials and products based on fossil P challenges the viability of many P recovery technologies. Struvite somehow fails the market mainly due to lower prices of competitors and lack of required regulations to recognize it as fertilizer. However, the revision of European fertilizer regulations can pave the way to get the real value of struvite and better marketing options (Christian Kabbe, 2019). Struvite, given its unique and beneficial properties and purity is a superior fertilizer candidate (non-odorous and non-sludgy). The value of struvite not only lays in low energy requirement for production or production capacity but also in its ability to produce high-quality product (Muhmood et al., 2019). The level of organic micropollutants and pathogens is very low in struvite due to less tendency of them for incorporation in the struvite crystal (Egle et al., 2018). Struvite presents 10-12% P content (28% as P_2O_5) with high plant availability on acidic soils and less on alkaline soils. Struvite has the same performance as commercial fertilizers with respect to plant uptake within one or more growing periods (Egle et al., 2018). The low water solubility (i.e. slow release) of struvite makes it a suitable product for turf, horticulture, nurseries, and ornamental procedures, while it would be less suitable for agricultural row and grain crops. The value of struvite depends on region-specific demand, nutrient content and physical properties (Jeyanayagam, 2018). The estimated market price for nutrient based on historical dataset is 1.25-2.5 USD/kg for nitrogen and 5.8-7.5 USD/kg of phosphorus, while the predicted value for struvite would be 0.75-1 USD/kg if the value tied up to phosphorus (Latimer et al., 2016).

Although around 23 sources for the struvite production are identified (farm wastes, industry wastes and municipal wastes), the commercial scale recovery has been demonstrated only for human urine and wastewater, and the feasibility of other methods has been reported in laboratory scale (Kataki et al., 2016). A nutrient enrichment stage is usually necessary prior to struvite precipitation, so an enhanced biological phosphorus removal process followed by sludge dewatering process or anaerobic sludge digestion is the most feasible. Further, the recovery of phosphorus from sidestreams after sludge dewatering by struvite is prominent since struvite recovery technology has been implemented due to operational needs at WWTPs with the combination of EBPR and anaerobic digestion. Moreover, sidestreams are nutrient-rich streams which constitute ≈1% of the overall flowrate to the plant, which reduces the handling and chemical costs. The P is removed from the wastewater applying phosphorus accumulating organisms (PAOs), most of the removed P is accumulated in the biomass in form of polyphosphates.

During anaerobic digestion, biomass is degraded and after degradation of the biomass in the digester, these polyphosphates are redissolved into the sludge liquor as ortho-phosphate (PO_4-P). In presence of enough ammonium (NH_4^+) and magnesium ions (Mg^{2+}) struvite starts crystallizing and can precipitate in the digester itself as well as in the downstream piping system and de-watering devices. The mitigation or even prevention of the potential scaling and related increased demand for maintenance was the initial driver to develop and implement struvite recovery units beginning in the late 1990-ies. Struvite can be blended into an existing fertilizer, can be developed as slow-release fertilizer or even potentially suitable P source for organic farming (EGTOP European Commission, 2016)

Calcium phosphates as the other alternative for P recovery from wastewater have a P content in the range of 12-20% and soluble in citric acid like struvite. However, the bioavailability is considerably lower in neutral and alkaline soils (Egle et al., 2018). The recovered calcium phosphates in different technologies present manifold of different phases, so the bioavailability would be different. Calcium phosphates are directly comparable to phosphate rocks which make them a suitable option to be mixed with phosphate rocks for production of fertilizer. Generally, calcium phosphates are better alternative for the production of fertilizers based on electro-thermal processes since they do not contain ammonium compared to struvite (Cornel and Schaum, 2009). In some cases, with proper phosphate concentrations and low ammonium concentrations such as industrial wastewater, calcium phosphates are potential alternatives.

A wide range of technological solutions are available owing to very vibrant research activities for recovery of P from wastewater. However, there is great potential for improvement of current technologies to bring long-term societal benefits, reduce the fluctuating market prices and develop regional values chains. The following section summarizes in brief the available knowledge for P recovery by crystallization of struvite and calcium phosphates. It was concluded that upgrading and introduction of new generations of current nutrient recovery technologies is necessary. Further, struvite crystallization provides an economically feasible solution and easy to implement into existing wastewater treatment plants that makes it a superior candidate.

2.8 The current state of knowledge

The main components for precipitation of struvite are Mg^{2+}, NH_4^+ and PO_4^{3-}, although wastewater streams comprise a heterogenous mix of these ions and certain organic and inorganic impurities, which can limit the struvite crystallization process. Struvite crystallization is complex as it depends on several physico-chemical process parameters affecting the struvite crystallization including degree of supersaturation, solution pH, mixing, temperature, and presence of impurities. The wastewater effluent's origin and the treatment technology affect all these physico-chemical process parameters (Ariyanto et al., 2014).

The temperature variations during different seasons can affect the process as temperature affects both ion activities and solubility constant, and it has been reported that at higher temperatures the growth rate of the struvite was improved (Ariyanto et al., 2014). However, the contradictory results were reported that the reaction rate decreases with increase in temperature (Ben Moussa et al., 2011). The choice of method for improvement of the crystal growth depends on the growth mechanism as diffusion-controlled growth is the dominant mechanism at high temperatures (over 35 °C) while surface integration-controlled growth happens at low temperatures (Song et al., 2011). The proper hydrodynamic and mixing is necessary to avoid local supersaturation since even small degrees of local supersaturation may trigger nucleation and consequently smaller particles and higher coefficient of variance of the particle size distribution (Ali, 2005). The relationship between crystallization and hydrodynamics is complex as mixing state can create segregation (i.e. setting particles apart) and attrition (i.e. gradual reduction of particle strength), which affect the spontaneous nucleation rate and consequently change crystal number, size distribution, morphology and composition of the final product (Ye et al., 2016). Mixing intensity have impact on crystal growth stage where the specific impact of mixing intensity depends on the competition between mixing, reaction, and nucleation processes (Peng et al., 2018). The higher intensity of mixing enhances the mass transfer of precursors to crystal and thus increases the crystal growth rate. However, it is reported that velocity gradients beyond the optimal can revert this effect, reducing the particle size and disfavoring growth rates (González-Morales et al., 2019).

The presence of seeds decreases the activation energy barrier of forming crystals and proper seeding can potentially lower the activation energy of nucleation (Ali, 2005). Non-isomorphous seeds (e.g. quarts, borosilicate) change the nucleation type from homogenous primary nucleation to heterogenous primary nucleation. The required activation energy for heterogenous nucleation is lower, while nucleation is still required even in the presence non-isomorphous seeds (Mullin, 2001). The crystallization can occur without the need of nucleation when struvite seeds provide the surface area for integration of precursors and struvite clusters (Mersmann, 1995). The ideal properties of seeds are chemical inactive in the mother liquor, isomorph with mother crystal and proper surface area in suspension (Mersmann, 1995). The supersaturation regulators such as ion concentrations, pH, temperature, organic and inorganic impurities are important parameters in the P recovery process by crystallization. The solubility, impact on pH and supersaturation are the main reasons that different salts have different impact on phosphorus removal. The efficiency of different Mg-based chemical for phosphorus removal was found to be in order of $MgCl_2>MgSO_4>MgO>Mg(OH)_2>MgCO_3$ (Li et al., 2019b). In addition to magnesium salts, several alternative low-cost magnesium sources have been evaluated such as seawater, seawater concentrate (nanofiltration, reverse osmosis) (Kim et al., 2016; Lahav et al., 2013), bittern (a by-product in salt industry) (Ye et al., 2011) and wood ash (Sakthivel et al., 2012).

The solution pH is one of the most important parameters as it affects the conditional solubility, the activity of precursor ions and foreign ions (Liu and Qu, 2017). The impurities in solution may affect the growth rates of crystalline compound due to blocking of growth sites or the reduction of recovery potential by simultaneous precipitation of different compounds (Hutnik et al., 2012). Furthermore, the pH influences the growth rate and the size of struvite crystals, which consequently determines the process throughput and product quality. Recently the ferroelectric nature of struvite has experimentally confirmed at room temperature (Zaręba, 2020). Ferroelectricity is spontaneous polarization of the crystal and the direction of it can be switched by an external electric field.

The presence of suspended solids may positively or negatively influence the recovery efficiency of struvite. They might provide the surface for nucleation and enhance struvite precipitation or hinder the growth by blocking the active growth sites (Le Corre et al., 2005). The suspended solids pretreatment may be necessary for the stream with suspended solid concentration above 1000 mgL^{-1} (Schuiling and Andrade, 1999). The inhibitory effect of organic matters (organic acids, oxalate) depends on the molecular weight as high molecular weight strongly interferes with the phosphate removal, while low molecular weight organic acids (citric acid, succinic acid and acetic acid) have a moderate inhibitory effect on struvite crystallization (Shih et al., 2017). Another example of high molecular compounds in anaerobic digestion of sludge is the dissolved organic materials (protein and humic substances) with strong complexation ability with Mg^{2+}, while it was shown that VFAs have weak complexation ability with Mg^{2+} or NH_4^+ (Lin et al., 2020). The adsorption of carboxylic acids on the surface of struvite crystals and formation of defective crystals was observed in a study using acetic, oxalic, and tricarballylic acid on struvite crystallization (Polat et al., 2020).

Generally, the additional compounds in wastewater can be participating or non-participating in the crystallization process. The contents of additional compounds vary among wastewater types and even within the same type of wastewater. The participating compounds that compete for the reaction with struvite constituent ions may coprecipitate and reduce the product purity or inhibit the growth of struvite crystals (Kataki et al., 2016). The most common additional ions in the wastewater are (Na^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Cl^-, CO_3^{2-} NO_3^- and SO_4^{2-}). The reduction of particle size and change in crystal shape are the most common reported impacts of participating ions, as an example the presence of nitrate favors the tubular morphology of struvite (Kozik et al., 2014). Municipal wastewaters contain many other contaminants such as heavy metals and metalloids, pesticides, pharmaceuticals, personal care products, nanomaterials, perfluorinated compounds (PFCs), hormones, recreational drugs and pathogens (Melia et al., 2017). The fate of many groups of these materials is not clear but the general conclusion is that they would be fixed in the sludge with minimum contribution in the final recovered struvite.

Calcium phosphates are alternative compounds for the recovery of phosphorus from wastewater. The supersaturation (Ca:P, pH) mainly determines the type of obtained calcium phosphate to be as amorphous calcium phosphate (ACP), brushite (DCPD), octacalcium phosphate (OCP) and hydroxyapatite (HAP) where hydroxyapatite is the least soluble and most stable form of calcium phosphates. The water solubility of calcium phosphate precipitates, much like struvite, is low and they are highly soluble (>90%) in citric acid (i.e., citrate-soluble) which make better usefulness for them under acidic conditions (Szogi et al., 2012). The recovery of calcium phosphates in nanoparticulate form will improve the fertilizer value as it increases the solubility due to increased surface area for the crops growth in highly weathered soils (Montalvo et al., 2015). The calcium phosphates are mainly colorless and pure powder is white while slightly coloration (brown, green or yellowish) in the case of impurities (Hidalgo, 2014). It is reported that the N:P molar ratio affect the pH of precipitation and growth kinetics of both brushite and hydroxyapatite and lower N:P is favorable for the growth of crystals (Vasenko and Qu, 2017). The presence of amino acids (aspartic and glutamic acid) did markedly reduce the crystal growth rate of hydroxyapatite by adsorption and blocking of active growth sites on HAP crystals (Koutsopoulos and Dalas, 2000).

The presence of magnesium, bicarbonate and propionic acid can affect the precipitation of calcium phosphate (Angel, 1999; Cunha et al., 2018). Therefore, calcium phosphates are better alternatives for Pre-digested nutrient-rich streams. It is reported that the bulk pH and carbon source affect the granulation of CaP as microbial cells and extracellular biopolymers resulted from degradation of biomass (i.e. glucose) was beneficial to cover crystals and to improve granulation of [$Ca_x(PO_4)y$], while streams containing only VFA did not generate CaP granules. Further, the bulk pH of 7-7.5 was suitable to generate granules of >1.4 mm diameter and to reduce the co-precipitation of $CaCO_3$ (Cunha et al., 2019). The application of brushite or dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) for phosphorus recovery from phosphorus-rich streams, particularly with pH values below 6.5, has been recently recognized (Zhongtian Li, Menachem Tabanpour, 2018). Selection of the seed in calcium phosphate crystallization affects the process and the reuse of the recovered material. For example, apatite is not a good choice of the seed as it does not have proper enduring property in solution with carbonate while Juraperle ($CaCO_3$) has good performance by accumulation of the newly formed phosphate on its surface (SONG et al., 2007). The presence of natural organic matter (NOM) can reduce the free aqueous Ca^{2+} and block the nucleation site and inhibit the precipitation of CaP (Sindelar et al., 2015).

There are several technical, economic, social and regulatory challenges on the way of phosphorus recovery from wastewater. Variety of technologies are available in the market, although limited number of them have shown proven track of record in full-scale and under challenging operational conditions. Further, most of the available reviews cover the recovery techniques in the early stages of development (i.e., lab-scale, pilot-scale) (Li et al., 2019a; Peng et al., 2018; Perera et al., 2019). However, it is crucial to have an overview of the available technologies demonstrated in full-scale and to comprehend the current practices and state-of-the-art technologies for nutrient recovery in order to identify the emerging technologies and research gaps in order to develop a sustainable strategy for nutrient recovery from sewage sludge. Moreover, an updated investigation based on recent environmental regulations on process requirements and product properties is necessary.

Among available techniques, enhanced biological phosphorus removal (EBPR) provides great potential for the recovery of phosphorus form the dewatering streams of the biological sludge. However, it is crucial to identify and mitigate the main operational challenges associated with the implementation of the EBPR to keep the operational capacity and the potential of phosphorus recovery. Further, the difference in physicochemical properties of the Pre-digestion and Post-digestion sidestreams after sludge dewatering, as an input to a crystallizer, has not been fully elucidated. Therefore, there is a need to take these differences into consideration to mitigate the operational challenges in the sludge line and consider the physicochemical properties of Pre-digestion and Post-digestion streams. The uncontrolled precipitation of struvite in the digester, clogging of the pipes and pumps has been among common problems for the utilities using EBPR.

The key role of supersaturation as an inclusive and key parameter in all steps of crystallization (nucleation and growth) and operation of struvite crystallizer is identified. However, complex matrix of organic and inorganic impurities in the wastewater is a strong barrier on the way of direct calculation of supersaturation. Therefore, development of alternative techniques is necessary to overcome this barrier. Further, the development of struvite crystal morphology and the impact of different morphologies on the operation of crystallizer is overlooked in the literature.

While socio-political objectives are pushing the treatment owners towards the phosphorus recovery from wastewater, improving the operational benefits, quality of the yield material and economy of the P recovery process could be an effective approach. This approach will further make the investment in the nutrient recovery sector beneficial and provide better market for the recovered nutrients from wastewater. The improvement of technological aspects of the phosphorus recovery by struvite have been more in focus than the economics of the process, while economics is a key driver of implementation of the phosphorus recovery by struvite. Therefore, investigation of the alternative low-cost chemicals and their impact on process performance and product properties is important to improve the financial sustainability of the struvite production. Seawater is a relevant alternative Mg source for the plants in coastal areas, although a systematic study and comparison with current Mg sources is necessary to investigate the effect of additional ions in seawater, dilution of reject water and the increase of salt concentration in the treatment plant.

This study aims to combine the scientific outlook with an ambition to create knowledge and develop process solutions for application in full-scale. Therefore, we have identified the key parameters that improvement of them is critical to enhance overall efficiency of the phosphorus recovery by crystallization. These parameters are process efficiency, product quality and economics of phosphorus recovery process by crystallization. The multi-objective approach of this study is reflected in the presented papers, where the focus was on one objective while other objectives were also discussed.

Objective 1: Comprehending the current practices and state-of-the-art technologies for nutrient recovery with a view to identify the emerging technologies and research gaps in order to develop a more sustainable strategy for nutrient recovery from sewage sludge.

- **Paper I:** The global overview of the current and state-of-the-art technologies for nutrient recovery from sewage sludge and a proposal for sustainable development of nutrient recovery from sewage sludge.

Objective 2: Enhancing the process performance of phosphorus recovery in the treatment plants by enhanced biological phosphorus removal (EBPR).

- **Paper II:** Enhancing efficiency and economics of phosphorus recovery process by customizing the product based on sidestream characteristics – an alternative phosphorus recovery strategy.

Objective 3: Improving the overall process efficiency of struvite crystallization via coupling the recovery efficiency and product properties.

- **Paper III:** Integrated optimization of the recovery efficiency and product properties in struvite crystallization.

Objective 4: Improving the economics of struvite crystallization by using alternative low-cost magnesium sources.

- **Paper IV and V:** Improving the economics of struvite crystallization by using seawater as a low-cost alternative magnesium source including phosphorus recovery potential, economic and LCA evaluation, product properties and kinetic studies.

CHAPTER 3

SUMMARY AND DISCUSSION OF PAPERS

3.1 Summary of papers

The findings in this research are presented in five scientific papers, inter-linked as illustrated in Figure 5. Three main area of improvement are identified based on the performed review in the first paper, and they were addressed and investigated in the other papers. The main theme for each paper is illustrated in Figure 5 while each paper includes insights from other aspects too. Summary and discussion of the main findings from each of the papers are presented in the following, with full-length original papers included at the end of the introductory part of the thesis.

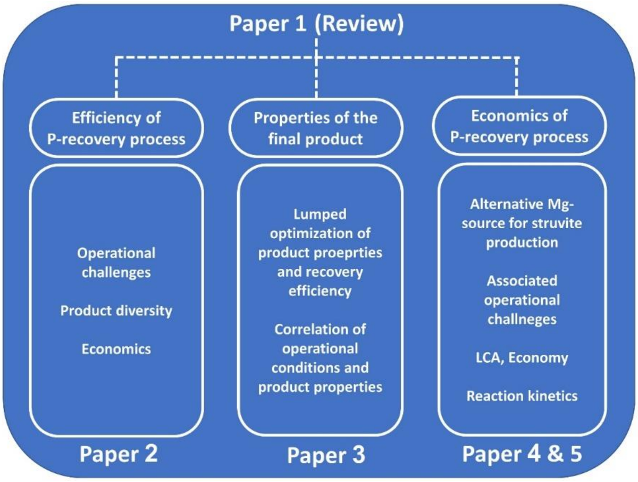


Figure 5: Illustration showing the structure of presented papers in this thesis

Paper I

A clear understanding of current and emerging technologies is beneficial to exploit the potentials of these techniques as well as their opportunities and obstacles. This understanding may further contribute to identify the research gaps and the areas for improvement, so this paper aims to review the practiced routes for nutrient recycling from wastewater as well as the emerging full-scale technologies. The global status of nutrient recovery from sewage sludge along with challenges and opportunities for the implementation were presented. Moreover, summary of the full-scale techniques for phosphorus recovery were presented and the key factors for the success of a P recovery technology / class of technologies were discussed. The environmental regulations and operational aspects are recognized to be both challenges and opportunities. The sustainability outlook and a proposal for a sustainable nutrient recovery from the sewage sludge was presented. It was concluded that applicable strategies and roadmaps need to be adapted to the local or regional economy and geographical context. The three pillars of sustainability (3 P’s), namely, people (societal), planet (ecological), prosperity (economy) should be considered in the development of sustainable nutrient recovery techniques. The ambitious goal is to reach a “zero net impact” associated with nutrient discharge from sewage sludge, while achieving the goal of over the coming years requires a dedication to overcome not only the technical barriers and financial constraints but also regulatory disincentives and societal aspects limiting nutrient recovery from wastewater. In other words, there will be more than one paradigm shift necessary to achieve the goal of a sustainable circular economy while it should be noted that there is no one-size-fits-all solution.

Paper II

Wastewater treatment plants using enhanced biological phosphorus removal (EBPR) may meet some operational challenges in the sludge treatment line due to unwanted release of phosphorus from the biological sludge under anaerobic conditions such as sedimentation stage that reduces the P recovery potential, imposes operational interruption and increases the costs. The early release of phosphate in sedimentation tanks, uncontrolled precipitation in the anaerobic digester and clogging of the pumps, pipes and equipment are among the most common operational challenges. This paper considers these operational challenges and proposes an alternative process configuration to improve the process flexibility and to improve the overall efficiency and economics of the P recovery process. Further, the impact of physiochemical properties of sludge dewatering sidestreams before anaerobic digestion (Pre-digestion) and after anaerobic digestion (Post-digestion) on the P recovery efficiency, product properties and economics of the P recovery process by struvite and calcium phosphate precipitation are investigated. The assessment of calcium phosphates and struvite were performed under similar conditions which enables us to select the proper product based on the physicochemical properties of the input material to the crystallizer. The presented alternative strategy considers the operational challenges associated with EBPR (i.e. clogging of the pumps and pipes, low dewaterability of the Bio-P sludge) and proposes to adapt the final product based on the characteristics of the sludge dewatering sidestream before and after anaerobic digestion. The thermodynamic equilibrium calculations followed by experimental validation of the results were performed to evaluate the efficiency of phosphorus recovery by struvite and calcium phosphates as well as the product properties such as phase characterization, morphology, particle size and dewaterability of the obtained products. The economic evaluation is also presented based on the obtained results in this study.

The results of this study show that introducing diversity in the final product of the phosphorus recovery process is an effective approach to improve the value chain of the recycled phosphorus. In addition, it increases the flexibility in handling different types of sludge dewatering sidestreams as well as mitigating the mentioned operational challenges. It was shown that both struvite and calcium phosphates are proper alternatives for phosphorus recovery from phosphate-rich sidestreams generated from dewatering of biological sludge in the EBPR process. However, the concluding choice mainly depends on process requirements and final application of the recovered product. It is concluded that phase transformation should be considered for calcium phosphate crystallization by supersaturation regulation (i.e, Ca:P molar ratio, pH, temperature) since it affects the purity, particle size and dewaterability of the final product. Considering both recovery efficiency and economic feasibility, the reaction pH=8.5 is optimal for production of struvite and calcium phosphate. The struvite showed lower water content and better dewaterability than calcium phosphates, although chemical expenses for production of calcium phosphate is lower under the same operational conditions. The results of this study can be used for optimization of the recovery efficiency and economics of the phosphorus recovery processes, reducing the potential of uncontrolled precipitation in the sludge handling line and increasing the flexibility and product variety in the P recovery from EBPR sludge.

Paper III

The production of struvite with desired quality is important in the struvite crystallization while engineering and control of the product properties require a sound understanding of the effects of reaction conditions on crystal properties. This can further be utilized to improve both the recovery efficiency and product quality of struvite as a fertilizer.

The effect of supersaturation on the phosphorus recovery and crystal properties was studied in the batch crystallization experiments were in laboratory scale. One of the aims was to utilize the supersaturation as an inclusive parameter to couple the recovery efficiency and product properties. Therefore, the synthetic solutions were used to eliminate the effects of impurities and to accurately calculate the supersaturation. The development of final crystal morphology was discussed in detail based on where supersaturation was followed as the main parameter.

In order to develop an operational strategy based on supersaturation regulation, a systematic approach was employed to investigate the effects of pH and molar ratios of constituent ions on the P-removal efficiency and product properties. By scanning through a relevant range of supersaturation values, efficient control on crystal size and morphology was attained and further correlation of these properties with settling and aggregation characteristics were evaluated. The impact of crystal morphologies on settling velocity and aggregation of crystals were also discussed. It was concluded that a well-controlled struvite crystallization requires an integrated optimization of both the recovery efficiency and product properties (i.e., size, aggregation and settling). Further, it was concluded that supersaturation regulation is an effective approach to define the proper operational window for this integrated optimization. Moreover, the operational conditions for production of three dominant struvite morphologies (i.e., well-faceted, hopper and rough) are presented and the recovery potential and properties of final crystals are discussed at each experimental condition. The results of this study showed that the supersaturation regulation is an effective strategy to optimize overall process efficiency by maximizing the recovery efficiency and by consistently attaining the desired struvite properties.

Paper IV

Generally, the recovery of phosphorus by struvite crystallization requires addition of magnesium source and pH adjustment. The costs related to the addition of Mg-based chemicals are a major part of the overall costs in the struvite crystallization and may stress the financial sustainability of the process, which prompted us to evaluate other suitable low-cost magnesium sources. The feasibility of various Mg sources is significantly correlated with Mg availability, solubility and reactivity. Seawater is available for the plants close to the costal line and it can be obtained at very low costs. The potential of seawater for struvite production is demonstrated, although a comprehensive understanding of this application still requires further systematic evaluation. The challenges mentioned above prompted us to evaluate the feasibility of using seawater as an alternative magnesium source for struvite production. The aim of this study is to systematically evaluate the potential of untreated seawater as a sustainable source of magnesium for struvite crystallization. For this purpose, a comparative approach is employed by using seawater and $MgCl_2$ as magnesium sources to precipitate struvite from real and synthetic reject water from sludge dewatering after municipal wastewater treatment. The equilibrium thermodynamic calculations and experimental studies were performed to evaluate the P recovery potential and the characteristics of the final precipitate. Subsequently, the results of the product characterization including product purity (X-ray diffraction and complete dissolution), particle size, and crystal morphology (scanning electron microscopy, SEM) are presented. The economic calculations and LCA analysis are presented for struvite crystallization by both $MgCl_2$ and seawater.

The results showed that satisfactory phosphorus recovery (80-90%) is achievable by using seawater as the magnesium source for struvite precipitation. The optimal selection of reaction pH and seawater volume (i.e. Mg:P and Mg:Ca molar ratios) was effective to control and minimize the simultaneous precipitation of calcium phosphates. The increase of temperature from 20 °C to 30 °C caused 15-20% reduction of phosphorus recovery while particle size increased by 30-35%. The phosphorus recovery was not influenced by presence of suspended solids in reject water, but it made the struvite separation difficult as the obtained struvite was mixed with suspended solids. Under operational conditions in this study, using seawater as magnesium source could reduce the chemical costs (30-50%) and CO_2-footprint (8-40%) in struvite production. The results of this study may be used for the development of struvite production by seawater in industrial scale in order to maximize the struvite purity by minimization of simultaneous precipitation of calcium phosphates and minimize the addition of unwanted ions to the wastewater treatment system.

Paper V

The reaction kinetics, in addition to the phosphorus recovery efficiency and product properties is important in the design and operation of a struvite crystallizer. In this study, the crystallization kinetics of struvite by seawater was studied versus the commonly used magnesium source, $MgCl_2$. The impact of ammonium concentration, magnesium concentration and pH on the growth kinetics of struvite in synthetic and real reject water were studied. Under the experimental conditions in this study, the simultaneous precipitation of calcium phosphates was not a major hurdle for struvite crystallization using seawater. The presence of struvite seeds was further diminished the insignificant precipitation of calcium phosphates in unseeded experiments. The presence of additional ions in the reactor reduces ion activities and available supersaturation for crystal growth which results in reduction of available supersaturation for crystal growth and consequently slower crystal growth kinetics with seawater. However, it was observed that at higher Mg:P and N:P molar ratios the struvite growth kinetics is comparable for both seawater and $MgCl_2$.

Among the supersaturation regulators, pH has the dominant effect on crystal growth kinetics, where the magnesium consumption rate at pH = 7.5 was increased by 32 and 45% at pH = 7.7 and 7.9, respectively. Further, the struvite crystal growth by seawater was enhanced at higher N:P molar ratios as the magnesium consumption rate at N:P = 12 was 20% and 40% higher than N:P = 9 and N:P = 6, respectively. Under experimental conditions in this study, it was observed that N:P > 6 improves the crystal growth kinetics while limited crystal growth kinetics was measured at a molar ratio of Mg:P < 0.2. The result of this study can be used for the design of a struvite crystallizer by using seawater as the magnesium source. Further, the presented results for the low supersaturation window of struvite crystal growth are useful for the optimization of reactor volume and hydraulic retention time which further affects the operation costs.

3.2 Discussion

Paper I

It has been noticed that despite frequent scientific outputs that emphasize the need and rationale to recognize wastewater as a resource, the implementation of full-scale nutrient recovery technologies is still very limited. Therefore, we aimed to improve the understanding about current practices and emerging nutrient recovery technologies to identify technical and non-technical challenges for implementation of resource-oriented processes in full-scale. Our review showed that the unsustainable nutrient cycle can be recognized both by the lack of nutrient management strategies in the wastewater sector and by ineffective use of nutrients in agriculture, although stringent environmental regulations and population growth are expected in coming decades. The global sewage sludge management can be classified into three different levels: developed, developing, and undeveloped where the common strategies are) without recycling (landfill, storage, dumping), 2) substance reuse (drying, land use), 3) substance conversion (compositing, anaerobic digestion, incineration, and wet oxidation), and 4) nutrient/energy recovery (incineration, anaerobic digestion, gasification). The different social, economic, and technical contexts is the reason that management of sewage sludge varies in different countries. The drawbacks of conventional practices (i.e., capture of nutrients in biomass) such as low confidence about the consistency and nutrient content and availability of sludge are other drivers to recover the nutrients (i.e., phosphorus and nitrogen) from sewage sludge. The phosphorus recovery technologies can be integrated with treatment process or at the downstream of treatment plant. Considering the available techniques, nutrient recovery is feasible from sewage sludge, sludge ash and concentrated sidestreams, while selection of the proper alternative route for nutrient recovery depends on several factors such as environmental regulations, technical and operational aspects and economy.

Ammonia stripping followed acid capture is the most applied technique for nitrogen recovery from concentrated streams with ammonium sulfate and ammonium chloride as the final products. We have concluded that short-circuiting of the nitrogen cycle is technically possible, but not very favorable from the energy point of view. Phosphorus recovery by struvite crystallization followed by calcium phosphate and phosphoric acid are identified as the leading products for these sidestreams. The input for the emerging phosphorus recovery technologies are mainly dewatering liquor, WAS thickening liquor and digestate. Reject liquor from sludge treatment (sludge dewatering sidestream) in a typical municipal WWTP has 7 to 12 times higher N and P concertation compared to the mainstream that makes them the first target for nutrient recovery due to smaller volume and higher recovery rates.

In addition to the technical challenges, several non-technical bottlenecks such as value chain development and economics, environment and policy issues have to overcome to successfully implement the nutrient recovery technologies. The eight key factors for the success of a P recovery technology are identified as applicability, recovery rate, side benefits, cost of implementation, operating costs, societal acceptance, known product and rollout potential in the market. Further, a proposal for sustainable nutrient recovery from sludge was presented and it was concluded that a sustainable nutrient recovery route from sewage sludge requires a multi-stock business model including policy makers, technology providers, and market developers. It can be concluded that the low market price for fertilizers from phosphate rocks challenge the economic viability of nutrient recovery technologies, especially when the candidate technology does not provide additional operational benefits or a directly marketable product. Moreover, considering potential technologies and addressing potential challenges in early phase of planning and process design is important. The current trend was shown that that P recovery has been mainly implemented in the case of operational needs or due to the reduction of operational costs, while environmental regulations can be a key driver to accelerate the recycling and recovery of resources and proper adjustment is necessary for adaption to the future challenges. It was concluded that achieving a sustainable nutrient cycle from secondary sources over the coming years requires a dedication to overcome not only the technical barriers and financial constraints but also regulatory disincentives and societal aspects limiting nutrient recovery from wastewater. The drivers for the development of a matrix of technological solutions for nutrient recycling range from low recovery efficiency and high costs, to high energy demands and large environmental footprints. However, it seems that there is a way to go for a shift from wastewater treatment plants towards water resource facilities. In other words, the question of which of the growing range of available technical options we should focus on remains open.

Based on the global status of nutrient recovery technologies in the first paper, three main parameters were recognized as the key parameters with the improvement potential: 1) the overall process efficiency, 2) the properties of final product and 3) the economics of nutrient recovery. Therefore, the following articles are mainly organized to address the proposals to improve these targeted parameters.

Paper II

The management of sludge dewatering streams in EBPR process is important as it can affect the overall process performance due to return of these streams to the inlet. Further, the early release of phosphate in sedimentation tanks and uncontrolled struvite precipitation in equipment and anaerobic digester are among the common operational challenges at plants using EBPR. Therefore, the process configuration should be designed as flexible as possible in order to adapt to the changes to meet consistently the process requirements and product specifications. The conventional approaches for P recovery in EBPR plants generally do not provide this flexibility as they target single product and largely ignore the variability and the impacts of physiochemical properties of Pre-digestion and Post-digestion sidestreams. Normally, the combined Post- and Pre-digestion sludge dewatering sidestreams have been considered for the P recovery in the plants using EBPR. However, we have proposed that P-release upstream of anaerobic digester and alteration of final product based on physicochemical properties of sidestreams are necessary for an effective phosphorus recovery process. Further, the operational difficulties including the risk of unwanted precipitation during anaerobic digestion and postdigestion operations will be reduced if the soluble-P diverts from the digester. The theoretical calculations showed that introduction of a P-stripper before anaerobic digestion and customizing the final product based on sidestreams characteristics have the potential to improve both overall efficiency and economics of phosphorus recovery process. Calcium phosphate production is advantageous on the streams with low ammonium content and low suspended solid content, while higher ammonium content is beneficial for struvite precipitation with higher tolerance for suspended solid content. Therefore, the calcium phosphate was chosen as the appropriate product for Pre-digested sidestreams and struvite as the relevant product for Post-digested sidestreams. The recovery of the phosphorus by this alternative process design have several advantages including: 1) reduction of operational problems and clogging of equipment, 2) reduction of the overall costs, 3) improving the product diversity and value chain of the recovered products and 4) potential for improvement of the environmental footprint of the phosphorus recovery process.

We have proposed that in the calcium phosphate precipitation, the phase transformation of calcium phosphates should be considered as recovery potential and product properties of different CaPs are not the same. The struvite has higher phosphorus recovery efficiency and preferable product properties such as better settleability and dewaterability. These desirable product properties can be found to some extent in brushite, although it has lower P recovery potential. We concluded that owing to better P-release from the sludge at lower pH values and less chemical consumption, calcium phosphate precipitation on Pre-digested P-rich sidestreams at low pH range (i.e., 4.5-6.5) combined with struvite precipitation on Post-digested sidestreams is beneficial with respect to conventional P recovery routes (i.e., combination of sidestreams). The proposed alternative process configuration introduces a higher degree of flexibility and modularity which can mitigate the mentioned operational challenges. In addition, this alternative process can improve the overall efficiency and financial sustainability of the phosphorus recovery process in EBPR plants.

Paper III

Increasing the phosphorus recovery in struvite crystallization without taking product properties into consideration may result in a final product with poor product properties (i.e. production of fine particles, low settleability). The properties of struvite crystals affect both the performance of the crystallizer and the post-handling operations. Producing struvite crystals with the desired quality often requires a sound knowledge of the elementary steps involved in the process: creation of supersaturation, nucleation, crystal growth, aggregation and other secondary processes. In crystallization, reaction conditions largely determine the product quality in terms of purity, size and aggregation properties. The control of supersaturation is possible by adjustment of supersaturation regulators such as ion concentrations (Mg^{2+}, NH_4^+, PO_4^{3-}) and pH. For struvite, the improvement of phosphorus recovery efficiency and product properties are not generally in the same direction. In other words, increasing supersaturation for improvement of phosphorus recovery efficiency reduces the size and settleability of the particles. Therefore, supersaturation regulation plays a key role in phosphorus recovery efficiency and shaping product properties in struvite crystallization.

The key role of supersaturation is clear, although determination of supersaturation for a complex composition such as wastewater is extremely challenging. Therefore, this study was performed to better understand the correlation between supersaturation and morphology of the final precipitation products, and further evaluate their consequent effects on downstream processes. The result showed that crystal morphologies can be categorized into three main groups (well-faceted, hopper and rough) based on the supersaturation level where the morphology of struvite crystals can reflect the supersaturation level. In this way, the indirect estimation of the supersaturation range was possible based on the crystal morphology. It was observed that the supersaturation regulators influence the spatial development of the struvite particles as for example ammonium concentration influences the lateral growth and thickness while the increase of pH causes longitudinal elongation of the crystals. The control of crystal morphology has other practical importance as the settleability of different struvite morphologies is different. The well-faceted particles showed the best settleability due to higher packing density. Moreover, maintaining sufficiently high levels of supersaturation during growth of particles can enhance particle aggregation, which further improves the particle settleability and reduce the wash out potential from the reactor.

We have concluded that the adjustment of supersaturation via regulation of the key supersaturation regulators (i.e., pH and constituent ions) is an effective strategy to achieve a lumped high P recovery efficiency and product quality. This can further improve the performance of the crystallizer reactor and the efficiency of downstream processes as well as enhancing the product quality.

Paper IV

Improving the financial sustainability of struvite production is a key driver and application of alternative low-cost magnesium sources is an effective measure in this way. Seawater is an example of these alternatives for the wastewater treatment plants close to the seashore. However, the associated challenges with the application of the seawater such as simultaneous precipitation of other precipitates (i.e., calcium phosphates) and the dilution effect of seawater should be addressed and investigated before further applications. This study showed that acceptable P recovery efficiency (80-90%) is achievable by using seawater without necessity for addition of large volumes of seawater. The slightly lower P recovery compared to $MgCl_2$ was attributed to higher ionic strength resulted from additional ions in seawater. The improvement of P recovery was achievable with increase of supersaturation, whereas the control of insignificant precipitation of calcium bearing minerals (i.e., calcium phosphate and calcium carbonate) was possible by regulation of pH, Mg:Ca and N:P molar ratios. This is mainly due to the faster kinetics of struvite compared to other potential precipitates and natural high Mg:Ca ≈ 5:1 molar ratio in seawater. The dilution effect of the seawater on the recovery efficiency should be considered, while it is not expected that the dilution effect of seawater within the relevant volumes (i.e., 10-20% of reject water volume) intensely reduces the recovery efficiency. Higher reaction temperatures reduce the phosphorus recovery efficiency while it increases the particle size mainly due to higher crystal growth rate. The supersaturation was still the most important factor affecting the morphology of the crystals, while the impact of additional ions in seawater and temperature was not significant. The potential cost reduction of 30-50% was achievable by using seawater under the operational conditions in this study. The reduction of struvite production costs is significantly positive considering the current market for struvite. Further, the replacement of Mg-based chemicals with a natural resource such as seawater can reduce the environmental footprint of the process. The LCA analysis revealed the importance of the optimized operational conditions for minimization of both costs and environmental footprint. It was concluded that it is possible to overcome the challenges of using seawater by optimization of operational conditions. Therefore, the concept of using untreated seawater as an alternative magnesium source for struvite precipitation is feasible both technically and economically.

Paper V

The optimum design of crystallizer is crucial to maximize the environmental benefits at minimum cost by using seawater for struvite production. The potential of seawater for offsetting operating the costs of struvite production is demonstrated, while an optimized design of a crystallizer requires data of reaction kinetics. The reaction kinetics determines the reactor volumes and flowrates, which further affect the operational costs. Current struvite reactors are mainly using pure Mg-based chemicals such as $MgCl_2$ and the design and performance data are based on these chemicals. However, the introduction of seawater to the system changes the ionic strength, alkalinity and ion concentrations. Therefore, using seawater as magnesium source requires modification of the design and operation strategy to provide both adequate recovery efficiency and product properties.

It has been noticed that the extent of impact of supersaturation regulators (i.e., pH and ion concentrations) on the reaction kinetics are not the same. This is because ammonium generally exists in surplus and magnesium is the limiting agent, while struvite crystallization occurs by stochiometric consumption of precursors of Mg^{2+}, NH_4^+ and PO_4^{3-}. Further, the concentration and activity of precursors varies during crystallization. The kinetic of consumption of magnesium and its correlation with pH is an important parameter in order to adjust the retention time and optimum dosing of seawater without sacrificing from the product quality. Further, identification of the reaction conditions (i.e., pH, Mg:P and N:P molar ratio) with unfavorable reaction kinetics (i.e., low crystal growth rate) is important to minimize the operational costs such as electricity consumption for pumping.

The consumption of magnesium for struvite precipitation reduces the Mg:Ca molar ratio, so it is important to reduce the precipitation potential of calcium phosphates. Therefore, high N:P molar ratio can both improve the kinetics of struvite growth by seawater and reduce the precipitation potential of calcium phosphates under the less competitive conditions for struvite (i.e., lower Mg:Ca molar ratios). It was shown that at higher Mg:P and N:P molar ratios the crystal growth kinetics of struvite is comparable with $MgCl_2$. Our results showed that seeding of struvite can further minimize the insignificant simultaneous precipitation of calcium phosphates compared to unseeded experiments. This study provides a better understanding about true benefits, challenges and operating strategies in struvite production by using seawater. Further, the presented results for the low supersaturation window of struvite crystal growth are useful to optimize the retention time of particle in the reactor and to optimize the reactor volumes and operational costs.

CHAPTER 4

CONCLUSIONS AND OUTLOOK

4.1 Conclusions

Based on the analyses in this thesis, main conclusions with respect to research objectives can be summarized as follow. The current standard processes for wastewater treatment are successful in meeting the legal effluent quality standards, although due to expected challenges in the future, the wastewater sector requires technologies that are sustainable and energy-positive to achieve resource recovery and reduce environmental footprints. The limited full-scale application of nutrient recovery technologies is mainly due to technical and non-technical barriers mainly related to environmental legislations, technical aspects and economic considerations. This requires dedication at different management levels to overcome not only the technical barriers and financial constraints but also regulatory disincentives and societal aspects limiting nutrient recovery from wastewater. Crystallization is a proper technique for the recovery of phosphorus from phosphorus-rich wastewater streams, where struvite and calcium phosphates are the most relevant alternatives when it comes to the P recovery from sidestreams after sludge dewatering in EBPR process. It was shown that the proposed alternative phosphorus recovery process (paper II) by selection of target product based on physiochemical properties of sludge dewatering sidestreams have the potential to improve the process stability and momentary benefits (mainly cost reduction and reduction of operational challenges) in phosphorus recovery by crystallization. Calcium phosphates are potential alternatives for P recovery from phosphorus-rich streams with low ammonium content (i.e., Pre-digestion sidestreams) while higher ammonium content in the input to the crystallizer improves the struvite crystallization (i.e, Post-digestion sidestreams). Considering phosphorus recovery potential, settleability and dewatering properties, struvite is superior compared to calcium phosphates. Successful struvite crystallization requires a sound knowledge of the elementary steps involved in the process where integrated optimization of recovery efficiency and product properties is important. The supersaturation regulation is an effective strategy to optimize the recovery efficiency and to consistently attain the desired struvite properties (size, morphology, settleability and aggregation) as well as to handle variational digester supernatant composition and operating conditions. Improving the economics of struvite crystallization is achievable by using seawater as a proper low-cost magnesium source with acceptable recovery efficiency and product properties. Seawater as an alternative magnesium source for struvite precipitation is feasible both technically and economically which can reduce the chemical costs and CO_2-footprint of struvite production. The crystal growth studies have shown that the crystallization kinetics of seawater is slower with respect to $MgCl_2$ but still in an acceptable range of crystallization kinetics. According to our results higher ammonium concertation improves the growth of struvite crystals by using seawater. Presence of the struvite seeds further improved the product quality by minimizing the insignificant simultaneous precipitation of calcium phosphates.

4.2 Outlook

Over the recent decades, nutrient recovery from wastewater has been subject to much research and innovation, and the trend looks set to continue. Resources in municipal wastewater are considerable and should be absolutely utilized, although it cannot fully satisfy the elemental or energy demand of industrialized societies. There is a need for implementation of a technically feasible resource recovery technologies that tackle operational challenges while exploiting synergies between resource and energy recovery. Unlike energy, water cannot be obtained from multiple sources so never forget that water itself is the most valued resource contained in municipal wastewater. Therefore, process solutions that include water reclamation along with resource recovery can provide an important alternative fresh water source in regions that expect lasting shortages in the future. The environmental impact of many of the available technologies is not clear, while it is crucial to use evaluation tools such as life cycle assessment (LCA) to identify and quantify the environmental impacts of a defined recovery technique. This was beyond the scope of the current work, although we aimed to target less energy- and resource demanding processes.

Economy and environmental regulations are the key drivers of resource recovery from wastewater, although proper adjustments are necessary for adaption to the future challenges as the current legal frameworks should be revised as they are mainly tailored to the existing structures. Generally, current techniques include three steps of nutrient capture, nutrient release and nutrient recovery. However, technologies are preferable that makes it possible to perform simultaneous removal and recovery of phosphorus. Less than 50% recovery of total P is achievable via P recovery on sidestreams after sludge dewatering, while solid fractions contain considerable amount of P and efficient conversion of inorganic P attached to mineral particles and conversion to dissolved P is necessary to improve the overall P recovery efficiency by crystallization.

The importance of wastewater as a resource is clear and emphasized in frequent scientific output, although wastewater treatment plants mainly collect and treat the wastewater rather than resource recovery. The interruption of current process configurations creates operational distraction while economic benefits cannot be justified.

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Paper 1

sustainability

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Sustainable Sewage Sludge Management: From Current Practices to Emerging Nutrient Recovery Technologies

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Abstract: Nutrient recovery from secondary resources, such as wastewater, has received increasing attention in recent years. Nutrient cycle sustainability and recycling approaches are important measures under development and considerations. This paper aims to present an overview of routes and technologies for nutrient recovery from sewage sludge and measures for improving their sustainability. First, current routes for nutrient recovery from sewage sludge are briefly reviewed. Next, an overview of commercial nutrient recovery technologies, projects, and emerging techniques around the world with the key factors for a successful phosphorus recovery technology is presented. Finally, a proposal for improving the sustainability of these practices is presented. It is concluded that the gap between demand and supply can be a major driver for the shift from 'removal and treat' to 'recovery and reuse'. Moreover, there is not, and will never be, a one-size-fits-all solution. Future strategies and roadmaps need to be adapted to the local economy and geographical context more than ever.

Keywords: nutrient recovery; sewage sludge; sustainability; phosphorus recovery; nitrogen recovery

1. Introduction

Rapid population growth, climate change, urbanization, and depletion of natural resources are obliging the global society to prepare for a stressful position for some natural resources. The wastewater (WW) sector, as one of the active players, needs to identify barriers and utilize creative strategies to cope with the expected challenges in the future.

The implementation of the European Council Urban Wastewater Treatment Directive (UWWTD) 97/271/EC (21 May 1991) triggered fundamental changes in wastewater treatment [1]. The ban on sludge dumping in the sea and limits for phosphorus and nitrogen discharge demanded more effective treatment methods and new infrastructures to address the increased volume of sludge. During recent years, on the one hand, population growth has led to a higher demand putting more pressure on resource supply and the environment [2], and on the other hand, legal, environmental and economic drivers have encouraged recovery and transformation of resources from wastewater into valuable products.

Wastewater contains nutrients vital for human food production. Modern agriculture is dependent on the massive use of mineral fertilizers (NPK fertilizers). The Haber–Bosch process and mining of phosphate rocks have been the most commonly used approaches to produce nitrogen-based and phosphorus-based fertilizers, respectively. Food production accounts for 90% of the mineral phosphorus consumption in Europe, split between fertilizers (79%) and livestock farming (11%). The ineffective use of P-fertilizers in food production has been stated in several studies. For instance, it has been stated that in Europe it takes 4 kg of reactive phosphorus to produce 1 kg as food with 40% surplus ending up in the soil and 50% loss from the system (17% to waterbodies), or in China it takes 13 kg of reactive phosphorus to produce 1 kg of food [3,4]. This reflects a not sustainable strategy with a subsidized and inefficient use of reactive phosphorus. In addition, phosphate rocks, which are the main source of P, are non-renewable and in the risk of depletion due to the expected population growth. The timeline of depletion of phosphate rocks has been disputed, but this should not distract from the instant effects of poor resource management. Phosphorus management strategies should be considered for several reasons, regardless of the exact time of global phosphate rocks depletion. Phosphorus has no substitute in agriculture, and in several locations (especially the tropics) the access to the P still limits the agricultural productivity. Moreover, there has been price instability for inorganic phosphate fertilizers with potential for future turbulence (i.e., food price spike) [5]. The world's population will increase 1.3 times by 2050 [6] with three times more phosphorus demand to produce enough food for the growing population [7]. Quality phosphate rocks are available in only a few countries, and the European Commission added phosphate rocks to the list of 20 Critical Raw Materials back in 2014 [8] for which supply security is at risk, and economic importance is high. Phosphorus recovery from wastewater is one effective strategy to compensate for the increasing demand and to slow down the depletion rate of phosphate rocks [9].

Among waste sources, such as animal feeding, crop farming, industrial pre-treatment facilities, septic systems, stormwater and wastewater treatment plants (WWTPs), nutrient recovery (NR) from wastewater and sewage sludge has been the most practiced approach and has received significant attention over the last decades due to practical considerations and available infrastructure at WWTPs. However, sewage sludge produced in a wastewater treatment process carries not only nutrients but also hazardous organic and inorganic pollutants, and this must be considered before any application.

This study describes the current practices and status of handling nutrients in wastewater and an overview of nutrient recovery practices, projects, and commercial technologies in various parts of the world. Further, a proposal for improving the sustainability of these practices is presented.

2. Methodology

This work aims to present an overview of nutrient recovery routes from sewage sludge and current practices and emerging technologies for nutrient recovery. Challenges and opportunities in the implementation phase of the nutrient recovery approach was considered as a ground to propose the requirements for a sustainable nutrient management strategy (recovery and recycling). The presented study mainly covers centralized infrastructures and technologies that are already implemented or at the brink to the market. Therefore, decentralized infrastructures or technologies at research stage were not addressed in this study. The data collected and analyzed from the available literature (reference list) and the market intelligence is based on direct contacts with technology suppliers and utilities operating the different technologies.

3. Nutrient Recovery Routes from Sewage Sludge

Currently, some nutrients in WW sludge are being recycled back to agricultural soils via direct land application, generally after treatments, such as composting, liming, and/or anaerobic digestion. This approach, however, has drawbacks, such as lack of full confidence about the consistency and nutrient content and availability as well as human health risks arising from the presence of pathogens, organic contaminants, and heavy metals in land-applied sludge.

The most practiced routes for capturing nutrients from wastewater are concentrating them in biomass (biological treatment or algae), or physicochemical separation. Reject liquid from sludge treatment (sidestream) in a typical municipal WWTP has 7 to 12 times higher N and P concertation as compared to the mainstream and therefore, is the first target for NR due to smaller volume and better recovery rates. However, different N and P concentrations have been stated in other studies, too [10,11].

Principally, in the current phosphorus removal methods, reactive phosphorus is removed from wastewater by converting soluble phosphorus (mainly orthophosphates, PO_4-P) to a solid state that becomes a part of the total suspended solids (TSS) and is removed as sludge. The sludge may be further treated to solubilize the captured phosphorus and make it available for recovery purposes. Strategies that are only based on P-removal cannot be entirely sustainable and may cause operational and treatment difficulties in wastewater treatment plants.

Theoretically, phosphorus recovery is possible from the liquid phase, sludge, and sludge ashes. Ninety percent to ninety-five percent of the incoming phosphorus is incorporated into the sludge, and phosphorus recovery from the liquid phase at the current stage of development will not exceed 20% to 40% while P-recovery technologies from the sewage sludge and sludge ash have a higher potential for P-recovery [12]. It seems essential that more innovative methods with higher efficiency for recycling of phosphorus should be developed and applied.

Figure 1 illustrates prominent and already applied concepts for P-recovery and recycling from sewage sludge. Discussion on these alternatives and their pros and cons is not the aim of this paper. Struvite precipitation from sludge liquor or sidestream has been proven viable for various WWTP operations. Mostly, it is an enhanced biological phosphorus removal (EBPR) process combined with anaerobic digestion followed by struvite precipitation on sludge liquor [13].

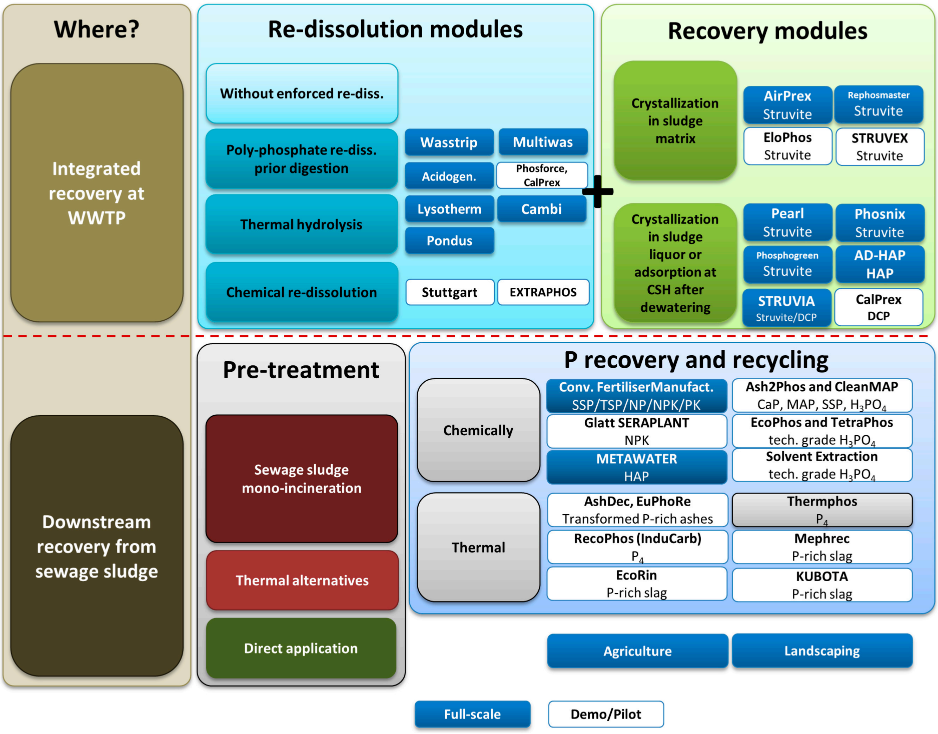

Figure 1. Prominent and already applied concepts for P-recovery and recycling from sewage sludge (Adapted from [14]).

The main goal of nitrogen recovery (i.e., reactive nitrogen recovery) is to short circuit the nitrogen cycle and to convert nitrogen in WWTP sidestreams to artificial fertilizer (precursors). In this way, the production of nitrogen fertilizer may be reduced with positive environmental impacts. Preferred recovered compounds are ammonium sulfate or ammonium nitrate. These products are suitable when the agricultural soil has a surplus of phosphorus. The amount of nitrogen in the reject water depends on the sludge type as well as the extent and configuration of the wastewater treatment. About 30% of the nitrogen in the sidestream, accounting for 4% of the nitrogen in wastewater, can be recovered [15,16]. Although this is far less than the agriculture needs for artificial fertilizer, N-recovery from wastewater might be part of a bigger sustainable solution. Ammonia synthesis from N_2 and H_2 via the Haber–Bosch process is energy intensive. Moreover, while nitrogen is abundant in the atmosphere, natural gas as the main source of hydrogen is non-renewable. Therefore, the conventional approach, i.e., removing ammonia from wastewater as nitrogen gas and then synthesizing ammonia from nitrogen and hydrogen to produce N-fertilizer, should be revised to enhance the overall energy efficiency, increase N-cycle sustainability, and satisfy greenhouse gas regulations and goals.

In general, short-circuiting of the nitrogen cycle is technically possible, but not very favorable from the energy point of view. From the cost perspective, the large amount of required chemicals makes the present and expected future technologies noncompetitive. Nevertheless, in special cases with the availability of residual chemicals or waste heat, N-recovery can be cost-effective and sustainable. There is a need for new techniques with reduced use of electricity, heat, and/or chemicals to have a more competitive and feasible N-recovery process for sidestream of WWTPs in the future.

4. State-of-the-Art and Current Practices around the Globe

4.1. Current Practices

For years, sewage sludge treatment has been considered a secondary issue compared to main wastewater treatment. However, importance of sludge management, is on the rise due to the fast increase of sludge generation owing to sewage network extensions, new installations, and upgrading of facilities [17]. Wastewater or treated wastewater effluent has been used in some countries as an alternative for irrigation to moderate the water use and to recover nutrients and water at the same time. However, the associated risks should be properly assessed owing to the extensive risk of wastewater reuse in agriculture. This requires the consideration of local regulations and to ensure that the pollutants will not be transferred to soil. Further, possible alterations of the soil texture properties, biomass, and microbiota should be considered [18].

Our review shows that global sewage sludge management can be classified into three different levels: developed, developing, and undeveloped. The common strategies are (1) no recycling (landfill, storage, dumping), (2) substance reuse (drying, land use), (3) substance conversion (compositing, anaerobic digestion, incineration, and wet oxidation), and (4) nutrient/energy recovery (incineration, anaerobic digestion, gasification) [19]. Europe, North America, and East Asia are the main sludge producers in the world [17]. Land application as the major route for the use of sewage sludge in western members of the EU has now been banned in several countries (Germany, Netherlands). In the USA about 55% of the produced sludge is applied to soil for agronomic and land restoration, and 45% is in municipal solid waste (MSW) landfills and incineration plants. However, the broad perspective on the management of biosolids has changed a little in recent years in the USA. In South America, little priority has been given to sewage sludge management due to a shortage of legal bases and basic facilities [17]. There is a lack of attention to sewage sludge management in Africa, with the exception of South Africa, due to lack of regulations and economic support where landfilling or direct discharge to the environment are the most common practices. The approaches for sewage sludge management are different in Southeast Asia. This varies from a poor situation in some countries to well-designed treatment systems in others due to the variety in population and development level of countries in this region. The current approaches in Japan and South Korea as two neighboring developed countries present a major contrast. Incineration of sewage sludge (70%) and landfill application are main disposal routes in Japan, while in South Korea sewage sludge was dumped into the sea until 2012 and currently there is a shift towards landfill application [20]. The favored option in China is land application due to disposal cost and environmental benefits [17].

The management of sewage sludge varies in different countries due to dissimilar social, economic, and technical contexts. Wastewater networks and wastewater treatment plants are essential infrastructures for the realization of the nutrient recovery from sewage sludge. Still, low-cost solutions have been preferred by utilities except for limited cases owing to the introduction of legal frameworks from authorities. The level of urbanization, livestock density index, and available land area are important factors in the selection of a favored strategy for sewage sludge management. Land application of sewage sludge can reduce the sludge disposal cost significantly. This approach is mainly practiced in an area with low population density and abundant available land, while high population density and limited land encourages alternative routes, such as nutrient recovery and product export (Netherlands, Singapore). For instance, a country, such as India, with a huge population requires a mature sanitation system as a prerequisite for the implementation of sludge management. Eastern Europe countries are in the stage of implementation, while a proper state of centralized sanitation in Western Europe has paved the way for the implementation of nutrient recovery from sewage sludge.

4.2. Emerging Technologies

Despite having a major potential for contributing to better nutrition management, the nutrient recovery sector is still facing a variety of issues on the business level, including legislative challenges, public awareness, and marketability of recovered material. Nevertheless, NR technologies have undergone accelerated development in the past decade, mainly due to operational benefits, increased environmental awareness, supply security, and stricter discharge limits on these nutrients.

N-recovery has received less attention than P-recovery due to lower operational need and economic motivation. At the current stage, the extraction of only N is cost-effective when ammonia has an immediate use on site [21]. However, in the years to come, N-recovery will gear up, especially for the case of manure, where the nutrient loads are much higher compared to sewage sludge.

Figure 2 presents an overview of the main products and commercial technologies for phosphorus recovery [14]. The most applied approach is struvite precipitation from the sludge sidestream or industrial WW (mainly food processing) with high P concentration, followed by calcium phosphate precipitation, and phosphoric acid production [21]. P-recovery, especially in treatment plants with enhanced biological phosphorus removal (EBPR) and anaerobic digestion may help improve plant economy via improved sludge treatment and dewaterability and additional income due to product sales. An improved plant operation (reliability) by lowering the operational challenges (blockage frequency of valves and pipes) is the additional driver. Other technologies are still either in research (laboratory) or development (pilot) phase, improving maturity, lowering costs, and gathering data for full-scale design.

Figure 3 presents some of the key factors that define the success of a P-recovery technology or a class of technologies, which should be considered for comparison and evaluation of different processes. A well-defined product and market potential (ready-to-use product or a compatible raw material for industry) should be considered when evaluating a technology (known product). The proper power for successful rollout (rollout potential) and general applicability in existing systems will increase the chance of success (applicability). A high P-recovery rate and high purity (recovery rate) and low/moderate investment cost (cost of implementation) along with low/moderate operation cost and low amounts of waste generated (operating costs) are essential elements for success of a technology. In addition, societal and political acceptance (societal acceptance) and side benefits, such as reduced operational costs (side benefits), are also necessary for a sustainable business in the P-recovery sector [22].

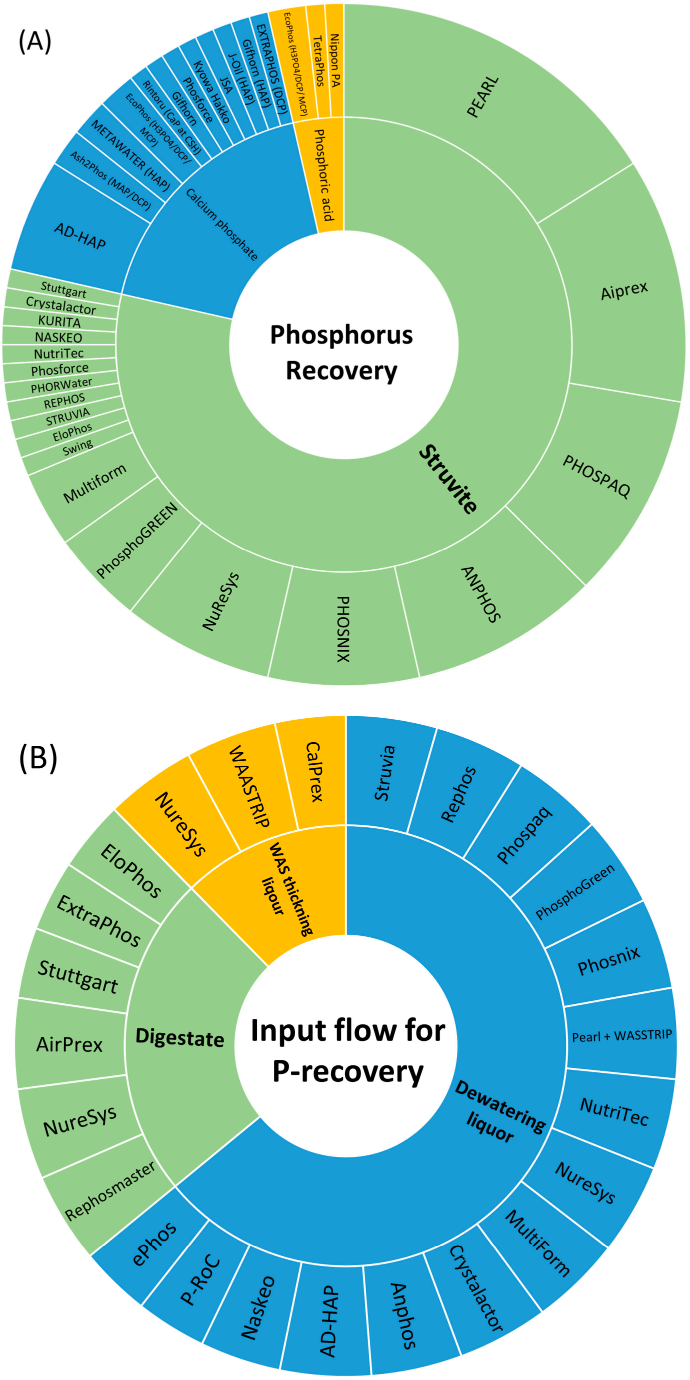

Figure 2. (**A**) Overview of the main products and the commercial technologies for phosphorus recovery, where area dedicated to each technology corresponds to the number of facilities in operation. (**B**) The input flow for P-recovery in different P-recovery technologies.

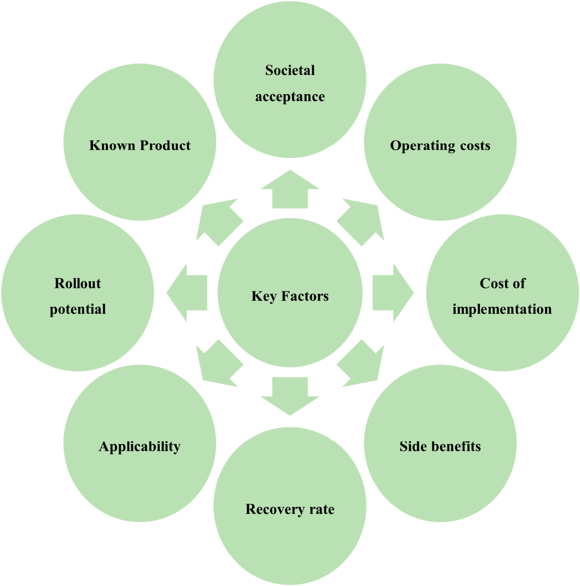

Figure 3. The key factors for the success of a P-recovery technology.

4.3. Current Global Status

Despite lack of strong financial drivers, the number of full-scale operational nutrient recovery units in WWTPs has been continuously increasing in the past decade with the majority of them in developed countries and installed on sludge liquor stream. Table 1 presents a high-level summary of NR practices and projects around the world. The EU is the region with the highest number of installed full-scale units followed by North America and Japan [23]. The EU is also the leading area based on number of full-scale installations predominantly producing struvite, although the volume of recovered struvite is currently higher in North America. Figure 4 presents the worldwide map of operational plants for P-recovery, among all of which more than 80 plants recover struvite, and more than 60 plants are municipal wastewater treatment plants. Normally, it is expected that phosphorus scarcity stimulates the recovery and recycling of phosphorus, although the available installations are in the countries or regions with a nutrient surplus, often linked to excessive livestock farming, limited land area, and high population density [14].

The EU commission has an extensive program for sustainable nutrient recovery (from bio-waste) and reuse, under which several platforms and projects are undertaking (or already have been undertaken) research, development, and commercialization of NR technologies. Japan is an early mover that since the 1980s has realized the importance, potential, and advantages of P-recovery. In Japan, strong nationwide collaborative programs between industry, academia, and government are in place, and business models and market development strategies for integrated P-recovery and recycling from WWTPs, steel production, agriculture, and chemical industries have been established producing both struvite and calcium phosphate (HAP: hydroxyapatite) [24,25]. Learning and adapting Japan's experiences in the NR sector could be a useful strategy for other regions and countries. Records on NR units in other parts of the world are scarce. Wastewater collection and treatment is still undeveloped or under development in several regions in the world which contribute to a significant percentage of the world's population, especially in rural areas. Therefore, the prevalence of NR would only be conceivable in a long-term perspective.

Table 1. Overview of some of nutrient recovery practices and projects in various parts of the world adopted mainly from [21,23].

Geographical Area	Plants	Technology/Product	Remarks
North America	More than 15 full-scale units mainly producing struvite	Pearl, Multiform, Airprex see [10]	Lack of economic drivers and regulations for nutrient recovery [10]
Europe	Germany (10), Netherlands (10), Belgium (6), France (2), Spain (2), Italy (1), UK (2), Denmark (4)	Variety of technologies including Airprex, Anphos, Elophos see [10]	Mainly producing struvite from both municipal and industrial wastewater
China and India	China (Tianjin, Nanjing), India nor record found	Airprex, Crystalactor	China is planning new facilities with biological phosphorus removal and anaerobic digestion for energy recovery
Africa	No plants, feasibility studies in South Africa on P-recovery from sludge and source separated urine	NA	High costs, immature market and lack of acceptability
Japan	16 full-scale plants producing struvite and calcium phosphate	Gifu, PHOSNIX	Strong nationwide collaboration on market development, integrated production from steel, agriculture and chemical industries

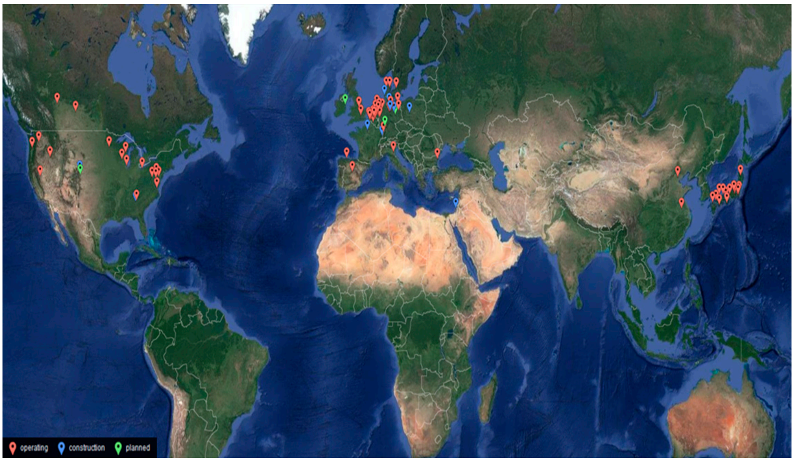

Figure 4. The worldwide map of operational plants for P-recovery [26].

It can be concluded that the low market price for fertilizers from phosphate rocks challenge the economic viability of nutrient recovery technologies, especially when the candidate technology does not provide additional operational benefits or a directly marketable product. The integration potential of a technology or a recovered material into existing infrastructure increases the chance to be in the successful class technologies. The direct involvement of potential users is as an important factor to reduce the complication of the emerging technologies and increase the chance for market deployment. Moreover, the higher recovery rates and additional operational benefits are important factors that should be considered in the development of the new generations of nutrient recovery technologies [22].

5. Implementation—Challenges and Opportunities

5.1. Environmental Regulations

Environmental legislation can be a key driver to accelerate the recycling and recovery of resources where the additional associated costs are against it. However, the current legal frameworks are mainly tailored to the existing structures. Thus, proper adjustment is necessary for adaption to the future challenges. Germany in 2017 and Switzerland in 2016 announced legal requirements for P-recovery. The EU fertilizer regulation (EC 2003/2003) is an example of such a regulation that can support the quicker transition towards nutrient recovery from wastewater. The way of monitoring and enforcing the discharge limits should be relevant and flexible. The phosphorus recovery from wastewater requires a proper and realistic discharge criterion since, where absolutely no flexibility is given to the plant operator, the final choice may be chemical P-removal rather than biological P-removal which reduces the potential for recovery.

5.2. Technical and Operational Aspects

The current trend shows that P-recovery has been mainly implemented in the case of operational needs or due to the reduction of operational costs. The current incentives for on-site nutrient recovery were recognized as prevention of uncontrolled scaling along the sludge train, improvement of sludge dewaterability, reduced polymer consumption, reduced sludge volume for disposal, partly better energy recovery, and better compliance with regulations. Excessive livestock farming and lack of land area for disposal of the sewage sludge may affect the selection of P-recovery technique. This is because the nutrients in the sludge exceeding the capacity or demand for domestic agriculture may make the concentration or volume reduction of the nutrients through incineration or thermal mineralization relevant options. Therefore, in the case of sludge incineration, technical needs for plant owners are not the driver; it is the compliance with regulation and/or cost reduction for disposal. To manage the investment risks, the recovery technologies and recovered materials should have the potential to be integrated into existing infrastructure and market with minimum change to the current operational regime. Moreover, the downstream market potential and security of supply of the raw material are crucial factors that determine the vulnerability of recovery technology.

5.3. Sustainability Outlook

A sustainable phosphorus management strategy requires recovery and recycling. There are several technologies for recovery and recycling available, while under current conditions, only some of them are economically viable. The process stability and momentary benefits (mainly cost reduction) are the main drivers for implementation of current recovery techniques rather than the sole recovery of phosphorus. However, expected regulatory policies can accelerate the transition towards more comprehensive recovery and recycling in the future. A few countries are frontrunners in nutrient recovery from wastewater. However, there is a visible demand for streamlining global knowledge to cover nutrient recovery from wastewater as well as other relevant nutrient containing wastes. There is a need to have a better link between stakeholders, policymakers, and researchers to bridge the gap between knowledge and practice. Figure 5 is an attempt to illustrate a high-level strategy for sustainable development of NR from sewage sludge. The overall strategy for the NR sector forms a nutshell in which four main elements; technology, policies and legislations, market and economy; interact with their corresponding stakeholders, i.e., investors, politicians, legislators, consumers, technology vendors as well as research and development and academia. This strategy has incorporated the key challenges that the NR sector is facing today and has proposed some proper high-level actions addressing those challenges. These actions have been predominantly formulated by taking into consideration the requirements of "sustainability" as the governing approach (3Ps: people, planet, and prosperity), such as creating/sustaining jobs, development of rural areas while promoting fair mechanisms for legislation, and rewarding mechanisms for involvement of stakeholders that are hesitant to contribute. This is in line with similar studies which proposed a 5R strategy (Re-align P inputs, Reduce P losses, Recycle P in bio-resources, Recover P in wastes, and Redefine P in food systems) to achieve a more sustainable P use [27]. In brief, it is necessary to secure economic routes to utilize secondary P in agricultural stores and consider wastewater as a potentially valuable source of P rather than a waste product and to develop sustainability indicators which are needed for long-term P sustainability.

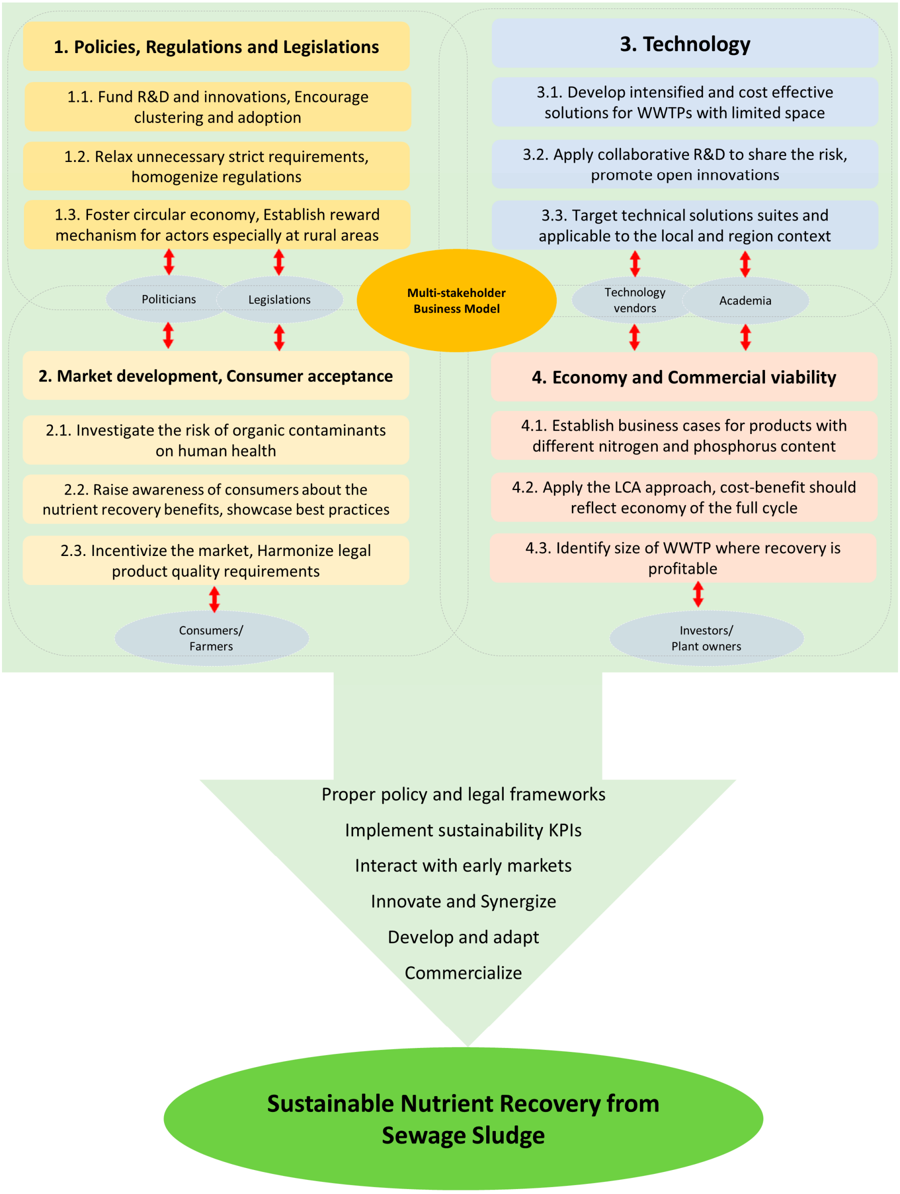

Figure 5. The proposed high-level strategy for sustainable development of nutrient recovery from sewage sludge.

6. Conclusion

Where wastewater is considered a renewable resource, nutrient recovery from sewage sludge requires a sustainable approach by utilization of appropriate technical options. Applicable strategies and roadmaps need to be adapted to the local or regional economy and geographical context. This is important to protect and improve the water quality, to enhance the operation and performance of waste treatment units, and to improve food security. Marketing of produced fertilizer from waste resources could be beyond the WWTP operators' job, and relevant stakeholders should be involved.

There is no one-size-fits-all solution, while there is a definite need to facilitate collective actions by developing business models that involve all stakeholders.

Sustainable development of the nutrient recovery sector will have to be defined based on three pillars of sustainability (3 P's) namely People (societal), Planet (ecological), Prosperity (economy); covering key aspects of this vision with the aim of the aspirational goal to reach a "zero net impact" associated with nutrient discharge from WW sludge. Achieving this goal over the coming years requires a dedication to overcome not only the technical barriers and financial constraints but also regulatory disincentives and societal aspects limiting NR from WWTPs. There will be more than one paradigm shift necessary to achieve the goal of a sustainable circular economy. Sustainability measures should be developed for WWTPs via measurable sustainability indicators (greenhouse gas and carbon footprints), monitoring and certification of the plants based on those key performance indicators (KPIs).

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Paper 2

Enhancing efficiency and economics of phosphorus recovery process by customizing the product based on sidestream characteristics – an alternative phosphorus recovery strategy

Sina Shaddel, Seniz Ucar, Jens-Petter Andreassen and Stein W. Østerhus

ABSTRACT

The enhanced biological phosphorus removal process makes the phosphorus recovery feasible from the dewatering streams of biological sludge. The physicochemical properties of these sidestreams, as an input to a crystallizer, are different before and after anaerobic digestion. In this study, phosphorus recovery by calcium phosphate is proposed for pre-digestion sidestreams and by struvite precipitation for post-digestion sidestreams. The thermodynamic modeling followed by experimental tests was performed to evaluate the recovery efficiency and product properties of struvite and calcium phosphates. The variations in phosphorus recovery potential, reaction kinetics and particle size distribution emphasize the importance of the adjustment of initial supersaturation and pH of the reaction. The optimum pH, considering the economics and recovery efficiency, for both calcium phosphate and struvite precipitation was found to be $\mathrm{pH} = 8.5$, whereas further increase of pH will not improve the overall efficiency of the process. In the case of calcium phosphate precipitation, it was shown that possible phase transformations should be considered and controlled as they affect both process efficiency and product properties. The economic evaluation indicated that the optimized operational condition should be determined for the phosphorus recovery process and that chemical costs for the production of calcium phosphates is lower than for struvite.

Key words | calcium phosphate, crystallization, economics, phosphorus recovery, process efficiency, struvite

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INTRODUCTION

Phosphate rocks are the main source of phosphorus for most phosphorus fertilizers in modern agriculture. The quantitative and qualitative reduction of the primary phosphorus rock reserves has led to great interest in phosphorus recovery from secondary resources to ensure sustainable food production in the future. The sewage sludge is a rich secondary resource for phosphorus and the enhanced biological phosphorus removal (EBPR) process provides great potential for phosphorus recovery from sludge phase (Wan *et al.* 2013). The sidestreams of the sludge handling line in the EBPR process, both before and after anaerobic digestion, are rich in phosphate. The high phosphate concentration and small volume of these sidestreams make them attractive for phosphorus recovery by chemical precipitation.

The precipitation of struvite and different calcium phosphate compounds is widely studied for phosphorus recovery from wastewater (Mehta *et al.* 2015; Melia *et al.* 2017). In these studies, input material is the liquid phase of anaerobically digested sludge and P-recovery from phosphate-rich sidestreams of undigested sludge is not fully elucidated. Anaerobic digestion of sludge and the conceivable introduction of ammonium recovery in the process change the physical and chemical properties of these sidestreams. Therefore, adaption of final product to the physicochemical properties of the targeted sidestream is necessary for an effective phosphorus recovery process.

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The aim of this study is to evaluate P-recovery in pre-digestion and post-digestion mode. For this purpose, calcium phosphates are selected as the targeted product for sidestreams with low ammonium content, and struvite for sidestreams after anaerobic digestion with higher ammonium content. The assessment is based on the phosphorus recovery efficiency, economic feasibility and product properties such as purity, water content and particle size.

The anaerobic character of thickening and dewatering of EBPR sludge leads up to PO_4^{3-}-release to the sludge dewatering sidestream. Application of a P-stripper with proper retention time and adequate amount of volatile fatty acid will improve the PO_4^{3-}-release to the liquid phase at dewatering stage of undigested EBPR sludge. An acid digester has also been proposed to facilitate the PO_4^{3-}-release and dissolution of the crystallized and organically bound phosphorus in this stage (Li *et al.* 2018). However, the low ammonium content of these sidestreams makes them less suitable for struvite precipitation while P-recovery by calcium phosphates can offer a noteworthy advantage. The precipitation of phosphorus in this stage diverts the soluble-P from the digester and lowers the risk of unwanted precipitation during digestion and post-digestion operations. The P-recovery by calcium phosphate at low pH (i.e. $pH = 5–7$, low NH_4-content) on P-rich sidestreams of undigested sludge will reduce the soluble-P in the digester, improve the dewaterability of the sludge and reduce the total-P in the biosolids (Li *et al.* 2018). The pre-digestion P-recovery by calcium phosphates at low pH can reduce the CO_2 footprint of the process. This is due to less consumption of sodium hydroxide (NaOH) and less polymer consumption for sludge dewatering. The CO_2 footprint in the production of NaOH is several times higher than that in the production of $CaCl_2$ or $MgCl_2$ (Thannimalay *et al.* 2013).

Degradation of sludge substrate to methane and CO_2 in anaerobic digestion increases the carbonate content in the sludge dewatering sidestream (Chipasa 2003). The coexisting carbonates (CO_3^{2-}), resulting from CO_2 dissolution, and production of amino groups ($-NH_2$) and ammonium increase the alkalinity of the dewatering sidestream from anaerobically digested sludge with respect to the undigested one (Möller & Müller 2012). The higher ammonium concentration increases the nucleation pH of calcium phosphates, and was shown to reduce the growth rate of brushite ($CaHPO_4{\cdot}2H_2O$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Vasenko & Qu 2017). Moreover, the required amount of caustic chemicals for pH elevation increases since the ammonium reaction tends to neutralize the hydroxyl ions (Gerardi 2003). However, increased ammonium concentration in solution boosts both the nucleation and growth kinetics of struvite precipitation. Therefore, the sidestreams after anaerobic digestion are better alternatives for struvite precipitation. In addition to anaerobic digestion, thermochemical treatments (incineration, liquefaction, gasification, pyrolysis) and hydrothermal treatments (thermal hydrolysis, wet oxidation) are among emerging techniques to treat sludge with phosphate release to aqueous phase (Munir *et al.* 2017).

Phosphorus recovery from the sidestreams of undigested sludge can be advantageous also from other aspects. The reduction of phosphate load to the anaerobic digester is proposed as an effective sludge handling strategy since during the anaerobic digestion a fraction of dissolved-P will mineralize and associate with suspended solids (Wilfert *et al.* 2018). This P-loss, which can be lower than 10% and up to 36%, will decrease the water-extractable P-fraction for further crystallization (Warren 1981; Massé *et al.* 2007; Marcato *et al.* 2008). The addition of iron or aluminum salts as support for an EBPR process to meet the effluent requirements or to resolve the sulfide production and odor problems is a common practice (Frossard *et al.* 1997; Wilfert *et al.* 2018). However, these ions will strongly reduce the availability of soluble phosphorus for further recovery. In these cases, P-recovery by calcium phosphate precipitation at the P-rich sidestreams of thickened bio-P sludge is still feasible.

In the context of a circular economy to achieve a sustainable phosphorus chain, the recovered phosphorus requires conversion into products that have diverse applications. Struvite, due to being composed of primary macronutrients (N and P) and secondary macronutrient (Mg), is a potential fertilizer while calcium phosphates have the potential to be used as secondary materials for the phosphorus industry since they are directly comparable to phosphate rocks. Calcium phosphates that precipitated from the wastewater can be mixed with normally mined phosphate rocks in fertilizer factories if they meet the standards for rocks (i.e. magnesium content, organic contamination). However, struvite, unlike calcium phosphates, is not suitable as an alternative raw material in electro-thermal processes because of its ammonia content (Cornel & Schaum 2009). Further, phosphorus recovery by calcium phosphates may make economic sense for small-scale wastewater treatment plants (Law & Pagilla 2018). Calcium phosphate compounds are potential alternatives for P-recovery when nitrogen is not available in the targeted stream such as industrial wastewater treatment plants, which in many cases do not accept nitrogen compounds since they do not have a biological treatment (Cichy *et al.* 2019).

The recovery of phosphorus in the form of high purity chemicals for applications in agriculture and industry will improve the economics of the phosphorus recovery process

(Vasenko & Qu 2017). The affinity of heavy metals is higher for volatile organic solids than for inert solids (Gould 1977). Due to degradation of volatile organic solids in the anaerobic digester, a higher concentration of heavy metals is expected in the dewatering sidestream of anaerobically digested sludge. Thus, in the case that contamination of final product by heavy metals is a concern, pre-digestion P-recovery can reduce this risk. Different forms of calcium phosphates have different potential for inorganic and organic contamination. Therefore, it is important to consider the phase transformation of calcium phosphates during precipitation from wastewater (Monballiu *et al.* 2018). However, this aspect is little studied for the wastewater applications.

The aim of this study is to evaluate the P-recovery efficiency, product properties and economics of the P-recovery process by struvite and calcium phosphate precipitation. The assessment of calcium phosphates and struvite under similar conditions enables us to select the proper product based on the physicochemical properties of the input material to the crystallizer. Further, this study aims to propose a alternative P-recovery strategy to improve the process flexibility and to improve the overall efficiency and economics of the P-recovery process. The proposed alternative strategy is to select the final product based on the characteristics of the sludge dewatering sidestream before and after anaerobic digestion. For this purpose, we performed a series of laboratory-scale crystallization experiments of struvite and calcium phosphates. The potential phosphorus recovery is calculated by thermodynamic equilibrium calculations followed by experimental validation of the results. The product properties such as phase characterization, morphology, particle size and dewaterability of obtained products are presented. The economic evaluation is also presented based on the obtained results in this study. The results of this study can be used for optimization of efficiency and economics of the phosphorus recovery processes.

MATERIALS AND METHODS

Materials

Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), ($CaCl_2$), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), ammonium chloride (NH_4Cl) and NaOH were used for the synthesis of struvite and calcium phosphates. All chemical reagents were purchased from Merck and were analytical grade, unless stated otherwise. Milli-Q water (18.2 MΩ·cm) was used for all purposes.

Methods

All experiments were carried out using a laboratory-scale crystallization system, composed of a 1 L glass reactor, stirred with a Teflon two-blade propeller controlled by a mechanical stirrer operated at 200 rpm. Temperature was regulated by a water bath and maintained at 20 ± 0.5 °C for all experiments. The pH was constantly measured and recorded by a combined glass electrode with KCl reference electrolyte connected to EasyDirect™ pH software (Metrohm), and calibrations were carried out daily. In the case of constant pH experiments, the pH was maintained by addition of 1 M NaOH. Nitrogen atmosphere presaturated with water was constantly preserved on top of the solutions throughout the crystallization reactions to prevent intrusion of atmospheric carbon dioxide. The chemical speciation and activity-based supersaturation were determined by the thermodynamic calculation program Visual MINTEQ 3.1 by including all the presented ions in the solution and NaOH that had been used to set up the initial pH. The precipitates were collected at the end of each experiment by vacuum filtration through a 0.2 μm pore size filter (polypropylene membranes). In the case of stopping crystallization reactions, the mixing was stopped and followed by quick filtration to collect the sample. The crystal samples were dried at the room temperature and their weight measured until reaching a stable weight. The water content and dewaterability of samples was measured at room temperature (≈20 °C) based on weight difference of the wet (collected sample after experiment) and dried states. The ion concentrations in the filtrate were determined via spectrophotometry (Hach DR Lange 1900). Solid phases were characterized via powder X-ray diffraction (XRD) (D8 Advance DaVinci, Bruker AXS GmBH) in the range of 2–75° with a step size of 0.013° and a step time of 0.67 s. Scanning electron microscopy (SEM) analyses (Hitachi S-3400N) were performed where samples were placed on carbon tape and sputter coated with gold. The particle size distribution (PSD) was analyzed with a laser diffraction particle size analyzer (Beckman Coulter LS230) in the range of 0.35 to 2,000 μm. The presented particle size distributions are based on dynamic light scattering technique and derived based on sphericity of the particles. Thus, the presented results are the nominal size of crystals for the comparison of the results. The filterability of the products was compared by filtering 50 mL of final sample with 0.2 μm filter paper (polypropylene membrane) under the same vacuum pressure for qualitative comparison.

Preparation of solutions

Stock solutions of $CaCl_2$, $MgCl_2 \cdot 6H_2O$), $NaH_2PO_4 \cdot 2H_2O$ and NH_4Cl were prepared from their corresponding crystalline solids (Merck, reagent grade) using MQ-water. The solution concentrations in this study were selected based on sludge dewatering sidestreams at a municipal wastewater treatment plant. The feed to the digester is a mixture of the thickened primary sludge and dewatered sludge that resulted from the EBPR process. Synthetic concentrate sidestream was then prepared from the stock solutions according to the original composition of total ammonium nitrogen ($NH_4\text{-}N = 745$ mg/L) and total phosphate ($PO_4\text{-}P = 137$ mg/L), where the final composition in each experiment was adjusted to achieve the target compositions. The supersaturated solutions with respect to struvite or calcium phosphates were prepared by the addition of magnesium- or calcium-containing solution to synthetic concentrate sidestream under constant stirring.

Equilibrium modeling

The calcium, magnesium and phosphate ions may form ion complexes that lower the effective concentration of free ions in solution. Therefore, the activity-based supersaturation is calculated for each experiment to identify the supersaturated phases and calculate the effective concentration of ions. The thermodynamic calculations of solution speciation were carried out with Visual MINTEQ 3.1 program (Figure S1, available with the online version of this paper) and the activity-based supersaturations are calculated by Equation (1) (Mullin 2001):

$$S_a = \left(\frac{\mathrm{IAP}}{K_{\mathrm{sp}}}\right)^{\frac{1}{\nu}} \tag{1}$$

IAP = ion activity product
K_{sp} = thermodynamic solubility product
ν = number of moles in one mole of solute

The experimental P-recovery yield and the theoretical value are calculated based on Equation (2):

$$\text{P-recovery (\%)} = \left(\frac{\mathrm{P_{initial}} - \mathrm{P_{final}}}{\mathrm{P_{initial}}}\right) \times 100 \tag{2}$$

The supersaturated solid phases based on thermodynamic modeling and under current experimental conditions are identified as $MgNH_4PO_4 \cdot 6H_2O$ (struvite), $Mg_3(PO_4)_2$ (magnesium phosphate) and $MgHPO_4 \cdot 3H_2O$ (magnesium hydrogen phosphate) in the struvite precipitation experiments. In the calcium phosphate experiments the supersaturated phases are amorphous calcium phosphate, $CaHPO_4$ (dicalcium phosphate), $CaHPO_4 \cdot 2H_2O$ (brushite), $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ (octacalcium phosphate, OCP) and $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite, HAP). Table S1 (available online) presents the overview of targeted products in this study. The formation of calcium phosphates is reported in the literature as a complex phenomenon by formation of multiple possible phases (Tsuge *et al.* 2002; Ferreira *et al.* 2003; Mekmene *et al.* 2009). Temperature, supersaturation, reaction pH, ionic strength and the presence of impurities affect the out coming phase (Lundager Madsen & Thorvardarson 1984). However, in this study doing the experiments at similar temperature and in the synthetic mode limits the governing parameters to supersaturation and reaction pH.

Design of experiments

The experiments are designed in desupersaturation mode since the different growth kinetics of calcium phosphates and struvite requires distinct experimental conditions for seeded growth experiments (seed amount and mixing). For the calcium phosphate precipitation experiments the Ca:P molar ratios of 1:1 and 1.67:1, and for the struvite experiments Mg:P molar ratios of 1:1 and 1.67:1, are selected. The Ca:P = 1 represents the minimum addition of calcium with respect to phosphate and Ca:P = 1.67:1 is selected to provide the equivalent molar Ca:P for the precipitation of HAP at the startup of the experiment. The Mg:P = 1 is the stoichiometric ratio in struvite and Mg:P = 1.67:1 is selected based on preliminary experiments to optimize the magnesium addition. The calcium phosphate precipitation is investigated in the pH range of 6.5–10.5 and struvite in the pH range of 7.5–9.5 with one pH-unit step. The experiments are designed in two modes: (1) drifting pH: without pH control to extend solid–liquid equilibration to 300 minutes and to compare with equilibrium modeling calculations and (2) constant pH: by keeping the reaction pH constant for 60 minutes. The results of drifting mode experiments are used to assess the thermodynamic equilibrium calculations and to identify the startup of phase transformation by slope changes in pH graphs. All experiments were performed in duplicate.

RESULTS AND DISCUSSION

Phosphorus recovery

The theoretical yield of phosphorus recovery at each experimental condition was calculated using thermodynamic software Visual MINTEQ 3.1. In these calculations, P_{final} is determined by the solubility of struvite and HAP, which is the thermodynamically most stable phase in the corresponding pH range and is constant under constant temperature. $P_{initial}$ is equal in all conditions in terms of total concentration; however, the effective initial concentration that determines the precipitation yield varies highly with solution pH. The equilibrium calculations assume precipitation of pure HAP with the theoretical yield and neglect the reaction kinetics. However, in calcium phosphate precipitation, kinetic factors play equally important roles in determining the precipitating phase (Wang & Nancollas 2008). It is well known that the final product may differ from the thermodynamically most stable one, where kinetically favored phases precipitate earlier according to Ostwald's rule of stages and transform to more stable ones under sufficient driving force (Muster *et al.* 2013). Therefore, a series of experiments in drifting pH mode were performed to compare the experimental P-recovery yield with the theoretical value, and results are presented in Figure 1.

The experimental results show that phosphorus recovery at Ca:P = 1:1 molar ratio does not significantly change by increasing the pH beyond 8.5 (Figure 1(a)). This is because the calcium concentration with respect to phosphorus is the limiting factor and the precipitated phase is the same (i.e. HAP), so further increase of P-recovery requires higher Ca:P molar ratios. It was observed that increase of Ca:P molar ratio to 1.67:1 significantly increased the phosphorus recovery and the increment was more significant for lower pH values. A long induction time (≈ 3 h) was observed for the experiment Ca:P = 1.67:1 at pH = 6.5, which is another reason for difference between the equilibrium and experimental P-recovery. The results show that increasing the Ca:P molar ratio beyond 1.67:1 and pH = 9.5 does not improve the phosphorus recovery in the corresponding experimental conditions (Figure 1(a)). In the case of struvite precipitation, Figure 1(b) shows that the increase of pH improves the P-recovery more than increasing the Mg:P molar ratio. This is because in the range of pH = 7.5–9.5 the HPO_4^- and $H_2PO_4^{2-}$ are the most abundant phosphate species and increase of pH will increase the PO_4^{3-} concentration as the final phosphate species in the struvite crystal along with decrease of struvite solubility. Increasing the Mg:P molar ratio did not significantly improve the P-recovery at pH = 7.5 during 60 minutes of reaction time due to slow precipitation kinetics at low pH. The faster reaction kinetics at higher pH values is the main reason that the experimental values of P-recovery were closer to the theoretical yield.

The role of starting pH on precipitation of different calcium phosphates is significant since pH governs the ion activities and ion complexation that further affect the supersaturation (Zhu *et al.* 2017). The results show that the increase of reaction pH and molar ratios (Ca:P or Mg:P) increases the supersaturation with respect to calcium phosphates and struvite (Figure S1). The increase of supersaturation, as the driving force for precipitation, increases the final P-recovery; however the equivalent P-recovery based on HAP precipitation is only obtained

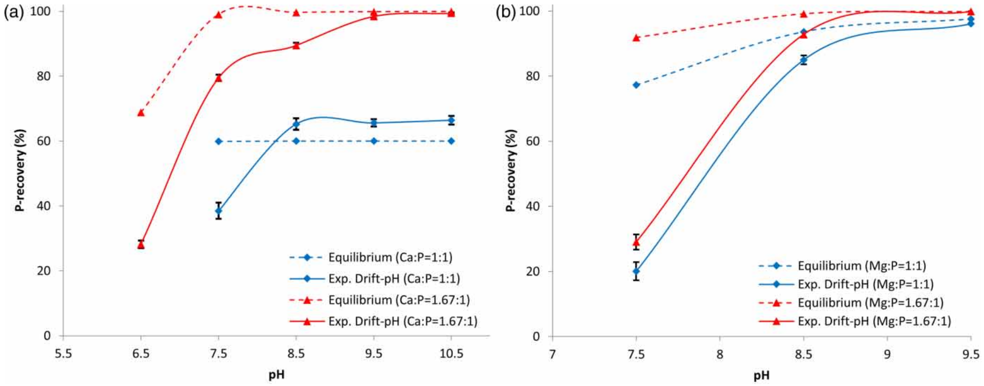

Figure 1 | Percent phosphorus recovery calculated from equilibrium modeling and measured in drifting pH experiments for (a) calcium phosphate (HAP) and (b) struvite precipitation under varying experimental conditions.

at pH ≥ 9.5. This can result from either slow reaction kinetics or nonstoichiometric precipitation due to low crystallinity of HAP or presence of multiple phases with changing Ca:P ratios in the precipitate. To investigate this, the precipitates were characterized by XRD and SEM analysis at different time points (Figure 2, panel 1). The XRD results show that HAP is the final precipitated product for pH = 7.5–10.5. At pH = 6.5, the initially precipitating phase was characterized as brushite without further phase transformation (Figure 2, panel 1(a)). Figure 2, panel 1(b), shows that at pH = 7.5, a mixture of brushite and HAP was present initially, which then completely transformed to HAP. In the presence of a thermodynamically more stable phase, metastable phases go under transformation and, in solution, this process mostly follows a dissolution–reprecipitation mechanism (Johnsson & Nancollas 1992). The multi-step precipitation behavior at pH = 7.5 can also be observed from the pH change as a function of time during the reaction (Figure S3, available with the online version of this paper). The control of the precursor phase and phase transformations is important for wastewater applications since different phases have different potentials for P-recovery and adsorbing impurities. Although OCP is also a supersaturated phase in these experiments, it was not detected by XRD analysis. The precipitated phases for pH ≥8.5 are identified as HAP from the initial time points of the reaction and no phase transformation was observed for these experiments (Figure 2, panel 1(c)).

The results of struvite experiments show that the precipitated phase in all experiments is struvite (Figure 2, panel 2 and Figure S2, available online). The phosphorus recovery increases by increasing the reaction pH. The XRD spectra of precipitated struvite at different pH values corresponds to different morphology of struvite crystals (Figure 2, panel 2). The crystals at pH = 7.5 showed a well-faceted morphology (bipyramidal). Further increase of pH to 8.5 produced hopper crystals (X-shape) and the dendritic crystals observed at pH = 9.5 (Figure 2, panel 2). A detailed insight into the development of different struvite morphologies is given in our recent publication (Shaddel *et al.* 2019).

Constant pH mode

The full-scale crystallization processes are mainly practiced at constant pH. The neutralization of H^+ by

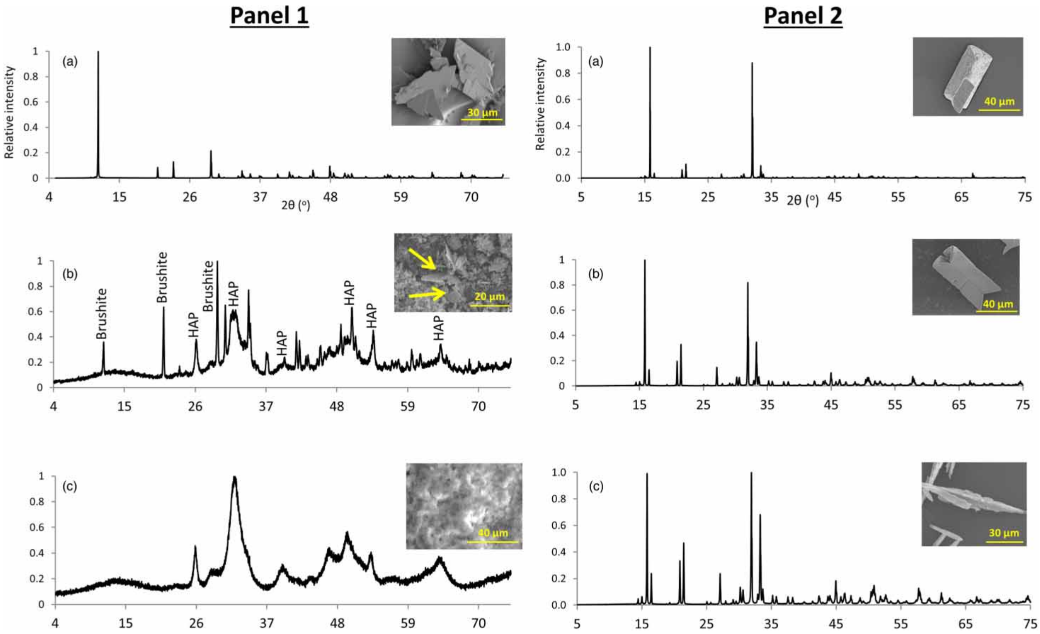

Figure 2 | The XRD spectra and SEM images. Panel 1: (a) Brushite at pH = 6.5 as single-phase, (b) mix of brushite and HAP at pH = 7.5 during the first 20 minutes of precipitation (the arrows point out brushite particles among HAP particles) and (c) HAP at pH ≥ 8.5; panel 2: (a) pH = 7.5, (b) pH = 8.5 and (c) pH = 9.5 with Mg:P = 1:1 molar ratio.

addition of alkali and keeping a constant pH keeps the driving force for deprotonation of phosphate species. This strategy retains higher precipitation rates to achieve the final recovery in shorter time, so the same series of experiments were designed at constant pH and the results are presented in Figure 3. The phosphorus recovery for both calcium phosphates and struvite increases with increasing the reaction pH. The results show that for the same reaction pH and molar ratio, the final P-recovery is higher with struvite precipitation than with calcium phosphates. In addition to the potential for phosphorus recovery, the product properties are also important in the phosphorus recovery process. Moreover, particle size and purity are important factors that define the value and application of the final product.

The XRD analysis confirmed that for constant pH experiments under the experimental conditions in this study, the final product was HAP when adding $CaCl_2$ and struvite when adding $MgCl_2$ (data not shown). The observed morphology of crystals by SEM showed similar results as presented in Figure 2. In full-scale applications there is a tradeoff between maximum P-recovery and product properties, because pH values higher than 8.5 and low Ca:P molar ratios may trigger the coprecipitation of carbonates and magnesium phosphate (Monballiu *et al.* 2018).

Particle size distribution

In the nutrient recovery by crystallization the uniform distribution of big particles with minimum contribution of fine particles is favorable (Li *et al.* 2019). The bigger particles will settle faster and bring fewer challenges in post-handling like drying and filtration, while fine particles will settle slower, and increase the chance of wash-out from reactor, especially in fluidized bed reactors. Thus, the product properties are important parameters in design and operation of the crystallizer, which require an overall optimization for P-recovery and particle size.

The PSD of obtained crystals is presented in Figure 4. Differences in the PSD and median size of the final products under different reaction conditions can be explained by the different levels of initial supersaturation, different degrees of aggregation and possible phase transformation for calcium phosphate experiments. Supersaturation is the main driving force for the crystallization process and highly influences particle size and size distribution due to its strong effect on the nucleation and growth rates. Smaller particles observed with increasing initial supersaturation result from boosted nucleation rates that produce higher number of particles (Mehta & Batstone 2013). Then, division of the remaining supersaturation for growth of many particles leads to production of particles with smaller size at the end of the experiment. In the case of calcium phosphate crystallization, median size does not decrease significantly with increasing initial supersaturation at higher pH values. This is probably due to aggregation of the produced particles that compensate for the higher nucleation rate at higher supersaturations (Collier & Hounslow 1999; Andreassen & Hounslow 2004). It can be observed that for both the Ca:P molar ratios the median size of the produced particles at $pH = 7.5$ is two times bigger than the produced particles at $pH \geq 8.5$. This is because the initial phase is brushite with further transformation to HAP, and lower nucleation rates,

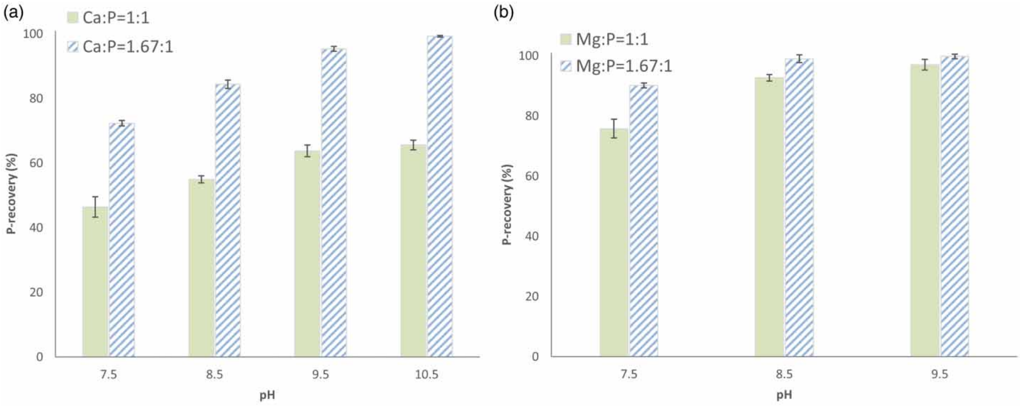

Figure 3 | Experimental values for phosphorus recovery in constant pH experiments with the precipitation of (a) hydroxyapatite and (b) struvite.

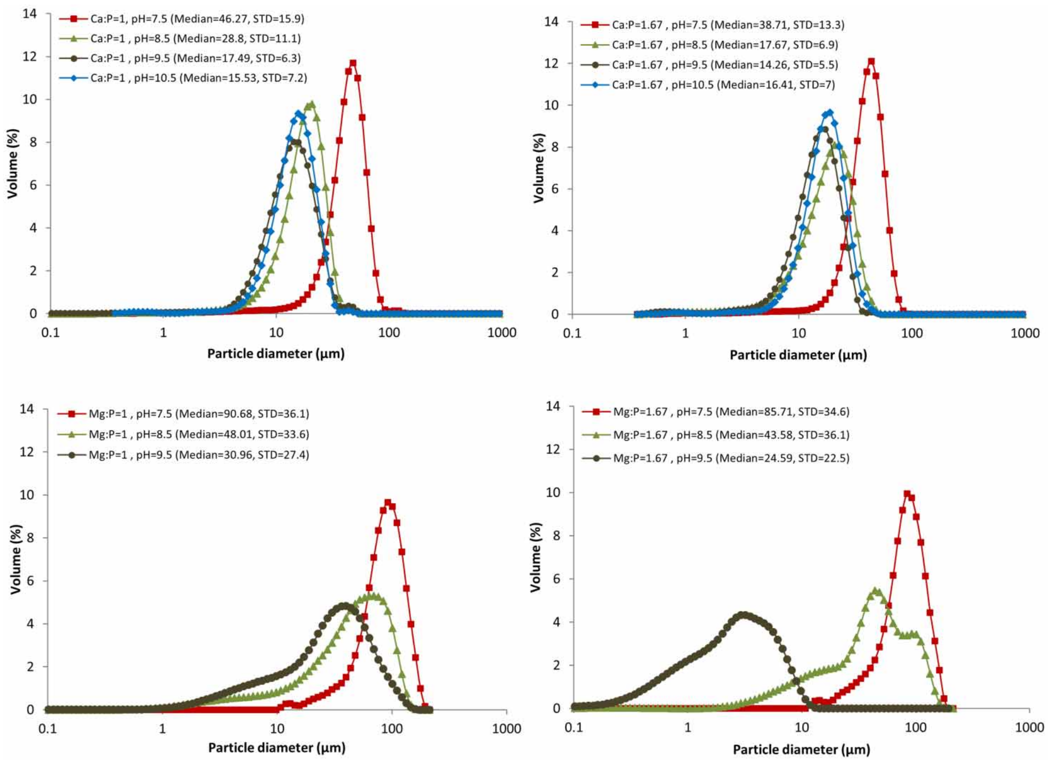

Figure 4 | Particle size distribution and median particle size for calcium phosphate experiments (final product as HAP) and struvite particles at constant pH and different operational conditions (STD: standard deviation).

which can explain the bigger particle size in this case (Ucar *et al.* 2017).

The desired size of crystals mostly depends on their final use. The less brittle crystals are desirable for agricultural purposes as they can be used by current fertilizer spreading machines. The bigger and denser crystals facilitate the handling and shipping. On the other hand when it comes to release rate, the smaller particles have higher release rates due to their high surface area/volume ratio (Forrest *et al.* 2008; Muster *et al.* 2013).

An easily filterable and washable product is desirable in wastewater applications. The filterability depends on PSD but this dependence is complicated (Liu & Qu 2016). In our experiments, the filterability followed the trend of struvite > brushite > HAP. The PSD at $\text{pH} = 7.5$ for different molar ratios resulted in the best filterability, which corresponds to the narrow size distribution and largest median particle. Increasing the reaction pH lowers the homogeneity of PSD and this effect is more pronounced for the struvite particles (Figure 4). Generally, the crystals with narrow PSD and larger size show better filterability of crystalline product (Liu & Qu 2016). The homogeneity of size distribution is more important in determining the filterability. The filling of the voids between the larger particles will reduce the overall porosity and consequently lower the filterability of the product (Dorf 2004). The average standard deviation of PSD for struvite was 35.1 μm at $\text{pH} = 7.5$ and 8.5, and 25 μm at $\text{pH} = 9.5$. The higher standard deviation at lower pH is due to the effect the initial supersaturation has on the aggregation of struvite crystals. The aggregation of struvite crystals is higher at lower initial supersaturation (i.e. $\text{pH} = 7.5$ and $\text{pH} = 8.5$), and no aggregation was observed at high initial supersaturation (i.e. $\text{pH} = 9.5$) (Shaddel *et al.* 2019). The average standard deviation of PSD for calcium phosphates was 14.6 μm at $\text{pH} = 7.5$ and 7.0 μm at $\text{pH} \geq 8.5$. The lower homogeneity of the obtained calcium phosphate particles at $pH = 7.5$ is due to phase transformation of brushite to HAP. Therefore, the solid retention time should be appropriately determined to obtain a more homogeneous product in full-scale reactors.

Water content

The settleability and water content of the product are important factors for agricultural applications (e.g. no humidity, no reactivity) (Egle *et al.* 2016). For wastewater applications, higher water content means lower purity of final product. Figure 5 shows the percent water content for calcium phosphates and struvite precipitated at different pH values. The average water content trend is HAP (48%) > brushite (23%) > struvite (8%).

The average dewaterability rate of struvite at room temperature was better than CaP products and in the order of struvite (1.5 days), brushite (2 days), HAP (4 days). The dewaterability rate, in addition to the type of the product, depends on the particle size. The struvite particles have bigger size than the calcium phosphate particles. The smaller particles have larger surface area, so their water content would be higher and consequently longer time is required for dewatering of the product. The final product of all experiments at $pH > 7.5$ is HAP. However, the HAP that resulted from transformation of brushite at $pH = 7.5$ showed lower water content than HAP that directly precipitated at higher pH values. The product at $pH = 9.5$ consisted of big flocs, which results in highest water content among calcium phosphates (Figure S4, available online).

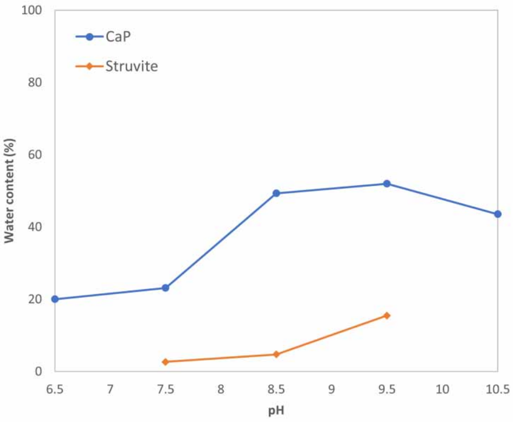

Figure 5 | The percent water content of different products for Ca/Mg:P = 1:1 molar ratio.

Economics and application as fertilizer

The chemical cost constitutes an important fraction of the operational costs. It represents a major part of the overall struvite production cost and is deterministic on payback time (Vaneeckhaute *et al.* 2017; Li *et al.* 2019). Therefore, an economic evaluation was performed by considering the chemical consumption (i.e. $CaCl_2$, $MgCl_2$ and NaOH) based on the experiments in this study. The cost of electricity (8.1% of the total costs) and operational and maintenance costs (16% of the total costs) were acquired from a full-scale struvite reactor. The total cost for each case was calculated by Equation (3) which is related to 1 kg of phosphorus recovered and presented in Figure 6. The total cost in the presented economic evaluation should be considered for comparison purposes, as the total cost in full scale would be lower due to a lower chemical costs in big scale.

$$\text{Total cost} = \text{chemical costs} + \text{electricity costs} \\ + \text{operational and maintenance costs} \quad (3)$$

The chemicals used as Ca^{2+} and Mg^{2+} source and the chemical cost for pH adjustment are major expenses in the P-recovery process by calcium phosphate or struvite precipitation. The results show that the molar ratio of Ca:P or Mg:P = 1.67:1 and $pH = 8.5$ are the optimum reaction conditions with respect to the cost and P-recovery efficiency for both struvite and calcium phosphates. The combination of $Ca(OH)_2$ and $CaCl_2$ may further reduce the chemical cost since $Ca(OH)_2$ is less expensive than $CaCl_2$ while providing the source for both calcium and pH adjustment. The price of $MgCl_2$ is higher than $CaCl_2$ and the amount of NaOH used for pH control in struvite precipitation was higher than for calcium phosphate. Increasing the pH beyond 8.5 is not cost-effective as high buffer capacity of phosphate ion implies addition of considerably higher amount of NaOH. In this study the base requirement for adjustment of initial pH to 9.5 and 10.5 was respectively 3.3 and 6.2 times higher than base requirement for $pH = 8.5$.

Calcium phosphates and struvite are potentially secondary resource materials for the phosphorus industry. However, the agronomic effectiveness of recovered product depends on its final use and soil characteristics. Therefore, the economic value and the desired characteristics for struvite or calcium phosphate precipitates should be thoroughly investigated based on process requirements and final application. From the application perspective, the fertilizer value of struvite is higher than the products in the calcium phosphate family since struvite contains N and P as primary

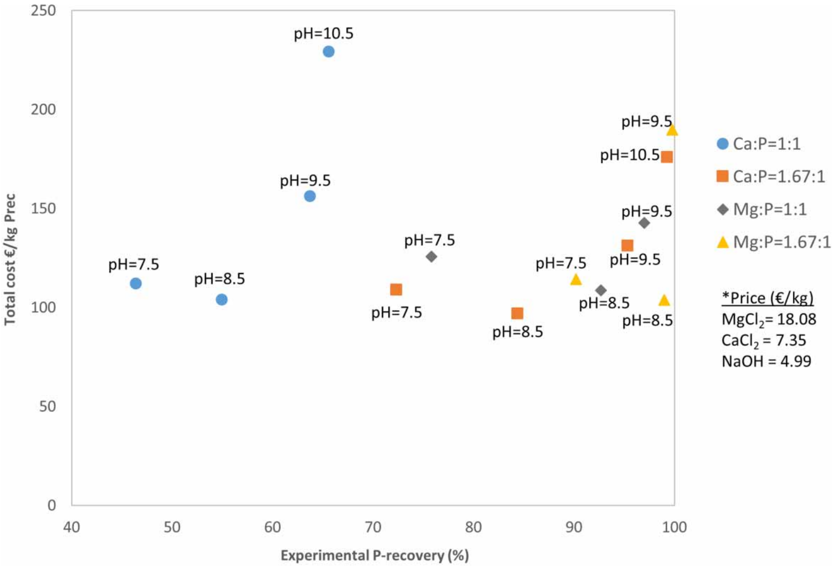

Figure 6 | The calculated total cost for different operational conditions in euros per kg phosphorus recovered (€/kg Prec). *Price quoted by VWR international, for technical grade material in 25 kg bag (September 2018).

macronutrients and Mg as secondary macronutrient. However, the calcium phosphate products are better alternatives as raw materials for production of artificial fertilizers since the magnesium in the struvite may interfere with the chemical processes based on sulfuric acid for production of NPK artificial fertilizer (Van Nieuwenhuyse 2000). In the case of comparison based on fertilizer potential, generally struvite is preferred over HAP. The slow release rate of struvite lowers the chance of rapid leaching and allows the plants to take up the nutrients, so less frequent application is needed (Caddarao *et al.* 2018). The fertilizer efficiency of calcium phosphates and struvite has been investigated by several researchers. There are several studies that reported struvite effectiveness is the same as the effectiveness of monocalcium phosphate for plant growth, and of diammonium phosphate and superphosphate for crop growth (Ghosh *et al.* 1996; Hao *et al.* 2013). Römer & Steingrobe (2018) evaluated 32 recycled P-products and they reported struvite as a good fertilizer with proper availability for plants.

Evaluation of the proposed strategy (case study)

A wastewater treatment plant with EBPR was considered as a case study to evaluate the performance of the proposed alternative strategy. The reject composition that has been used in this study imitates the current reject composition in the plant. However, mass balance calculations and different scenarios for P-recovery were used to evaluate the performance of the proposed strategy under a more generic condition. Figure 7 shows the simplified flow chart for the intended plant. The four feasible scenarios for P-recovery on the sludge dewatering sidestreams were defined as: (1) without P-stripper via mixed reject, (2) without P-stripper on post-digested reject, (3) with P-stripper via post-digested reject and (4) with P-stripper via calcium phosphate on pre-digested reject and via struvite on post-digested reject.

First, it should be noticed that application of P-stripper is necessary since exclusion of the P-stripper in scenario 1 and 2 implies significant reduction of P-recovery potential and operational problems. The operational problems can be uncontrolled struvite precipitation in the anaerobic digester, and clogging in downstream pipes and post-digestion dewatering equipment. In addition, mixing the two reject streams in scenario 1 is not favorable as it reduces the phosphorus concentration in the mixed flow, which reduces the P-recovery potential. However, the pre-digestion sidestream should be considered for P-recovery as it contains considerable amount of the soluble phosphorus, and return of this flow to the inlet of the plant will increase the phosphorus load to the biological treatment stage. The ultimate

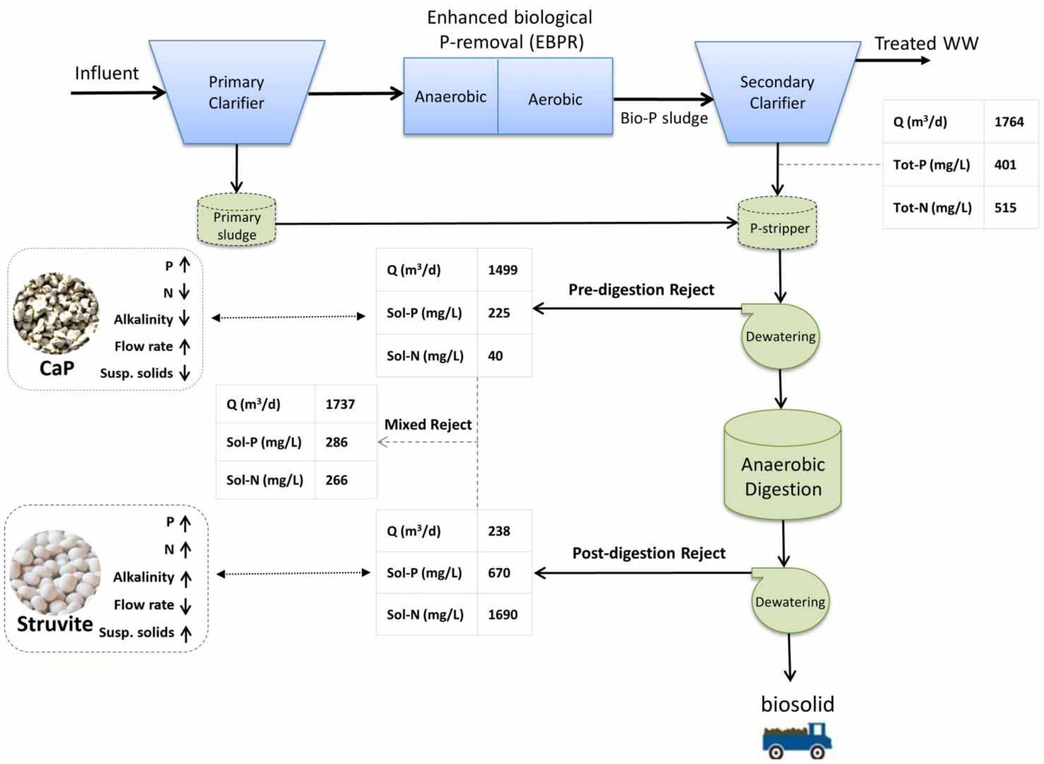

Figure 7 | The simplified flow chart for a wastewater treatment with enhanced biological phosphorus removal and mass balance data for the targeted streams.

comparison of scenario 3 and 4 in this case study requires dedicated experimental data, while the equilibrium P-recovery calculations were used for comparison purposes. It was noticed that the overall P-recovery in scenario 4 depends on the P-recovery efficiency on pre-digestion reject. The associated costs for recovery of 1 kg P in scenario 4 were 40–60% lower than scenario 3, whereas using a mix of $CaCl_2$ and $Ca(OH)_2$ can further reduce the costs in scenario 4. This is because $Ca(OH)_2$ is less expensive than $CaCl_2$ and it can be used to increase Ca:P molar ratio and pH at a lower cost. Assuming that product value would be tied to phosphorus content, brushite is a better option for pre-digestion P-recovery due to higher P-content and lower transport cost.

Therefore, it can be concluded that customizing the product based on sidestream characteristics, in addition to operational benefits, has a great potential to improve efficiency and financial sustainability of the phosphorus recovery process. However, it should be noted that there is not a one-size-fits-all solution and process requirements along with local needs should be considered in identification of an ideal process solution.

CONCLUSION

The results of this study show that introducing diversity in the final products of the phosphorus recovery process is an effective approach to improve the value chain for recovered phosphorus. In addition, it increases the flexibility in handling different types of sludge dewatering sidestreams. It was shown that both struvite and calcium phosphates are proper alternatives for phosphorus recovery from phosphate-rich sidestreams in the EBPR process. However, the final choice among these products mainly depends on process requirements and final application of the recovered product. Supersaturation as an inclusive parameter can be used for optimization of phosphorus recovery by crystallization as it governs both the recovery efficiency and reaction kinetics. The effective regulation of supersaturation is achievable by adjustment of the reaction pH and chemical dosing of magnesium and calcium. It is concluded that phase transformation should be considered for calcium phosphate crystallization since it affects the purity, particle size and dewaterability of the final product. The overall optimum pH for both struvite and calcium phosphate precipitation, by considering both recovery efficiency and economic feasibility, was found to be $pH = 8.5$. The low pH values result in slow precipitation rates and high pH values trigger the nucleation and production of fine particles. The struvite has lower water content and better dewaterability than calcium phosphates. However, under the same operational conditions, the chemical expenses for phosphorus recovery by calcium phosphate precipitation are lower than those of struvite.

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NOTES

The authors declare no competing financial interest.

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Supplementary data (Paper II)

Table S1: Overview of calcium phosphate products and struvite (Chow 2001)

Compound	**Reaction equation**	**pK$_{sp}$**	**P-content (% weight)**
Amorphous calcium phosphate	variable	variable	variable
Brushite	$Ca^{2+} + HPO_4^{2-} \rightarrow CaHPO_4 \cdot 2H_2O$	6.6	18
Octacalcium phosphate	$8Ca^{2+} + 6HPO_4^{2-} \rightarrow Ca_5H(PO_4)_6 \cdot 5H_2O$	46.9	7
Hydroxyapatite (HAP)	$5Ca^{2+} + 3HPO_4^{2-} + 4OH^{-} \rightarrow Ca_5(PO_4)_3OH$	58.3	6
Magnesium ammonium phosphate (struvite)	$Mg^{2+} + PO_4^{3-} + NH_4^{+} \rightarrow MgNH_4PO_4 \cdot 6H_2O$	12.6	12

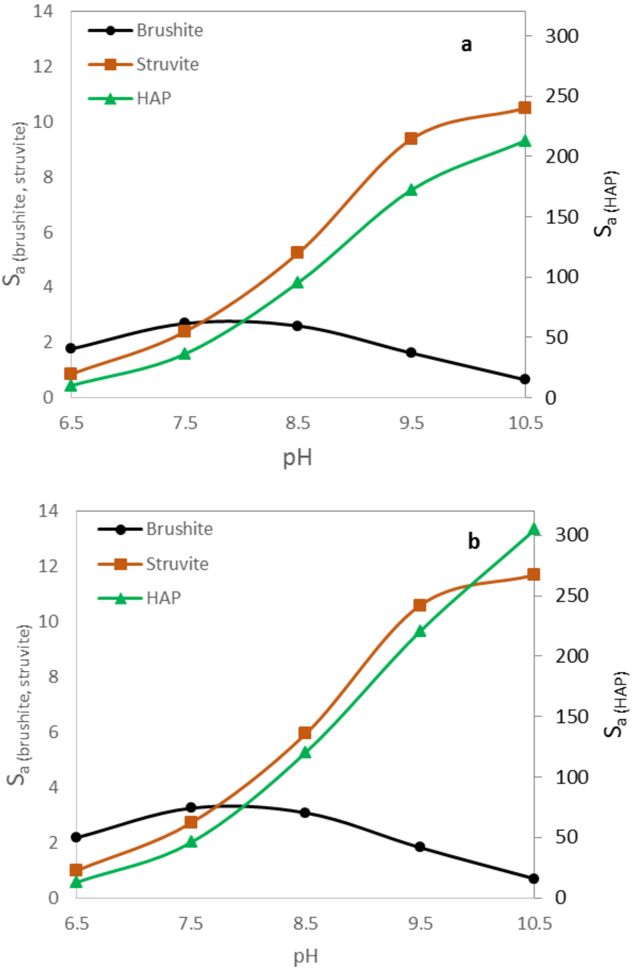


Figure S1: Activity based supersaturation with respect to brushite, HAP and struvite calculated at (a) Ca:P / Mg:P = 1 and (b) Ca:P / Mg:P = 1.67 molar ratios and at 20 °C.

Phase transformations and reaction kinetics

The degree of deprotonation (release of H^+) is an indirect signal that can be monitored to follow the progression of calcium phosphate and struvite precipitation reactions. For both minerals, nucleation and growth of the solid phases are accompanied by the release of H^+ ions, and a stable pH represents equilibrium in solution. Therefore, it is possible to determine the endpoint of precipitation for both minerals, and phase transformations between calcium phosphate phases with varying acidity through the pH signal. In addition, the slopes of the pH curves can be used to evaluate the rates of precipitation reactions.

The results showed a single drop and then stabilization of the pH for struvite precipitation, which implied a single precipitation event with no phase transformations (Figure S2). On the other hand, calcium phosphate precipitation at pH 7.5 showed an initial drop, followed by a weakly declining plateau and a second abrupt drop before stable pH is achieved, which implies formation of at least two different phases with varying composition (Cardew & Davey 1985) (Figure S3).

It was observed that increasing the initial supersaturation through increasing the molar ratio of precursor ions or pH accelerates the drop of pH to its final stable value that shows higher rates for precipitation. The experiment at pH = 6.5 and Ca:P = 1.67:1 showed a long induction time (≈150 min) due to the low supersaturation at this condition.

At high pH and supersaturation the amorphous calcium phosphate is usually the first phase that precipitates and this phase hydrolyzes almost instantaneously to more stable phases (Johnsson & Nancollas 1992). In experiments conducted at pH = 8.5–10.5 immediate precipitation was observed after the addition of calcium ion to the reaction medium. This makes the study of phase transformation challenging; however, we expect maturation of precipitated phases towards more crystalline HAP (Ucar *et al*. 2017).

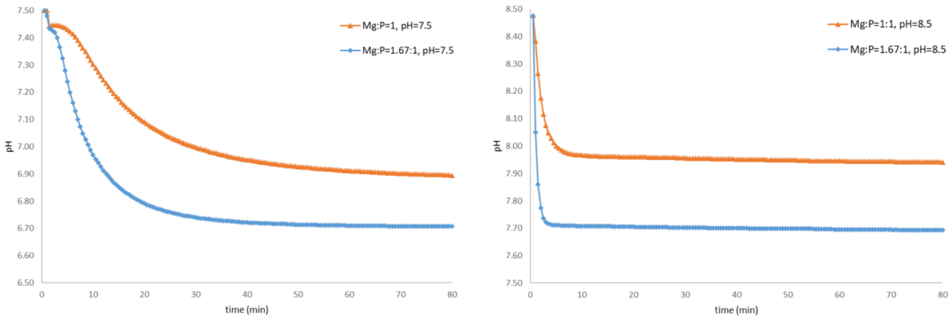


Figure S2: The pH graphs for struvite precipitation at different pH and Mg:P molar ratios.

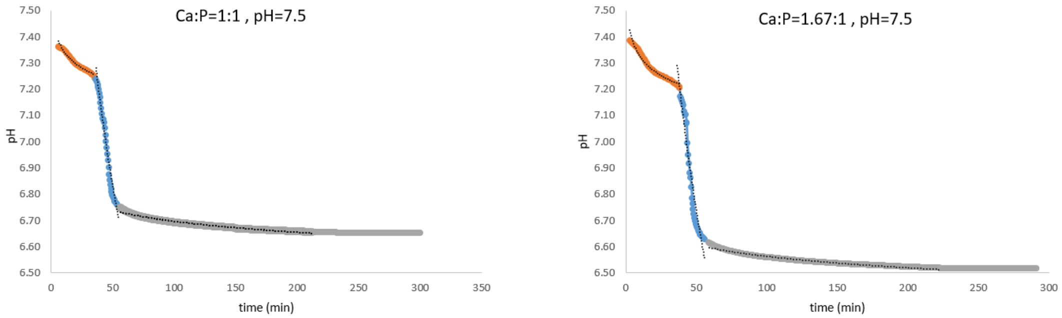
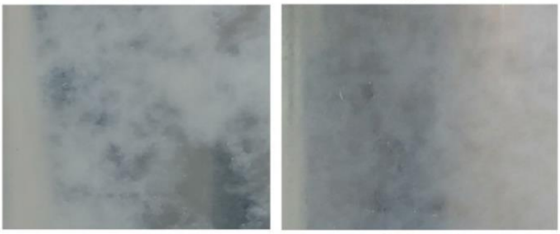


Figure S3: The pH graphs for calcium phosphate precipitation at pH = 7.5 and different molar ratio (note the change of pH graph slope as a sign of phase transformation).

a) pH=7.5 b) pH=8.5



c) pH=9.5 d) pH=10.5

Figure S4: The image of final sample of calcium phosphate experiments. (a) and (b): well dispersed solutions, (c) big flocs of particle at pH = 9.5 and (d) smaller flocs of particles at pH = 10.5.

Paper 3

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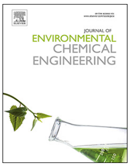

Engineering of struvite crystals by regulating supersaturation – Correlation with phosphorus recovery, crystal morphology and process efficiency

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ABSTRACT

Struvite crystallization is widely applied for nutrient recovery from wastewater streams. The better understanding of the effects of reaction conditions on final crystal properties will contribute to improve both the recovery efficiency and product quality of struvite as a fertilizer. In this study, batch crystallization experiments were performed in laboratory scale to reveal the effect of supersaturation on the phosphorus recovery and crystal properties. For this purpose, supersaturation is regulated through varying the pH, magnesium and ammonium concentrations in solution. The effects of these parameters on controlling crystal properties such as size and morphology are highlighted through their role as supersaturation regulators.

The potential implications of different crystal morphologies on settling velocity and aggregation of crystals are also discussed. This improved understanding could aid in improved struvite crystallization processes for wastewater treatment.

1. Introduction

Phosphorus (P) is one of the essential elements in living organisms and an irreplaceable ingredient for agricultural fertilizers that are used in crop and livestock production. However, phosphate rocks, which are the main source of P, are non-renewable and in danger of depletion [1]. In addition, beside diminishing phosphate rocks, P content has increased notably in the hydrosphere because of human activity through domestic and industrial waste, which can cause eutrophication [2]. Therefore, its efficient use, recovery and recycling are important steps towards environmental safety and a sustainable development.

P-recovery from wastewater is an effective strategy to address both problems and has gained great attention [1]. The most commonly used approach has been the precipitation of P-bearing minerals from wastewater, such as struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4{\cdot}6H_2O$). Struvite has the advantages of being composed of primary macronutrient (nitrogen and phosphorus) and secondary macronutrient (magnesium), and being a slow-release fertilizer that can be used directly as precipitated [3,4]. In addition, controlled precipitation of struvite in wastewater treatment plants aids in avoiding pipe clogging and extra costs of equipment cleaning [5,6].

Efficiency of a P-recovery process and struvite product quality can be enhanced by controlling the precipitation reaction to optimize the reaction time as well as the size and morphology of the crystals. The shape and size of crystals have strong impact on the properties of final product as well as the efficiency of downstream processes like settleability, filtering and drying. Therefore, it is important to be able to tailor process conditions for optimization of these properties. It could be misleading to measure the process efficiency in terms of soluble-P removal as the fine particles can be washed-out and redissolve in downstream processes, which affect the reliability of modeling and economic predictions for the whole process [7]. Therefore, improving the efficiency of downstream processes via regulating reaction parameters enhances the phosphorus recovery efficiency and ensures the quality of effluent. The consistency in the quality and properties of final product is one of the determinative factors for the success of struvite production. The particular processes in wastewater treatment plants, feed and seasonal variations often create changes in the composition of the input material to the crystallizer. Therefore, the operational conditions should be properly adjusted to minimize the risk of fail to meet the product quality and process requirements.

Supersaturation is the main parameter that governs size and morphology of the precipitated struvite and the phosphorus recovery efficiency [8,9]. Crystal size is determined dominantly by supersaturation since the nucleation and growth kinetics are correlated with the thermodynamic driving force in the crystallizing system. The application of the kinetic models for nucleation and growth can be used to control the size related settling characteristics of struvite crystals [10]. The crystal

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morphology is an outcome of the internal (crystal lattice structure and crystal defects) and external factors (supersaturation, the presence of impurities, temperature, etc.). The modification of crystal morphology has been receiving growing attention due to both theoretical interest and industrial needs [11,12]. However, a systematic correlation of struvite morphology with supersaturation and transition boundary between different morphologies for wastewater application is not yet fully explored in the literature. The dependency of struvite morphology on supersaturation, mixing energy and retention time has already been mentioned by previous studies [8,13,14]. Although it is well established that crystal morphology is highly effective on the settling velocity, this aspect has not been reported for struvite previously.

Previous work also implicitly reported the dominant effect of supersaturation on precipitation kinetics and aggregative properties of crystals [15,16]. The liquid from dewatering of anaerobically digested sludge is the main feed for the majority of struvite reactors [17]. Although, the reported studies are not directly applicable for wastewater applications due to distinct compositions and characteristics related to wastewater. The equimolar and low concentration of struvite constituents ions or the high phosphate concentrations in swine wastewater are not representative for wastewater applications.

High initial supersaturation in the vicinity of inlet ports of struvite reactor can favor nucleation over crystal growth at the onset of crystallization. Improving aggregation of the generated crystals in this stage is important; otherwise distribution of them in the space and time will reduce the chance of collision and aggregation in later stages. Moreover, improved aggregation contributes to better granulation and will further reduce the chance of product loss from reactor by wash out. While the struvite aggregation is mainly explained based on zeta potential in previous studies [18,19], the effect of initial supersaturation on crystal aggregation is mainly disregarded.

Numerous studies have investigated the feasibility of P-recovery via struvite precipitation from laboratory to pilot scale and the existing full-scale struvite crystallization techniques all advertise high recovery efficiency (80–90%) [7,19–21]. However, the impacts of operational conditions on the different characteristics of obtained products remain unclear. Thus, large-scale processes are yet to be optimized in terms of product quality and efficiency, where variations can be expected due to individual processes employed at different plants. The individual optimization of reaction parameters such as pH and struvite constituent ions (Mg^{2+}, $NH_4{}^+$) is the most common approach to enhance the phosphorus recovery. However, this approach without a clear understanding of benefits and disadvantages on product properties will not improve the overall efficiency of the process. Further, owing to the complexity of crystallization processes, considering a comprehensive parameter is necessary to consistently achieve the desired recovery efficiency and product properties. Supersaturation is an inclusive parameter independent of reactor type which takes into account the effect of several parameters (struvite constituent ions, ionic strength, pH and temperature). Although supersaturation regulation is crucial to improve the overall process performance, lack of a fundamental understanding on lumped recovery efficiency and struvite properties hindered the utilization of supersaturation as a design parameter. Therefore, coupling the recovery efficiency and product properties requires a better understanding of the role of supersaturation from a fundamental viewpoint.

The aim of this study is to explore the central role of supersaturation on phosphorus recovery efficiency and shaping product properties. Revealing the correlation between supersaturation and the size and morphology of the final precipitation products, and further evaluate their consequent effects on downstream processes is the main focus of this work.

One of the objectives of this study was to utilize the supersaturation as an inclusive parameter to couple the recovery efficiency and product properties. Therefore, the effects of impurities were eliminated by conducting the experiments with synthetic reject water that enables accurate calculation of supersaturation. Both reaction conditions and crystal properties are evaluated for discussing the final crystal morphology where supersaturation was followed as the main parameter.

In order to define a proper operational strategy for supersaturation regulation, a systematic approach was employed to investigate the effects of pH and molar ratios of constituent ions on the P-removal efficiency and product quality. By scanning through a relevant range of supersaturation values, efficient control on crystal size and morphology was attained and further correlation of these properties with settling and aggregation characteristics were evaluated. This fundamental understanding is crucial for improving full-scale applications of phosphorus recovery by struvite crystallization via optimization of operational conditions and their effects on crystal properties.

2. Materials and methods

2.1. Materials

Magnesium chloride hexahydrate ($MgCl_2·6H_2O$), sodium dihydrogen phosphate ($NaH_2PO_4·2H_2O$), ammonium chloride (NH_4Cl) and sodium hydroxide (NaOH) were used for the synthesis of struvite. All chemical reagents were purchased from Merck with analytical grade. Milli-Q water (18.2 MΩ.cm) was used for all purposes.

2.2. Methods

All experiments were carried out using a lab-scale crystallization system, composed of a 1 L glass reactor, stirred with Teflon two-blade propeller controlled by a mechanical stirrer operated at 200 rpm. Temperature was regulated by a water bath and maintained at $20 \pm 0.5^{\circ}$ C for all experiments. The pH was constantly measured and recorded by a combined glass electrode with KCl reference electrolyte connected to EasyDirect™ pH Software (Metrohm), and calibrations were carried out daily. The precipitation reaction was initiated by addition of $MgCl_2$ solution to a synthetic reject solution and the reactions were let to proceed for 60 min. The pH was kept constant during experiments by addition of 1 M NaOH. In the case of terminating crystallization reactions for further studies, the pH of reaction was lowered to pH = 7 by adding appropriate amounts of HCl followed by quick filtration to prevent dissolution. Nitrogen atmosphere was constantly preserved on top of the solutions throughout the crystallization reactions to prevent intrusion of atmospheric carbon dioxide. The chemical speciation and activity based supersaturation were determined by thermodynamic calculation program Visual MINTEQ 3.1. The precipitates were collected at the end of each experiment by vacuum filtration through a 0.2 μm pore size filter (PP membranes). The ion concentrations in the filtrate were determined via spectrophotometry (Hach DR Lange 1900). The particle size distribution was performed and analyzed with Beckman Coulter LS230 laser diffraction particle size analyzer. The presented particle size distributions are based on dynamic light scattering technique and derived based on sphericity. Thus, the presented results are nominal size of crystals for the comparison of the results.

Solid phases were characterized via powder X-ray diffraction (XRD) (D8 Advance DaVinci, Bruker AXS GmBH) in the range of $5 - 75^{\circ}$ with a step size of 0.013° and a step time of 0.67 s. The analysis of XRD data was performed by DIFRACC.SUITE EVA software (Bruker) and the International Centre for Diffraction Data database (ICDD PDF-4 + 2018) was used to characterize the precipitates. SEM analyses (Hitachi S-3400 N) were performed where samples were placed on carbon tape and sputter coated with gold. The zeta potential measurements were conducted by Malvern Zetasizer Nano ZS in a dip cell at 20 °C.

2.3. Design of experiments

The solution concentrations in this study were selected based on a dewatering reject of anaerobically digested sludge at a municipal wastewater treatment plant. The feed to the digester is a mixture of the thickened primary sludge and dewatered sludge that resulted from an enhanced biological phosphorus removal (EBPR) process. The operation strategy for supersaturation regulation is important in order to keep high recovery efficiency and product quality. The Mg:N:P = 1:1:1 is the theoretic requirement for struvite precipitation, while there is an imbalance between molar ratios of these ions in practical implications. The reagent cost for magnesium and alkali may affect the economic feasibility of struvite production [22]. In this work, different pH and Mg:N:P molar ratios were evaluated for struvite crystallization. The reaction kinetics at pH $<$ 7.5 were very slow and pH $>$ 9.5 may result in precipitation of other phases than struvite [23], thus the reaction pH were selected as pH = 7.5 (low), pH = 8.5 (medium) and pH = 9.5 (high). By combining different molar ratios with different pH values, struvite crystallization was investigated under a broad range of supersaturation and growth kinetics. The addition of magnesium beyond the consumption potential by struvite crystallization increases the operating cost, may result in formation of various magnesium phosphate precipitates and increases the chance of unintentional struvite precipitation in other processes [24]. Therefore, a series of preliminary experiments were performed to maximize P-recovery with minimum increment of Mg:P molar ratio beyond the stoichiometric value of 1:1. The Mg:P = 1.67:1 was selected based on the result of these experiments. The dewatering sidestreams of EBPR sludge both before and after anaerobic digestion are rich in phosphorus, while the reject flows after anaerobic digestion have significant surplus of ammonium with respect to phosphate and magnesium [25]. Therefore, the ammonium concentration to the crystallizer (N:P molar ratio) can be controlled by regulating the contribution of phosphate rich and ammonium rich streams or by control of recycle ratio of the reactor. According to technology providers N:P > 6 is optimal to maximize the recovery efficiency and purity of struvite and struvite precipitation would be of interest if N:P > 1 [19,26]. The molar ratio of N:P = 12 is the original N:P in the selected reject water and the other N:P molar ratios were selected based on these criteria. All experiments were performed in duplicates and Table 1 shows the experimental conditions and the thermodynamically calculated activity based supersaturation, S_a, for each experiment by using Eq. (1) [27]:

$$S_a = \left(\frac{IAP}{K_{sp}}\right)^{\left(\frac{1}{3}\right)} \tag{1}$$

IAP = ion activity product = $a_{Mg}{}^{2+} \cdot a_{NH4}{}^{+} \cdot a_{PO4}{}^{3-}$

K_{sp} = thermodynamic solubility product

The thermodynamic equilibrium calculations for struvite precipitation were performed by Visual MINTEQ 3.1 software to calculate the theoretical yield for each solution and the thermodynamic evaluation was followed by lab-scale batch experiments with a reaction duration of 60 min. The presented theoretical and experimental results of percent phosphorus recovery were calculated by using Eq. (2).

Table 1
Experimental conditions and calculated activity based supersaturation values ($P = 137\ mgL^{-1}$).

ExP.	Mg:N:P	pH	Sa
1	1:2:1	7.5	1.5
2	1:2:1	8.5	3.3
3	1:2:1	9.5	5.8
4	1:6:1	7.5	2.1
5	1:6:1	8.5	4.5
6	1:6:1	9.5	7.9
7	1:12:1	7.5	2.4
8	1:12:1	8.5	5.3
9	1:12:1	9.5	9.5
10	1.67:12:1	7.5	2.7
11	1.67:12:1	8.5	5.9
12	1.67:12:1	9.5	10.6

$$P\text{– recovery}\,\% = \left(\frac{P_{initial} - P_{final}}{P_{initial}}\right) \times 100\% \tag{2}$$

2.4. Preparation of solutions

Stock solutions of magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$) and ammonium chloride (NH_4Cl) were prepared from their corresponding crystalline solids (Merck, reagent-grade) using MQ-water. Synthetic reject water was then prepared from the stock solutions following the original composition of the reject water with total ammonium nitrogen (NH_4-N = 745 mg/L) and total phosphate (PO_4-P = 137 mg/L) conforming N:P = 12:1, and the final composition in each experiment was adjusted to achieve the compositions in Table 1. The supersaturated solutions with respect to struvite were prepared by addition of the magnesium-containing solution to synthetic reject water under constant stirring.

2.5. Measurements of settling velocity

Sedimentation tests were conducted on an experimental set-up which was a modified form of the Andreasen pipette method [28]. The set-up consisted of a cylindrical glass burette with 8 mm internal diameter filled with water pre-saturated with respect to struvite to avoid dissolution. The sieved crystals were dispersed in 1 mL of the same liquid and allowed to make a distinct front before measurements. The measuring system was based on visual space-time registration and travel time of the particles measured by digital-display stopwatch.

3. Results and discussion

3.1. Efficiency of phosphorus recovery

The initial phosphorus concentration is equal in all conditions and the final phosphorus concentration is determined by the solubility of struvite, which is constant at constant temperature, for the calculation of theoretical yield. Fig. 1 presents the experimentally measured and theoretically percent P-recovery values for all determined conditions. The increasing values of P-recovery shown with thermodynamic calculations reflect the effect of higher supersaturation in the reaction medium that is achieved either by increasing the pH or molar ratio of the constituent ions with respect to P. The results for struvite yield

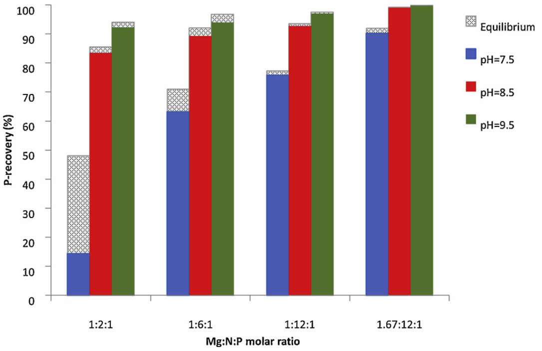


Fig. 1. The P-recovery measured in the experiments and equilibrium theoretical P-recovery calculated from Visual MINTEQ.

based on thermodynamic equilibrium calculation are presented in Figure S1.

The strong influence of pH on supersaturation results from its deterministic effect on phosphate and ammonia speciation in solution (Table S1) [60]. Increasing pH shifts the equilibrium reactions of struvite constituents, which consequently increases the supersaturation with respect to struvite. A satisfactory fit was observed between theoretical and experimental results within the reaction time of 60 min determined for this study, except for two sets of experiments at pH = 7.5 with lowest supersaturation values due to slower reaction kinetics (Mg:N:P = 1:6:1 and Mg:N:P = 1:2:1). Higher supersaturation means a higher chemical potential for the crystallization of struvite and consequently a higher phosphorus recovery as observed in the thermodynamic calculations. Increasing Mg:P and N:P molar ratio at low pH (7.5) caused a greater effect on P-recovery efficiency than that in higher pH values.

Moreover, experimental results also showed the strong effect of supersaturation on the kinetics of the precipitation reaction and indicated that supersaturation is a key parameter for efficient P-recovery by precipitation. Both nucleation and crystal growth rates scale with supersaturation, thus, the reaction times for completing the precipitation shorten under high supersaturation. The rate of NaOH addition for maintaining the solution pH during the precipitation reactions was an indication of the reaction progression [22] and it was found that among the studied factors, pH showed the major effect on the reaction time. Increasing the reaction pH from 7.5 to 8.5 and from 8.5 to 9.5, reduced the time for completing the reactions by a factor of ≈5 and ≈3, respectively (data not shown). According to the results of ion and complex speciation by Visual MINTEQ 3.1 (Figure S2) the increase of pH changes the ion speciation and ion complexations towards a higher PO_4^{3-} and $MgPO_4^-$ content while decreasing free Mg^{2+} and NH_4^+. This implies that higher rates of the precipitation reactions at higher pH can mainly be explained based on higher amounts of available phosphate precursors. This hypothesis is in line with the findings of Abbona et al. deducted from molecular modeling based on periodic bond chain (PBC) theory [8].

The slow reaction kinetics observed at low supersaturation levels can be disadvantageous in the case of full-scale application specially for big treatment plants with high flows of reject water. Therefore, supersaturation adjustment via pH and precursor concentration is of vital importance for enhanced recovery efficiency. The struvite rectors must be optimized to not only convert the soluble phosphorus to struvite but also to maximize the quality and collection of the product [29]. However, the dissimilarities associated with reactor type (i.e. fluidized bed, air-agitated and stirred) make this optimization challenging. Aeration is mainly practiced for pH increase by CO_2 stripping, while process regulation by aeration adjustment could be challenging due to complex dependency of turbulence on bubble size and reactor dimensions. Further, it has been reported that adjustment of aeration intensity did not improved the struvite recovery and particle settling [30]. In stirred reactors, the mixing improvement enhances the struvite recovery by more homogenous distribution of supersaturation and preventing local peaks in supersaturation, otherwise mixing by itself can not be considered as the main parameter for optimization. Therefore, process optimization requires selection of a proper control parameter. Supersaturation incorporates the impact of essential parameters (constituent ions, pH and temperature) and has the privilege to uncouple the optimization to a great extent from reactor type. Moreover, supersaturation regulation approach can be further utilized for crystal growth and kinetics studies as a well-established theoretical and practical knowledge is available on the supersaturation role in different aspects of crystallization process [10,27,31].

3.2. Product characterization: purity and crystal morphology

In the crystallization systems with sufficient concentrations of Mg^{2+}, NH_4^+ and PO_4^{3-} ions, struvite and various magnesium phosphate minerals can potentially precipitate. However, the final precipitate is the result of both thermodynamic and reactions kinetics. The thermodynamic calculations showed that at the defined experimental conditions, the supersaturated phases were limited to struvite, newberyite ($MgHPO_4{\cdot}3H_2O$) and trimagnesium phosphate ($Mg_3(PO_4)_2$).

The intensity and positions of XRD patterns matched with the reference powder diffraction file for struvite (PDF 00-015-0762) that further confirmed presence of pure struvite under all experimental conditions (Figure S3). Further, based on defined experimental conditions, obtaining pure struvite is in accordance with previous studies. It is reported that nucleation rate of struvite is greater than that of newberyite and newbryite is the stable form at low pH (pH < 6) and high magnesium concentrations [32]. Trimagnesium phosphate has never been observed in the pH range of 6–9.5 and is reported to have low precipitation rate. Therefore, in the pH range of this work, neither newberyite nor trimagnesium phosphate are kinetically favorable phases and struvite precipitation is more abundant [23,32,33].

The morphology (external shape) of a crystalline particle is determined by the intrinsic characteristics of the crystal structure and the external factors of growth conditions such as solution composition and temperature. The final crystal morphology arises as a result of the relative growth rates of each of its faces which are affected by both internal and external elements of growth [24,34]. Fig. 2 shows the wedge shape morphology of struvite crystals with corresponding miller indices for different faces.

The effects of reaction conditions on the final crystal morphology are investigated in detail and Fig. 3 summarizes the different morphologies observed at varying conditions of supersaturation and ammonium concentration. The represented morphologies in Fig. 3 are selected after thorough inspection by SEM in order to report the dominant crystal morphology in each experiment. The observed morphologies are categorized in three groups as polyhedral (well-faceted), hopper and rough (dendritic) morphologies with a possible transition boundary between them.

3.2.1. Effects of supersaturation on struvite morphology

Struvite morphologies observed at low supersaturations (S_a = 1–3) showed a well-faceted structure with a bipyramidal appearance and generally free of major defects (zone 1). The crystals at S_a = 1.5 (Fig. 3a) reflected the most basic morphology of struvite crystal that is hemimorphic with unequally developed [001] and $[00\bar{1}]$ faces. In this zone, increasing the ammonium concentration triggered the growth of [001] face which appeared as a sharp and narrow face on the top of the crystal (Fig. 3b, c and d). It can be seen that in zone 1 increasing pH by one unit caused longitudinal elongation of the crystals (Fig. 3e). Increasing the supersaturation beyond S_a = 3, either by increasing the pH or the concentration of constituent ions, initiated the transition between zone 1 with well-faceted crystals and zone 2 with hopper crystals. The crystals observed in zone 2 seemed to be twin crystals with the

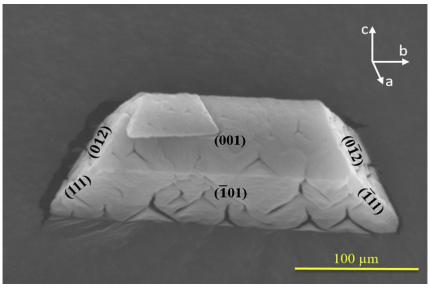


Fig. 2. The wedge shape morphology of struvite crystals. The facets are defined with corresponding Miller indices.

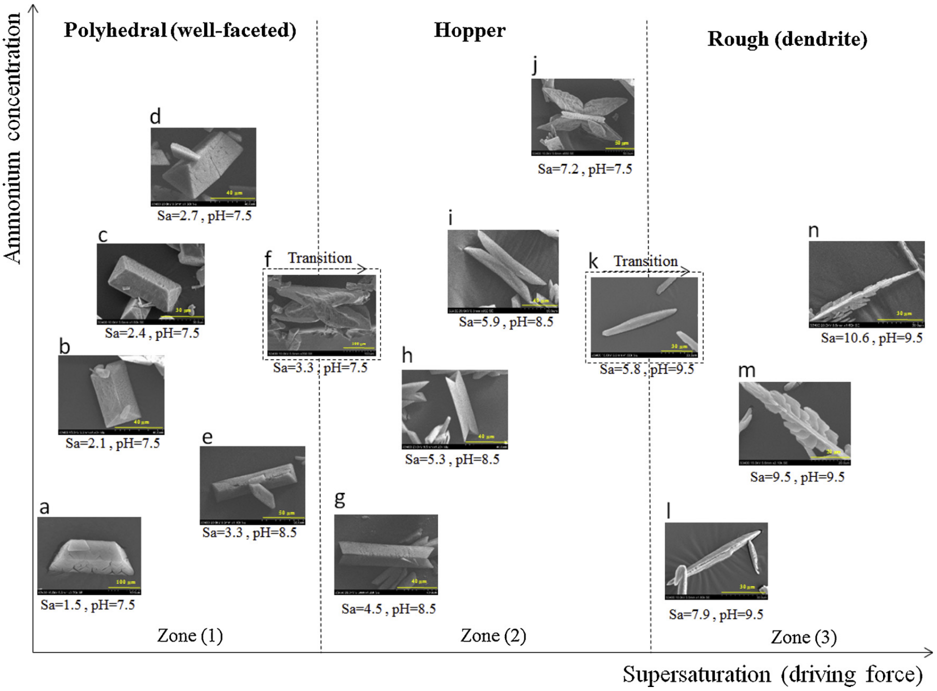


Fig. 3. Crossover of the struvite morphology versus activity based supersaturation and ammonium concentration (note that the placement of f and k do not follow the placement with respect to axes).

X-shape morphology. It was noticed that as the supersaturation was increased, the area of the [012] planes became smaller and it eventually disappeared at higher supersaturation. The further increase of supersaturation resulted in the formation of needle-like and dendritic crystals with high aspect ratios as shown in zone 3. It was observed that higher levels of supersaturation attained by increasing the ammonium concentration within zone 3 amplified the branching of struvite crystals and shifted the needle-like morphology to a dendrite. (Fig. 3m, n).

The transition exhibited by the crystals from polyhedral to dendritic morphologies was induced by changing growth mechanisms as a result of the increasing supersaturation. Under low to moderate supersaturation levels growth is surface reaction controlled and monocrystalline particles with polyhedral morphologies are the expected outcomes of the advancement of smooth faces along the crystal lattice. With increasing driving force, surface roughness increases due to extensive surface nucleation and stimulates a change in the growth mechanism from reaction-controlled to diffusion-controlled growth. The diffusion field around crystals becomes prominent on their development under these conditions and concentration gradients along the diffusion field induce morphological instabilities at the crystal interface. Depending on the diffusion field, certain edges and corners of crystals can have access to higher supersaturation and consumption of supersaturation by growth of these locations prevents growth of the central part, which results in hopper crystals (Fig. 4a) [31]. Further elevation of the characteristics observed in hopper crystals results in a more efficacious advancement in the direction of high supersaturation along the same lattice and give rise to dendritic growth. The X-shape morphology can be considered as an intermediate stage of evolution between the well-faceted and dendrite crystals or as an implicit boundary between slow and rapid growth (Fig. 3) [35,36].

Previous studies also showed that the internal structure of struvite induces surfaces with higher potential and probability of growth in certain directions, which will regulate the final morphology of struvite crystals [8]. However, the complex morphology of X-shape crystals has been explained by some researchers to be formed by self-assembly and fusion of independent crystals [37–39]. In order to investigate this hypothesis, crystallization reactions with different initial supersaturation values were terminated at varying time intervals and precipitates were examined by SEM (Fig. 4). Our results did not show any supporting evidence for mesocrystal formation, which proposes that a composite structure forms via oriented aggregation of small particles [36]. Instead, we suggest these complex morphologies are mainly surface patterns that reflect different shapes due to different growth rates of struvite faces. However, further interpretations cannot be made within the scope of this work and detailed investigations would be necessary to determine the underlying formation mechanism of these morphologies.

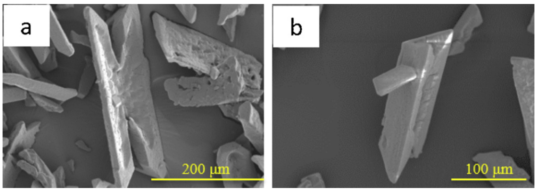


Fig. 4. The X-shape morphology of struvite crystals from a) bottom and b) side views.

From practical point of view, the regulation of supersaturation is achievable by adjustment of the nutrient rich flows, chemical dosing and pH. Although, the accurate measurement of supersaturation in full-scale applications is quiet challenging since the real wastewater is a complex matrix of organic and inorganic materials [40]. The crystal morphology yet can be determined by simple microscopy or an image analysis technique, which further can be used as an auxiliary indicator for approximation of the supersaturation extent (Fig. 3).

3.2.2. Effects of Mg^{2+} and NH_4^+ concentration

The effect of Mg^{2+} on struvite morphology was mainly observed as a regulator of supersaturation and reaction kinetics. The reflection of higher Mg^{2+} concentration on the morphology of crystal is observed in the development of $[00\bar{1}]$ face. The higher Mg^{2+} concentration slightly increased the longitudinal elongation of crystals along b-axis (Fig. 3c, 3d and 3h, 3i). This is in line with the molecular modeling and previous observations in other studies [36,37].

The ammonium concentration influences the lateral growth and thickness of struvite crystals (Fig. 3a, c and c, d). This deduction is based on several experiments in addition to presented experiments in this paper and it will be discussed in more detail. Struvite crystals consist of tetrahedral PO_4^{3-} and NH_4^+, and $Mg[H_2O]_6^{2+}$ species. In all observed morphologies the $[00\bar{1}]$ face is larger than [001] face and NH_4^+ concentration is efficient in shaping the outcrop of [00i] surfaces (i = 1–4) (Fig. 3). For moderately low values of pH (about 7.5) and low concentrations of NH_4^+, the [001] face appears as a flat trapezoidal surface which is elongated more along b-axis (Fig. 2). Higher concentrations of NH_4^+ produced a sharp outcrop for this face and it triggered the growth of [00i] (i = 1–4) faces. At medium pH = 8.5 the lower concentration of NH_4^+ hindered the formation of a smooth finished surface at [001] face and at high pH = 9.5 it can be seen that the higher concentrations of NH_4^+ induced the dendritic structure of the crystals which has started on the top face of [001] (Fig. 3). However, lower concentrations of NH_4^+ resulted in smoother top surface and less branching of crystals.

It has previously been reported that the [001] surface has the higher density of electropositive groups (NH_4^+) or in other words the NH_4^+ groups terminate the [001] surface [41]. PO_4^{3-} and $Mg[H_2O]_6^{2+}$ groups terminate the $[00\bar{1}]$ surface that makes the c-axis a dipole axis [36,41]. Thus, increasing the content of NH_4^+ affects the distribution of supersaturation around the growing crystal. The NH_4^+ groups on [001] faces are likely to be more polarized than the PO_4^{3-} and $Mg[H_2O]_6^{2+}$ groups on $[00\bar{1}]$ face [41]. The NH_4^+ groups can induce growth along the c-axis and outcrop on [00i] surface (i = 1–4) that results in such structures. The XRD results (Figure S3) further showed that the expression of observed peaks for [002] (2θ = 15.78) and [004] (2θ = 31.88) were higher in the case of higher NH_4^+ concentration.

3.3. Product properties

3.3.1. Size distribution

The final particle size, purity and crystal morphology are the key factors to the phosphorus recovery efficiency [42]. The desired size of struvite particles mostly depends on its final use. Smaller particles have higher release rate of nutrients because of their high surface area/volume ratio [43,44]. However, in the nutrient recovery by struvite crystallization, uniform distribution of big particles with minimum contribution of fine particles is favorable. Bigger particles settle faster and bring less challenge in post-handling like drying and filtration, while the fine particles increase the chance of wash out from the reactor, especially in fluidized bed reactors (FBR) [29,45].

Fig. 5 presents the nominal size distribution graphs for struvite particles precipitated at different conditions. As a general trend, the particle size decreased with increasing initial supersaturation and a more homogenous size distribution was obtained for the particles crystallized at lower supersaturations. The particle sizes were in the range of 70–90 μm in zone 1, 40–60 μm in zone 2 and 20–50 μm in zone 3.

The share of fine particles (smaller than 10 μm) in final products were also calculated at each experimental condition and given in Fig. 6. Results show that the share of fine particles increased with increasing supersaturation via both pH and ion concentrations. Experiments conducted at pH = 7.5 had no share of fine particles except for the lowest supersaturation condition at the case of Mg:N:P = 1:2:1. As shown in Fig. 1, 60 min reaction time was not enough for complete growth of crystals at that supersaturation (S_a = 1.5) which resulted in fine particle formation in this case.

Supersaturation is the main driving force for the crystallization process and highly influences particle size and size distribution due to its strong effect on the nucleation rate. Smaller particles observed with increasing initial supersaturation results from boosted nucleation rates that produces higher number of particles, which then consume the remaining supersaturation by crystal growth [10]. Similarly, the increasing share of fine particles detected at pH = 8.5 and pH = 9.5 is associated with high initial supersaturation which implies high nucleation rate [46]. Thus, lower initial supersaturation levels that result in large size crystals with a lower content of fine particles can be considered for process optimization.

3.3.2. Settleability

Crystal size and shape affect the efficiency of downstream processes like settleability, filtering and drying, so it is important to be able to tailor process conditions for optimization of these properties. Improving crystal settleability by optimization of reaction parameters to minimize loss of crystals due to wash out will enhance phosphorus recovery efficiency and ensure the quality of effluent [47].

There are different factors that affect the settling velocity of a particle like size, shape and density [48]. The settleability test was performed on the varying morphologies of struvite particles that were obtained at different reaction conditions. Sieving was used in order to investigate the effects of size and morphology separately on the settling velocity of struvite particles. Fig. 7 shows the results of statistical analysis for these measurements.

Results showed the strong dependency of the settling velocity on both size and morphology of the precipitates. The bigger crystals settled faster for all morphologies. Among different morphologies, the bipyramidal crystals had the highest settling velocity for all crystal sizes followed by X-shape crystals and the lowest settling velocity was observed for the dendritic (needle-shape) crystals. The difference of the settling velocities can be explained based on difference in mass and packing density of the particles [49]. Further, the needle-shaped crystals with high aspect ratio do not favor proper settling due to the higher drag force they experience, which might cause difficulties during settling and filtration [50].

These results reveal that for a more efficient solid-liquid separation and better settling properties, the struvite particles crystallized under low to moderate supersaturation conditions can be advantageous.

3.3.3. Aggregation

During crystallization, particles may grow as single particles or in aggregates. The aggregation of struvite crystals is favorable for wastewater applications since bigger aggregates settle faster and mediate the granulation in the reactor. It is reported that the higher structural strength of struvite pellets can be achieved by aggregation of fine struvite crystals [51].

The aggregation process affects the final particle size and it requires collision of particles and a sufficient period that particles stay together [52]. Previous research has shown that supersaturation affects the aggregation of struvite particles by influencing the adherence of particles and increasing the pH of the precipitation reaction leads to the production of particles with weak aggregation and settling properties [16,53]. In our study, we also observed that both pH and supersaturation are important parameters for aggregation of struvite particles. Fig. 8 shows SEM images of struvite crystal with stronger aggregation at low values of initial supersaturation and reaction pH (a, b and c), and their transition to weak aggregates and to single crystals (d, e and f) with increasing values of these parameters. In general, results

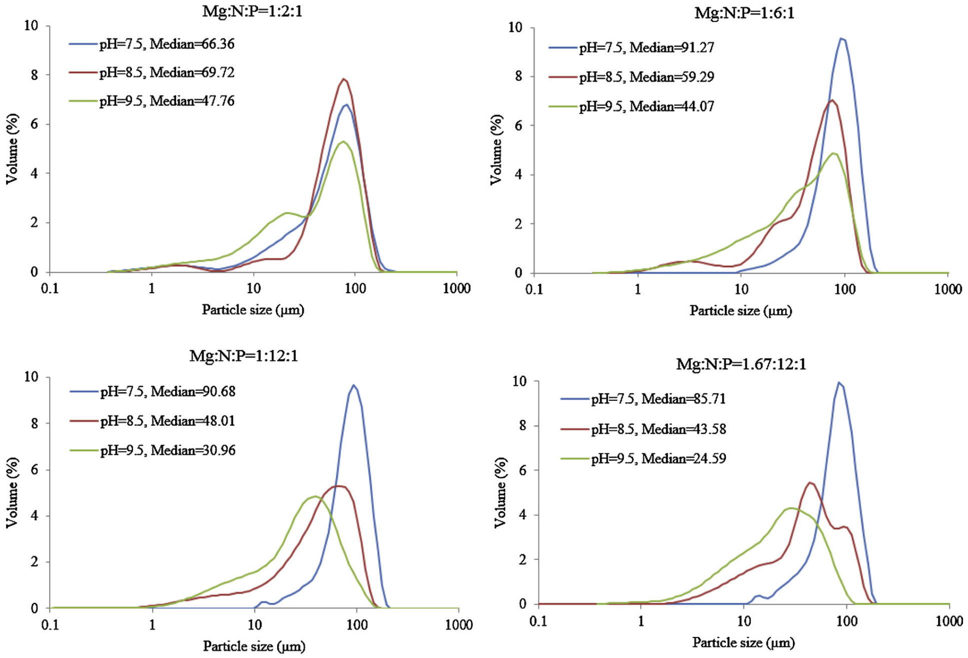


Fig. 5. Particle size distribution for struvite particles precipitated at different conditions.

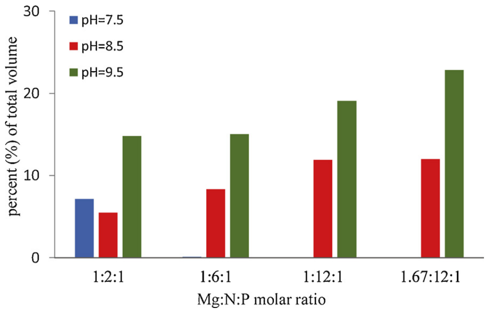


Fig. 6. The share of fine particles (< 10 μm) by volume percent in the final products precipitated at different experimental conditions.

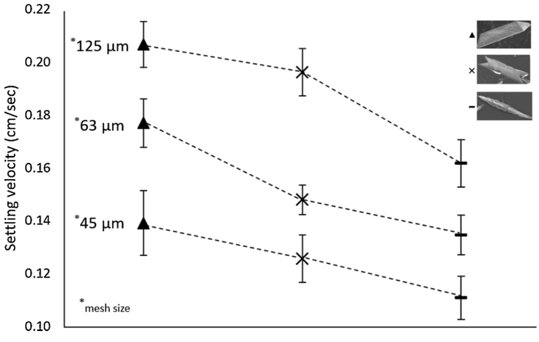


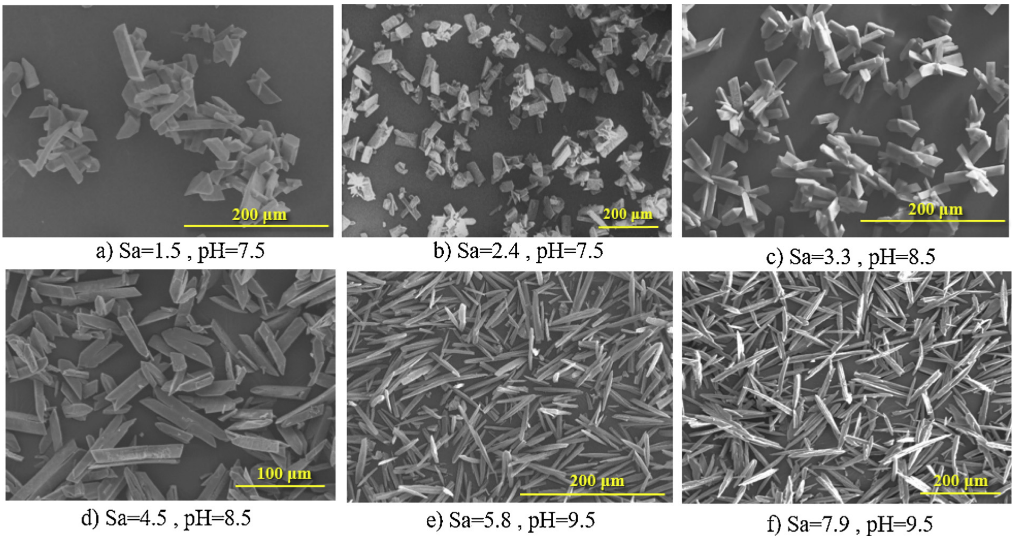
Fig. 7. The settling velocity of struvite particles with different size and morphologies (bars show standard deviations).

showed that struvite particles crystallized under conditions corresponding to zone 1 (Fig. 3) displayed better aggregation properties.

The measured zeta potentials for crystals at Mg:N:P = 1:12:1 and in different pH levels (ζ = -7.51 mV at pH = 7.5, ζ = -9.30 mV at pH = 8.5 and ζ = -17.06 mV at pH = 9.5) confirmed that struvite particles have higher negative zeta potential at higher pH values. It is known that the aggregation of particles is mainly governed by surface charge and struvite crystals showed higher negative surface charge at higher pH values, which disrupts the aggregation potential and settleability due to increased repulsive forces [18,54,55]. Therefore, crystallization reactions held at low pH can mediate stronger charge induced aggregates of struvite crystals termed as micro flocs that can initiate the formation of compact aggregates by adsorption and bridging in the case of sufficient supersaturation. The aggregation of micro flocs is an important step that affects the efficiency of solid/liquid separation [56]. As shown in Fig. 8e and f, when pH was increased to 9.5, no aggregation was observed due to the high negative zeta potential of crystals precipitated under this pH value.

Our results also showed the influence of initial supersaturation on the aggregative properties along with the reaction pH. The comparison of Fig. 8c and d (corresponding to Fig. 3e and g, respectively) showed better aggregated struvite crystals in the zone 1. Aggregation rate shows a linear relationship with crystal growth rate and scales with supersaturation [57]. Thus, maintaining sufficiently high levels of supersaturation during growth of particles can enhance their aggregation. Zone 1 lies low in the supersaturation scale of our experiments; however, in this work only the initial values of supersaturation are determined. High initial supersaturation induces high nucleation rates and generation of higher numbers of particles, which triggers faster consumption of supersaturation during growth regime. On the contrary, the low initial supersaturation in zone 1 implies maintaining of supersaturation for longer time during growth; hence, particle aggregation is improved.

The aggregation of struvite particles has practical implications since it favors the round granular shape of struvite. The granular struvite



a) Sa=1.5 , pH=7.5   b) Sa=2.4 , pH=7.5   c) Sa=3.3 , pH=8.5

d) Sa=4.5 , pH=8.5   e) Sa=5.8 , pH=9.5   f) Sa=7.9 , pH=9.5

Fig. 8. a, b and c) stronger aggregation of struvite crystal at low supersaturation, d, e and f) weak aggregates of struvite crystals and single crystals at higher supersaturation.

particles are preferable for ease of transportation and its applicability to the farmers' spreading equipment [58]. It was also reported that X-shape struvite crystals do not favor the production of struvite granules, which is undesired for agriculture purposes [59].

The results of this study show that struvite crystals precipitated at different reaction conditions have different aggregation properties. The electric charge of crystals plays an important role in granulation and particle-particle interactions, and solution pH is shown to be an effective parameter for its control [15]. Solution supersaturation is another important factor, where continuous measurement can impose some practical difficulties for full-scale applications; however, adjustment of initial values can be utilized for successful granulation.

4. Conclusion

Variational digester supernatant composition and operating conditions in wastewater treatment plants requires adjustment of operating parameters to ensure high P-recovery efficiency and product quality. This study presents how different concentrations of struvite constituents (Mg^{2+}, NH_4^+) and pH affect phosphorus recovery along with crystal size and morphology, and settling and aggregation properties of the final products.

It is concluded that an integrated optimization of both recovery efficiency and product properties (size, aggregation and settling) is necessary to achieve a well-controlled struvite crystallization. The supersaturation regulation is an effective approach to define the operational window for this integrated optimization. The proper control of supersaturation through controlling the pH and ion concentrations in the reaction medium demonstrated the combined effects of operating conditions and feed composition on the final properties of the struvite crystals. The operational conditions for production of three dominant struvite morphologies are presented and the recovery potential and properties of final crystals are discussed at each experimental condition. In brief, providing the operational condition in a way that it lies in zone 1 (Fig. 3) produced bigger crystalline particles with better settling and aggregation properties than zone 2 (Fig. 3) and the dendritic crystals in zone 3 (Fig. 3) were not favorable in terms of settleability and aggregative properties. Moreover, maintaining the sufficient levels of supersaturation after nucleation showed improved aggregation of struvite crystals. These results revealed that product properties, like crystal size and morphology, can be efficiently controlled by supersaturation. On the other hand, the general trend of phosphorus recovery did not follow the same trend where the efficiency was highest in zone 3 with high supersaturation values.

The overall process efficiency requires maximized phosphorus recovery and favorable product properties. The results of this study show that the supersaturation regulation is an effective strategy to optimize the recovery efficiency and to consistently attain the desired struvite properties.

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Notes

The authors declare no competing financial interest.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jece.2019.102918.

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Supplementary data (Paper III)

Table S1: Equilibria for speciation of struvite ion constituents at 25 °C , ref: [60]

Equilibrium	log K
$H^+ + PO_4^{3-} \rightleftharpoons H\,PO_4^{2-}$	12.375
$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$	7.198
$H^+ + H_2PO_4^{2-} \rightleftharpoons H_3PO_4$	2.148
$Mg^{2+} + OH^- \rightleftharpoons MgOH^+$	2.6
$NH_3 + H^+ \rightleftharpoons NH_4^+$	9.244

Figure S1: the theoretical struvite yield calculated based on thermodynamic equilibrium at different molar ratios and pH

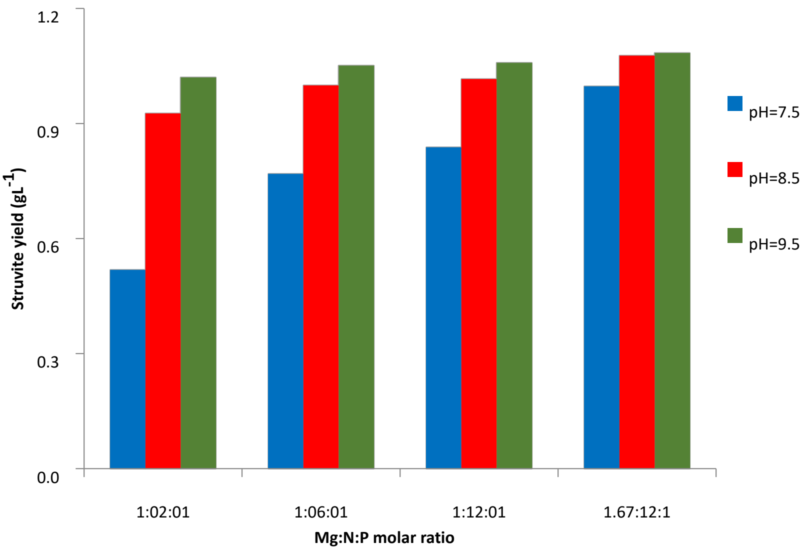
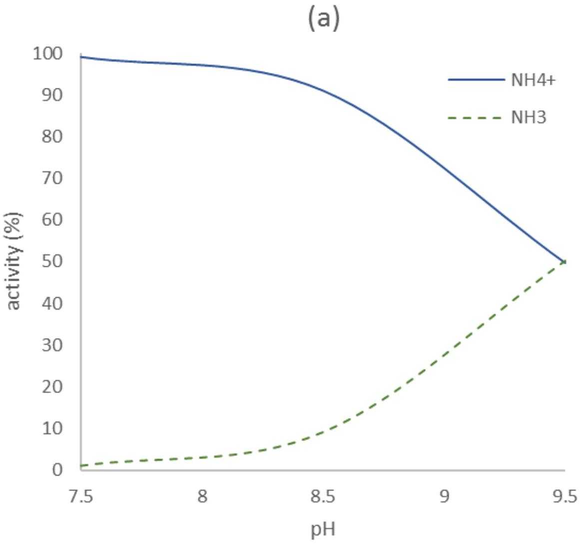
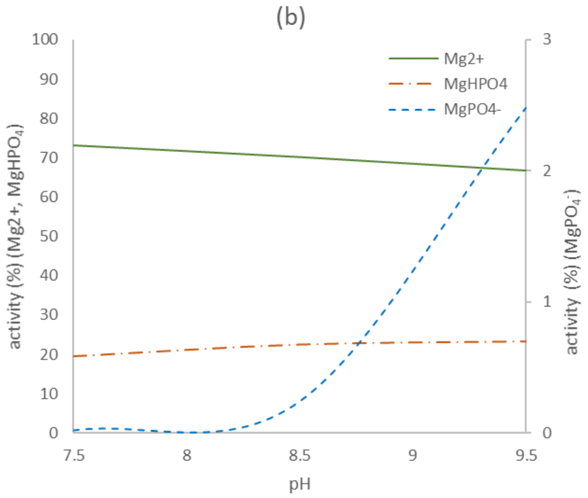


Figure S2: percentage distribution of selected ion and complex speciation for the struvite at different pH levels


(a)
100
90
80
70
60
50
40
30
20
10
0
activity (%)
NH4+
NH3
7.5
8
8.5
9
9.5
pH


(b)
100
90
80
70
60
50
40
30
20
10
0
activity (%) (Mg2+, MgHPO$_4$)
3
2
1
0
activity (%) (MgPO$_4^-$)
Mg2+
MgHPO4
MgPO4-
7.5
8
8.5
9
9.5
pH

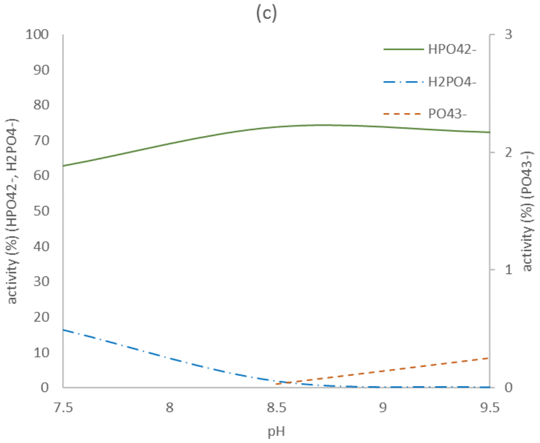
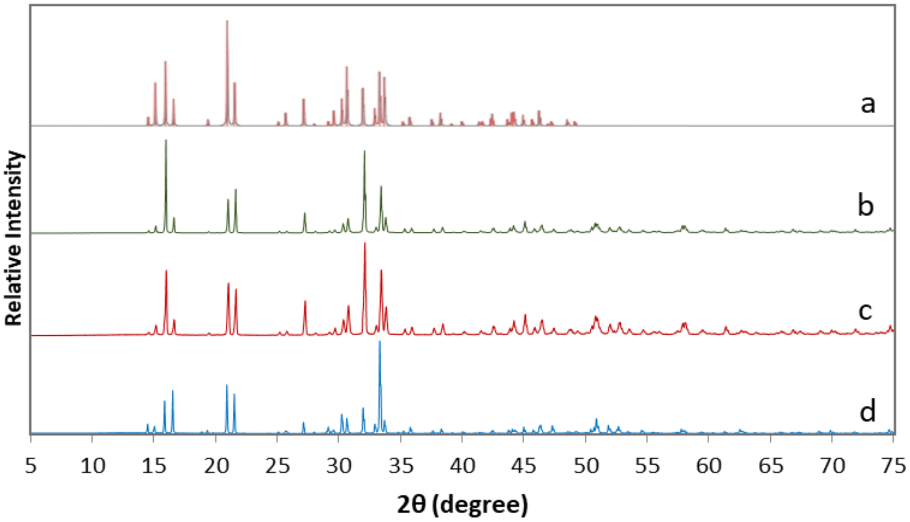
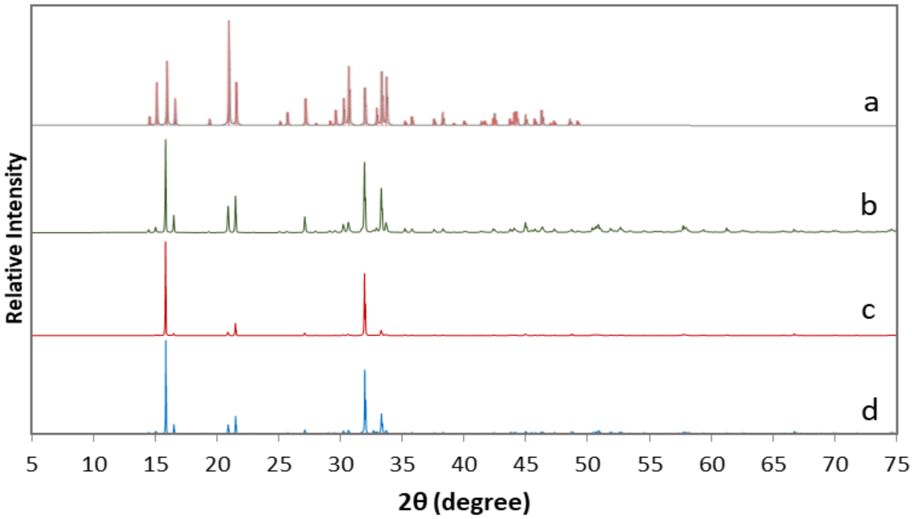


Figure S3: XRD patterns for precipitated struvite under different experimental conditions

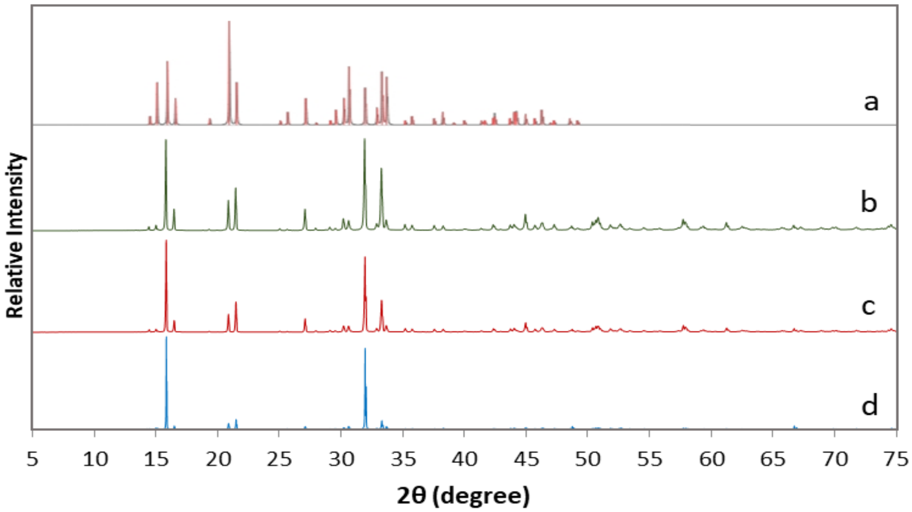


a) Reference struvite (PDF-00-015-0762) , b) Exp. #3 (Sa=5.8, Fig. 3k)

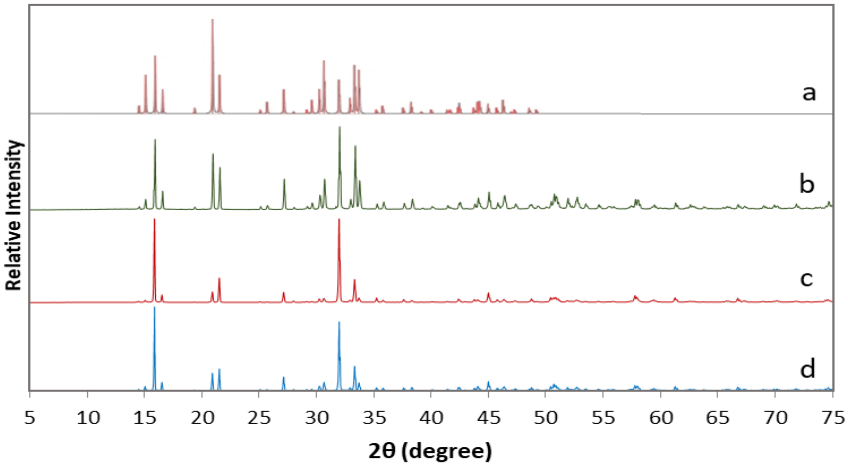
c) Exp. #2 (Sa=3.3, Fig. 3f) and d) Exp. #1 (Sa=1.5, Fig. 3a)



a) Reference struvite (PDF-00-015-0762) , b) Exp. #6 (Sa=7.9, Fig. 3i)
c) Exp. #5 (Sa=4.5, Fig. 3g) and d) Exp. #4 (Sa=2.1, Fig. 3b)

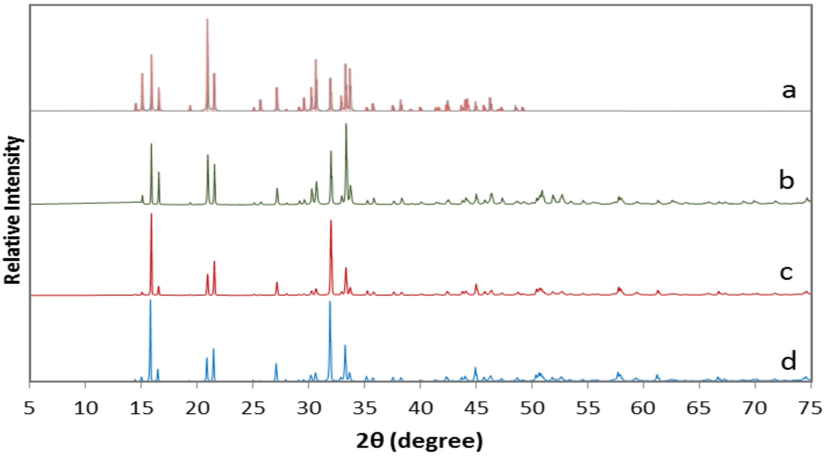


a) Reference struvite (PDF-00-015-0762), b) Exp. #9 (Sa=9.5, Fig. 3k) ,
c) Exp. #8 (Sa=5.3, Fig. 3h) and d) Exp. #7 (Sa=2.4, Fig. 3c)



a) Reference struvite (PDF-00-015-0762) , b) Exp. #12 (Sa=10.6, Fig. 3n)

c) Exp. #11 (Sa=5.9, Fig. 3i) and d) Exp. #10 (Sa=2.7, Fig. 3d)



a) Reference struvite (PDF-00-015-0762) , b) analytical grade struvite (>98%)

c) Sa=7.2 (Fig. 3j), d) Sa=3.3 (Fig. 3f)

Paper 4

Water Research 173 (2020) 115572

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Struvite crystallization by using raw seawater: Improving economics and environmental footprint while maintaining phosphorus recovery and product quality

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ABSTRACT

Seawater, as an alternative magnesium source, has the potential to improve the overall economics and environmental footprint of struvite production compared to the use of pure magnesium salts. However, the dilution effect and the presence of other ions in seawater can reduce the phosphorus recovery potential and the simultaneous precipitation of other compounds may reduce the quality of the produced struvite. This work presents a comparative study of seawater and $MgCl_2$ by performing a series of thermodynamic equilibrium modeling and crystallization experiments. The results revealed that acceptable phosphorus recovery (80–90%) is achievable by using seawater as the magnesium source for struvite precipitation. Further, the simultaneous precipitation of calcium phosphates was successfully controlled and minimized by optimum selection of reaction pH and seawater volume (i.e. Mg:P and Mg:Ca molar ratios). The increase of temperature from 20 °C to 30 °C reduced the phosphorus recovery by 15–20% while it increased the particle size by 30–35%. The presence of suspended solids in reject water did not have significant effects on phosphorus recovery but it made the struvite separation difficult as the obtained struvite was mixed with suspended solids. The experimental results and economic evaluation showed that the use of seawater can reduce the chemical costs (30–50%) and the CO_2-footprint (8–40%) of struvite production. It was concluded that seawater is a potential alternative to pure magnesium sources in struvite production, while studies in larger scale and continuous mode are needed for further verification before full-scale applications.

1. Introduction

The transition towards modern generations of wastewater treatment is being shaped by several developments that aim at improving effluent quality, cutting greenhouse gas emissions and recovering energy and valuable resources. Recovery of phosphorus, among all available resources, is a prominent action as phosphorus (P) is a vital nutrient for all forms of life, while it is expected that the quality and quantity of the main source for phosphorus (i.e. mineral rocks) will be reduced in coming decades (Cordell et al., 2011). Regardless of an exact timetable of global phosphate rocks depletion, phosphorus is a limited and irreplaceable resource. Therefore, the recovery of phosphorus from waste streams can be a promising approach to reduce the conventional mining and moderate the expected future shortage of phosphate (Shaddel et al., 2019b).

Among phosphorus compounds, struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$) has the advantages of being composed of primary (nitrogen and phosphorus) and secondary (magnesium) macronutrients and being a slow-release fertilizer that can potentially be used directly as precipitated. Therefore, struvite has been considered as an advantageous option to recover phosphorus from wastewater. The source of constituent ions in full-scale struvite production is mainly the dewatering reject of anaerobically digested sludge (NH_4^+ and PO_4^{3-}) with addition of an adequate amount of magnesium. However, the use of

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pure magnesium sources such as magnesium salts (i.e. $MgCl_2$ and $MgSO_4$) may stress the total sustainability and economic feasibility of the process (Shaddel et al., 2019a). The cost of struvite production is mainly influenced by chemical costs, especially that of the magnesium which can contribute up to 75% of overall costs (Hövelmann and Putnis, 2016). Therefore, a critical challenge for a sustainable phosphorus cycle is to improve the economics of struvite crystallization by using low-cost magnesium sources while ensuring the quality of the final product.

It has been reported that a low-cost magnesium source may reduce the costs by 18−81% (Gunay et al., 2008; Lahav et al., 2013). Some low-cost alternatives to conventional magnesium sources are seawater, seawater concentrate (nanofiltration, reverse osmosis) (Kim et al., 2016; Lahav et al., 2013), bittern (a by-product in salt industry) (Ye et al., 2011) and wood ash (Sakthivel et al., 2012). Bittern may not be available in many areas, whereas wood ash is considerably cheap but the high content of heavy metals makes it an unsafe alternative for struvite production (Sakthivel et al., 2012). Using seawater concentrate minimizes the intake volume but will not change the molar ratio of magnesium with respect to other ions. On the other hand, pretreatment of seawater for removing the interfering ions may not be economic as it introduces additional costs. However, raw seawater (untreated seawater) is an inexhaustible, cost-effective and environmentally friendly alternative. Generally, the availability of an alternative magnesium source in local context improves the economics of struvite production. After sodium, magnesium is the most commonly found cation in seawater ($\approx$1300 mg/L), which makes the application of seawater financially attractive and technically feasible, although it is not advantageous cost-wise for plants located away from the seashore. This is because long distances increase the power cost for seawater pumping as well as investment and maintenance costs.

There are several ions (i.e. sodium, chloride, calcium, and sulfate) that inevitably will be added into the system by using seawater, so simultaneous precipitation of other compounds (i.e. calcium phosphates, calcium carbonate) should be minimized to improve the quality of produced struvite. However, it is expected that adverse effect of some ions such as chloride on biological processes would not be significant. This is because the sidestreams constitutes $\approx$1% of the overall flowrate to the plant, and contribution of salt content from seawater to the main stream is likely to be marginal (Lahav et al., 2013; Matsumiya et al., 2000). Generally, calcium ions compete with magnesium ions for reaction with phosphate species. However, the interfering effect of these ions on struvite precipitation strongly depends on operational conditions. Previous studies have reported examples for both cases where calcium ions interfered with (Jaffer et al., 2002) or did not significantly affect the struvite crystallization (Krähenbühl et al., 2016; Le Corre, 2006). Therefore, further studies are required to define the optimum operational conditions for struvite crystallization by seawater to maximize the quality and quantity of the final product that determine the profitability of a full-scale struvite plant. Most of the reported studies for struvite production by seawater were carried out by using treated seawater for P-recovery from urine (Nur et al., 2018; Quist-Jensen et al., 2016; Rubio-Rincón et al., 2014) and a few studies were carried out by using untreated seawater for struvite production from municipal wastewater (Matsumiya et al., 2000). There are some associated challenges by using seawater for struvite production which should be addressed both theoretically and practically. The low Mg^{2+} concentration in seawater, compared to pure magnesium sources, requires addition of large amounts of seawater for obtaining similar magnesium concentration, which results in dilution and decrease in the concentrations of ammonium and orthophosphates in the reaction medium (i.e. reduction of the struvite precipitation potential). Also, overdosing of seawater beyond the demand for P-recovery can introduce residual magnesium and unwanted ions in the system. However, the dilution effect of seawater has mainly been disregarded in previous studies (Aguado et al., 2019; Wongphudphad and Kemacheevakul, 2019). The liquid from dewatering of anaerobically digested sludge (mesophilic: 30−38 °C) is the main feed for the majority of struvite reactors (Shaddel et al., 2019b). The feed temperature will be different depending on the process at the treatment plant and the seasonal variations of ambient temperature. Temperature is an important parameter for the activity of different ions in the reactor since it affects the solubility of struvite and other phases that can simultaneously precipitate. In addition, precipitation kinetics of different phases can vary with temperature. Despite its importance, the effect of temperature in struvite production by seawater has not been investigated in previous studies. The organic content of the obtained struvite from wastewater is a determining factor in the final application of the product as potential fertilizer. However, there is little information available on organic contamination of the struvite, specifically by using seawater. The environmental impact of any phosphorus recovery technology, in addition to technical feasibility, should be considered. To our knowledge, the life cycle assessment and comparison of using seawater with pure magnesium sources for struvite production has not been reported in the literature.

The potential of seawater for struvite production is demonstrated, although a comprehensive understanding is still necessary for further application. This study aims to systematically evaluate the feasibility of using seawater as a sustainable source of magnesium for struvite production compared to $MgCl_2$. The equilibrium thermodynamic calculations and experimental studies were performed by using synthetic and real reject water after sludge dewatering of municipal wastewater to evaluate the P-recovery potential and the characteristics of the final products such as product purity, particle size and crystal morphology. The chemical costs and LCA analysis are presented for struvite crystallization by both $MgCl_2$ and seawater. The results of this study can be used for the development of struvite production by seawater in industrial-scale. Further, it can be used to maximize the struvite purity and minimize the addition of unwanted ions to the wastewater treatment system.

2. Materials and methods

2.1. Materials

Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), ammonium chloride (NH_4Cl) and sodium hydroxide (NaOH) were used for preparation of synthetic reject water and readjustment of real reject water. All chemical reagents were purchased from Merck with analytical grade, unless stated otherwise. Milli-Q water (18.2 MΩ.cm) was used for all purposes. The seawater was obtained from Trondheim fjord (an inlet of the Norwegian Sea) where it was pumped from a depth of 70 m and 800 m away from land. The seawater was passed through a sand filter of ~70 μm and then kept in the fridge (1−4 °C) prior to further use without any pretreatment. Table 1 presents the properties of seawater.

2.2. Methods

All experiments were carried out using a lab-scale crystallization system, composed of a 1 L glass reactor, stirred with a Teflon two-blade propeller controlled by a mechanical stirrer operated at 200 rpm. Temperature was regulated by a water bath and maintained at 20 ± 0.5 C or 30 ± 0.5 C for different experimental sets.

Table 1
The characteristics of used seawater.

Parameter	Values (SD)	Molar conc. (mM)	Mol./Mol. (**Mg^{2+}**)
pH	7.9 (±0.01)	–	–
Conductivity (mS/cm)	31.6 (±0.3%)	–	–
Alkalinity (mM $CaCO_3$)	1.66 (±1%)	–	–
Na^+ (mgL^{-1})	10,570 (±1.7%)	459.8	8.8
Mg^{2+} (mgL^{-1})	1,276 (±2.6%)	52.5	1
Ca^{2+} (mgL^{-1})	447 (±6.9%)	11.1	0.2
K^+ (mgL^{-1})	393 (±4.5%)	10	0.2
Cl^- (mgL^{-1})	19,325 (±6.4%)	545	10.4
SO_4^{2-} (mgL^{-1})	2,740 (±1.5%)	28.5	0.5
NO_3^-(mgL^{-1})	160 (±4%)	2.58	0.05
Br^- (mgL^{-1})	67 (±0.3%)	0.83	0.02
F^- (mgL^{-1})	1.3 (±0.3%)	0.06	–

The pH was constantly measured and recorded by a combined glass electrode with KCl reference electrolyte connected to EasyDirect™ pH Software (Metrohm), and calibrations were carried out daily. Nitrogen atmosphere was constantly preserved on top of the solutions throughout the crystallization reactions to prevent intrusion of atmospheric carbon dioxide. An ion exchange chromatograph (940 Professional IC Vario, Metrohm) with an autosampler (813 compact) was used for characterization of seawater, wastewater and the composition of completely dissolved precipitates. The phosphate ion concentrations were determined by spectrophotometry (Hach DR Lange, 1900). The chemical speciation and activity-based supersaturation were determined by the thermodynamic calculation program Visual MINTEQ 3.1. The activity-based supersaturation, S_a, was calculated for each experiment by using equation (1):

$$S_a = \left(\frac{IAP}{K_{sp}}\right)^{\left(\frac{1}{3}\right)} \tag{1}$$

IAP = ion activity product = $a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}$
K_{sp} = solubility product of struvite

The theoretical and experimental results of percent phosphorus recovery were calculated by using Eq. (2):

$$P - recovery\% = \left(\frac{P_{initial} - P_{final}}{P_{initial}}\right) \times 100\% \tag{2}$$

The precipitates were collected at the end of each experiment by vacuum filtration through a 0.2 µm pore size filter (Polypropylene membrane). Solid phases were air dried at room temperature (≈20 °C) and characterized by powder X-ray diffraction (XRD) (D8 Advance DaVinci, Bruker AXS GmBH) in the range of 5–75° with a step size of 0.013° and a step time of 0.67 s. The analysis of XRD data was performed by DIFFRAC.SUITE EVA software (Bruker) and the International Centre for Diffraction Data database (ICDD PDF-4+ 2018) was used to characterize the precipitates. SEM analyses (Hitachi S–3400N) were performed where samples were placed on SEM stub using carbon tape and sputter coated with gold. The particle size distribution was analyzed with a laser diffraction particle size analyzer (Beckman Coulter LS230). The presented particle size distributions are based on volumetric standard distribution by dynamic light scattering technique and derived based on a sphericity. Thus, the presented results are nominal size of crystals for the comparison of the results. Alkalinity of the seawater was measured by titration with HCl (Jenkins et al., 1981). The soluble components were characterized after filtration of sample through 0.45 µm filter (PP membranes). In order to measure the elemental composition of the precipitates, the samples were dissolved in 1 M HNO_3 and the ion concentrations were measured by ion chromatography, 940 Professional IC Vario (Metrohm). The total organic carbon (TOC) content of the samples was determined by dissolving the samples in 21% v/v H_3PO_4 and measuring by Apollo 9000 (Teledyne Tekmar) total organic carbon (TOC) analyzer. Determination of solids including total suspended solids (TSS) and volatile suspended solids (VSS), in wastewater were performed according to Standard Methods 209 (American Public Health, 1960).

2.3. *Preparation of solutions*

The real reject water was obtained from a municipal wastewater treatment plant in the western part of Norway treating wastewater from 300,000 population equivalent (P.E.). The treatment comprises of the drum sieves for primary treatment followed by enhanced biological phosphorus removal in activated sludge mode, with anaerobic digestion for sludge stabilization. The characterization of real reject is presented in Table 2. The target composition of the reject water has total ammonium nitrogen (NH_4–N = 754 mg/L) and total phosphate (PO_4–P = 137 mg/L). Therefore, the final composition of the real reject was adjusted by addition of salts of sodium dihydrogen phosphate dihydrate and ammonium chloride. Synthetic reject water, composed only of ammonium and phosphate at the same concentrations, was prepared from stock solutions based on dissolution of the corresponding crystalline solids ($NaH_2PO_4 \cdot 2H_2O$ and NH_4Cl).

Table 2
The characteristics of the real reject water used for the precipitation experiments.

Parameter	Real reject
Tot-P (mgL^{-1})	148.1
PO_4–P (mgL^{-1})	137.1
NH_4–N (mgL^{-1})	754.3
Na^+ (mgL^{-1})	347
K^+ (mgL^{-1})	34.6
Ca^{2+} (mgL^{-1})	54.5
Mg^{2+} (mgL^{-1})	41.6
Initial pH	6.5
TSS (%)	2.05
VSS (%)	0.62
Total COD (mgL^{-1})	1,838
Soluble COD (mgL^{-1})	468

2.4. Design of experiments

All experiments in this study were performed in duplicate and Table 3 presents an overview of different series of experiments. The reactions were let to proceed for 60 min and the pH was kept constant during experiments by addition of 1 M NaOH. The preliminary experiments were performed for optimization of mixing speed, reaction time and the molar ratio of Mg:P. The Mg:P = 1.67:1 was selected based on a series of preliminary experiments to maximize the P-recovery beyond the stoichiometric ratio with minimum requirement of magnesium addition. The reaction temperatures 20 °C and 30 °C were selected based on the measured temperature at the targeted wastewater treatment plant in cold and warm seasons, respectively.

2.5. Life cycle assessment (LCA)

LCA was used to assess the environmental impact of both struvite production alternatives investigated in this study, namely: 1- using commercial magnesium chloride hexahydrate and 2- using seawater. The LCA was conducted following the ISO standards (International Organization for Standardization ISO, 2000; International Organization for Standardization ISO, 2006) in order to evaluate and quantify the potential CO_2 equivalent emissions (International Organization for Standardization (ISO), 2006; Ryding, 1999). It consisted of four main stages: i) goal and scope definition, ii) inventory analysis, iii) impacts assessment and iv) interpretation of the results (International Organization for Standardization ISO, 2006).

The functional unit used for this evaluation is one kg of produced struvite. The boundaries for both systems include only the direct and indirect emissions associated with operation and necessary chemicals (sodium hydroxide and/or magnesium chloride), transport of those chemicals, the pumping of seawater, and seawater. The process equipment was not included as the differences between both systems are considered negligible and it is reported in the literature that the impact from the system infrastructure is minor compared to the operation (e.g. Lundin et al., 2000; Machado et al., 2007). For this study, the production of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) has been modelled according to Linderholm et al. (2012) (Linderholm et al., 2012). Magnesium chloride salts are produced in Netherlands and transported to Norway by ship, representing a distance of 1000 km. Trucks are assumed to be the means of transport from the supplier to the facility and the distance is assumed to be 200 km. The rest of the inventory data were collected from relevant datasets from the Ecoinvent database and real data obtained from experiments performed in this study and provided in the supplementary documents. LCA was performed using the software SimaPro® 8 (PRé Sustainability, 2014). The equivalent CO_2 (CO_2 eq.) emissions were calculated using the CML2 method.

3. Results and discussion

3.1. Thermodynamic modeling

The thermodynamic modeling was performed to define the supersaturated phases (potential precipitates) and the theoretical P-recovery yields in the planned experiments, which are presented in Table S1 and Fig. S1, respectively. According to thermodynamic calculations when seawater is used as the magnesium source, the reaction solutions become supersaturated with respect to calcium phosphate (CaP) phases along with struvite due to high levels of Ca^{2+} present in seawater (Table S1). However, the final composition of the precipitates is governed by both thermodynamic and kinetic factors, and struvite has faster precipitation kinetics than most CaPs making it the dominant phase also in the presence of calcium (Lahav et al., 2013). P-recovery was therefore calculated solely based on struvite formation and the validity of this assumption was evaluated experimentally.

The general trend in theoretical yield shows that P-recovery increases by increasing Mg:P molar ratio and reaction pH (Fig. S1). This is due to the increasing supersaturation with respect to struvite with higher Mg:P molar ratio and higher reaction pH, which provides a higher driving force for precipitation of struvite that consequently enhances P-recovery (Fig. S2). The thermodynamic modeling shows that ion complexation and ion pairs lower the free concentration of magnesium. Therefore, Mg:P molar ratios higher than stoichiometric ratio in struvite is advantageous to enhance the reaction kinetics and to achieve P-recovery yields higher than 80% at low pH values. The calculations show the P-recovery to be higher than 95% at Mg:P = 1:1 at pH = 9 with $MgCl_2$ and at Mg:P = 1.67:1 at pH = 8 with seawater. Therefore, further increase of Mg:P molar ratio or pH beyond these conditions is theoretically not necessary since it increases the operational costs while improving the P-recovery marginally. However, in order to define the optimum operational conditions, the experimental results and the product properties should also be considered along with equilibrium modeling.

3.2. Crystallization experiments with varying magnesium sources

The thermodynamic equilibrium calculations are useful to define the potential supersaturated phases (solid precipitants). However, this approach does not take into consideration the kinetic differences between potential precipitates. Therefore, a series of crystallization experiments were planned to validate the results against experimental data. Fig. 1 presents the measured P-recovery in crystallization experiments by seawater and $MgCl_2$ by using Eq. (2). The experimental results for P-recovery show the same trend as equilibrium calculations where it increases by increasing the Mg:P molar ratio and reaction pH.

The experimental P-recovery results for seawater in this work were generally lower compared to a pure magnesium source (i.e. $MgCl_2$) which is in line with reported studies (Zhang et al., 2016). Application of seawater as the magnesium source increases the

Table 3
The overview of performed experiments in this study.

Experiment set		Mg:P	pH
$MgCl_2$ vs. seawater		1:1 and 1.67:1	7.5–9.5 (unit step = 0.5)
Dilution effect of seawater		1:1–3:1 (unit step = 0.67)	7.5
Temperature effect		1:1–3:1 (unit step = 0.67)	7.5
Reject type	real/synthetic filtered/unfiltered	1:1–3:1 (unit step = 0.67)	7.5–8.5 (unit step = 0.5)

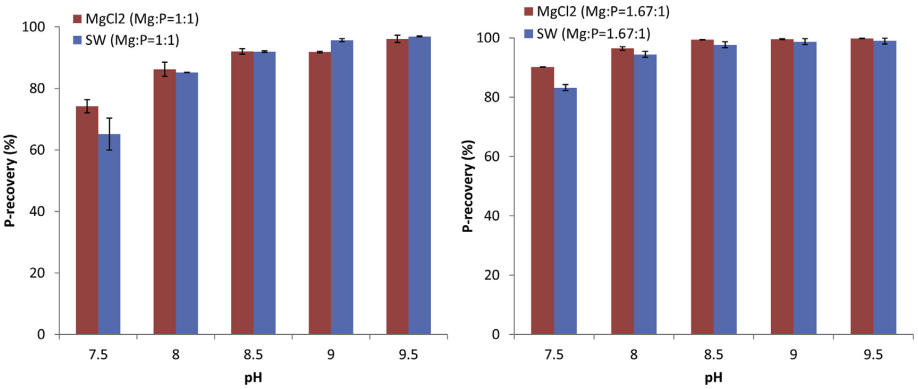

Fig. 1. The measured P-recovery in crystallization experiments by seawater and $MgCl_2$.

ionic strength of solution in the reactor and thus decreases the ionic activity product and supersaturation with respect to struvite. The higher ionic strength affects particularly the activities of multivalent ions such as Mg^{2+} and PO_4^{3-} via formation of ion pairs (e.g. $MgSO_4^0$, $NaPO_4^{2-}$), thus, maintaining higher reaction pH is required to compensate for this effect. However, under current experimental conditions pH values higher than 8.5 are redundant since the improving effect of higher pH values on P-recovery is minimal. The measured P-recovery in the experiments at pH values higher than 8.5 was slightly higher (up to 3%) than the calculated equilibrium P-recovery based on precipitation of struvite. This discrepancy is within the uncertainty range of the measurements and the simultaneous precipitation of other compounds was insignificant.

The consumption of magnesium by struvite precipitation reduces Mg:Ca molar ratio, and the consumption rate of magnesium is even higher at high pH values which lowers both Mg:Ca and Mg:P molar ratios. Therefore, it is important to keep the Mg:Ca molar ratio high enough during the course of precipitation to favor the struvite precipitation and minimize the simultaneous precipitation of calcium phosphates (Le Corre et al., 2005).

3.3. *Dilution effect of seawater*

The dilution effect of seawater on phosphorus recovery efficiency and product properties was studied by addition of varying volumes of seawater in the reaction media, which consequently results in different Mg:P molar ratios (i.e., different dilution factors). The experiments were conducted at pH = 7.5 for both synthetic and real reject water to optimize the Mg:P molar ratio including the dilution effect. This pH value was selected to minimize the costs regarding the use of NaOH since achieving maximum P-recovery at minimum cost was another objective. The initial ionic concentrations at different dilution factors and the P-recovery results are presented in Table S2 and Fig. 2, respectively.

The P-recovery was reduced by 4% and 6%, respectively owing to the dilution effect of seawater at Mg:P = 1:1 and Mg:P = 1.67:1 with respect to the experiments without any dilution. The similar experiments were performed with real reject water to test the efficiency of seawater under real conditions. The real reject contains suspended solids which can affect the struvite precipitation and the purity of final product. Therefore, the unfiltered and filtered real reject (filtered with filter paper, 1.2 μm pore size) were used to investigate the effect of suspended solids (Fig. 2A). It was noticed that the suspended solids had no noticeable effect on P-recovery, but it made the separation of final product difficult, as the final product was a mixture of struvite crystals and suspended solids (Fig. S3). The Mg:P molar ratios of 1.67 and 2.34 were found to be optimal, based on P-recovery, for the current reject composition at pH = 7.5, so the phosphorus recovery at these molar ratios were further investigated for real filtered reject at pH = 8 and 8.5 (Fig. 2B). According to Fig. 2B, Mg:P = 2.34:1 at pH = 8 can be considered as the optimum operational condition since the cost of increasing Mg:P molar ratio by seawater is less than increasing the reaction pH.

3.4. *Effect of temperature*

The reaction temperature determines the solubility products of all potential precipitates as well as their precipitation kinetics, which can affect the recovery efficiency and potentially induce simultaneous precipitation of calcium phosphates with struvite (Hanhoun et al., 2011). Therefore, the effect of temperature on struvite crystallization was investigated by performing the experiments with seawater and synthetic reject water at 20 and 30 °C and the results are presented in Fig. 2C. It was observed that increasing the temperature to 30 °C hindered the struvite nucleation at Mg:P = 1:1 during the 60 min duration of reaction in this study. The increase of reaction temperature increases the solubility product of struvite, which decreases its supersaturation in solution (eq. (1)). At other Mg:P ratios the P-recovery was reduced by 11–28% by the increase of temperature from 20 to 30 °C in accordance with decreasing supersaturation; however, no adverse effects were observed on the product quality. Results showed that higher Mg:P molar ratio can compensate the adverse effect of higher temperature on P-recovery (Fig. 2C).

3.5. *Product properties*

3.5.1. *Product purity*

The purity of struvite precipitated from aqueous solutions containing additional ions (i.e. calcium) is determining in the effective economical implementation of the final product. The presence of pure struvite in all experiments with $MgCl_2$ and seawater was confirmed by XRD (Fig. 3 and Fig. S4). The purity of struvite in the experiments with seawater was attributed to fast precipitation kinetic of struvite compared to calcium phosphate phases, which was facilitated by the presence of ammonium. Additional experiments showed that in the absence of ammonium

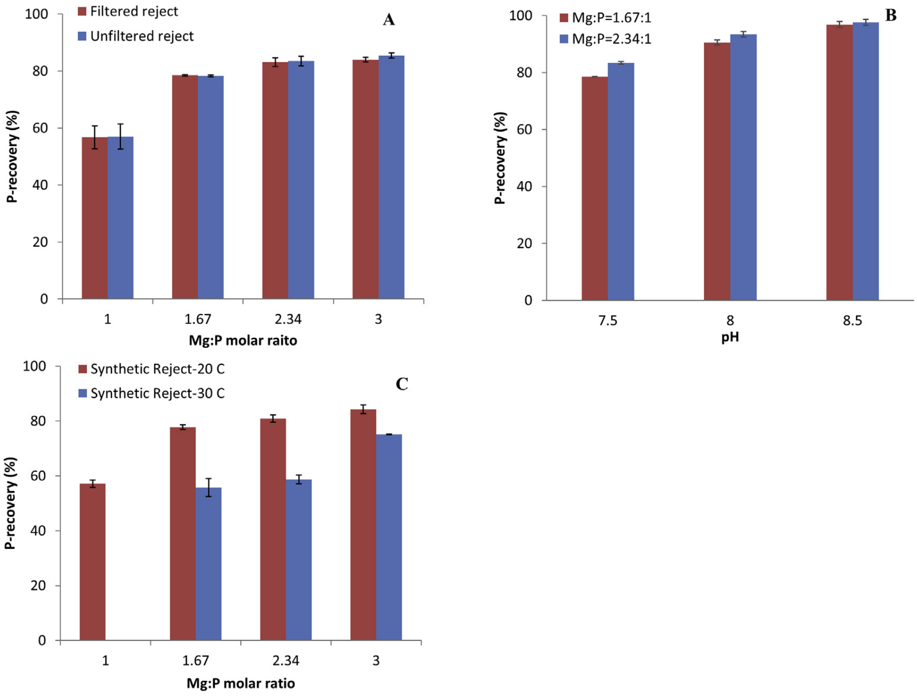

Fig. 2. The P-recovery in the experiments with seawater including dilution effect, A) filtered and unfiltered real reject at pH = 7.5, B) filtered real reject at varying pH values and C) synthetic reject at 20 and 30 °C at pH = 7.5.

the final precipitate phase was mainly amorphous calcium phosphate with traces of magnesium (Fig. S5). However, presence of ammonium even at a low molar ratio of N:P = 1 led to the precipitation of struvite rather than other phases (Fig. S6). The N:P molar ratio should not be the limiting factor in the struvite crystallization with seawater since ammonium concentration is one of the determining factors that can enhance struvite precipitation in the presence of calcium by inhibiting precipitation of calcium-bearing minerals (Aguado et al., 2019; Golubev et al., 1999; Gunnars et al., 2004).

Our review showed that simultaneous precipitation of calcium phosphates by using seawater has been mainly reported in the studies with unfavorable N:P molar ratio (i.e., urine or N:P < 4) (Aguado et al., 2019). An increase of N:P molar ratio increases the buffer capacity of solutions, precipitation kinetics and nucleation rate of struvite which makes it kinetically more favorable with respect to potential calcium phosphates at similar conditions (Crutchik and Garrido, 2011). Enhanced buffer capacity of the solutions results in lowering the required pH for nucleation of struvite, which in turn favors the precipitation of P as struvite and improves the product purity by reducing the share of other compounds (i.e. calcium phosphates) (Capdevielle et al., 2013).

In addition to XRD analysis, complete dissolution of final precipitate obtained by using seawater and real reject water was performed (Fig. 4A). This is because small crystalline size and low crystallinity of simultaneously precipitated phases can prevent their detection by XRD (Crutchik and Garrido, 2011; Le Corre et al., 2005; Lee et al., 2013). Trace amounts of sodium and potassium (<0.1 wt. %) were detected in the dissolved samples precipitated by using real reject water, which is in line with previous studies (Nur et al., 2018). Also, trace amounts of calcium carbonate were identified in the end product of the precipitation reaction conducted with real filtered reject water at Mg:P = 2.34:1 and at pH = 8.5 (Fig. S7). However, the calcium share with respect to struvite constituent ions in the final precipitate was less than 1% in all cases and the simultaneous precipitation of calcium-bearing minerals was shown to be insignificant at all experimental conditions used in this study (Fig. 4A). The results showed that Mg:P molar ratio higher than 1 is beneficial specially at higher pH values to keep Mg:Ca molar ratio high enough during the reaction. The increase of reaction temperature to 30 °C did not show any adverse effects on purity of struvite, although the XRD spectra differed in intensities of some peaks (Fig. S4G).

The total organic carbon (TOC) content of struvite is another important factor that defines the value of the final product as mineral fertilizer or an organo-mineral soil amendment (EU Parliment, 2019). Therefore, the TOC content of struvite obtained from seawater and real reject was analyzed (Fig. 4B). The results showed that increasing the reaction pH slightly increased the TOC of the sample that can be attributed to increasing nucleation and growth rates due to increasing supersaturation with pH. Increasing the crystallization pH increases the number of crystals and the surface area of crystals and the probability of organic compound incorporation in the final product. The higher contamination of final products by organic compounds at higher pH values has also been reported in previous work (Zhou et al., 2015). This contamination has been explained by the coprecipitation of organic compounds or complexation between organic acids and Mg^{2+} or NH_4^+. However, the TOC values in this study should be considered only for comparison purposes and not as absolute TOC of the final product.

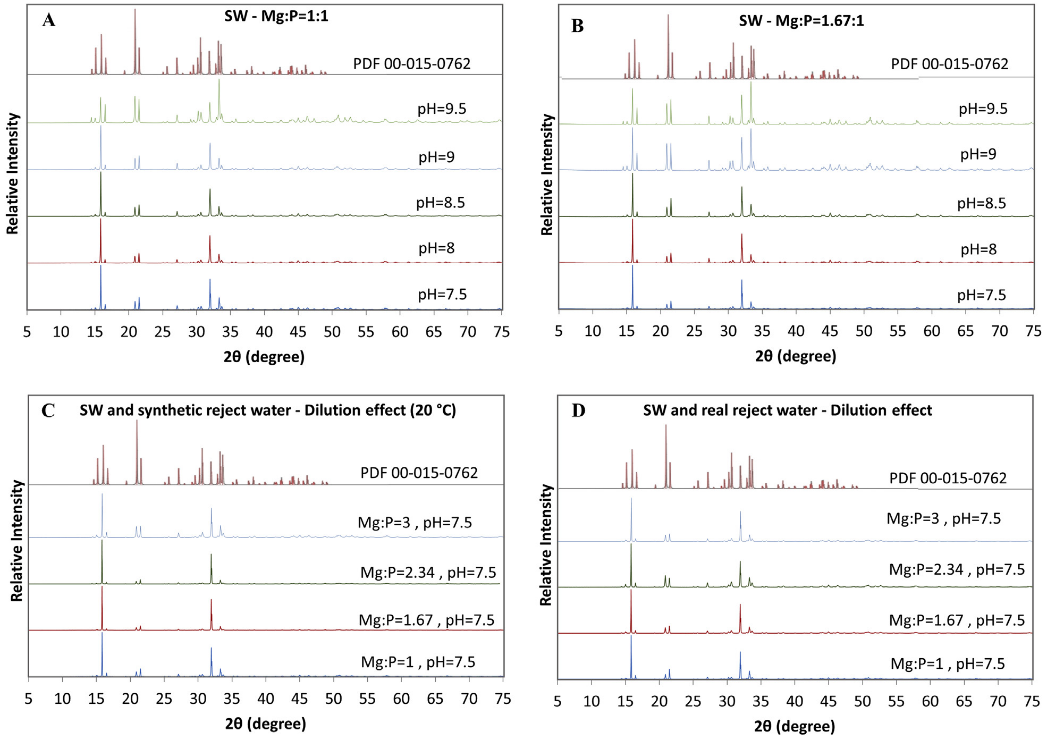

Fig. 3. The XRD spectra of obtained precipitates with seawater from, A) synthetic reject at Mg:P = 1:1 and varying pH, B) synthetic reject at Mg:P = 1.67:1 and varying pH, C) synthetic reject water with dilution effect and D) real reject water with dilution effect.

This is because seeded crystallization and washing of the product in full-scale application will reduce the TOC in the final product.

3.5.2. Crystal morphology

The final precipitates were imaged by scanning electron microscopy (SEM) to investigate the impact of additional ions in the seawater on the struvite morphology (Fig. 5). The obtained struvite crystals by both $MgCl_2$ and seawater had well-faceted bipyramidal shape at low supersaturation values (pH = 7.5). Increasing the supersaturation by increasing the pH produced hopper crystals with X-shape morphology (pH = 8.5) and higher supersaturations (pH = 9.5) produced needle-shape and dendritic shape crystals for both sets of experiments with $MgCl_2$ and seawater. This is due to the dominant impact of supersaturation on morphology development of crystals compared to the effects of additional ions in seawater. The development of struvite crystal morphologies in correlation with supersaturation has been explained in detail in our previous work (Shaddel et al., 2019c).

The initial supersaturation is an important factor also for aggregation of struvite crystals. It can be seen in Fig. 5-Panel A that at pH = 8, the struvite crystals formed with seawater show some degrees of aggregation unlike the crystals with $MgCl_2$. Maintaining sufficiently high levels of supersaturation during growth of particles can enhance their aggregation (Shaddel et al., 2019c). Seawater reduces the initial supersaturation with respect to struvite, which consequently reduces the nucleation rate. Thus, the supersaturation level could be maintained for aggregation of crystals. The increase of temperature from 20 to 30 °C had no significant impact on the morphology of the final struvite crystals (Fig. S8).

3.5.3. Particle size

The size distribution of the final particles of precipitation experiments were measured (Fig. 6) due to importance of the particle size in the design and the operation of struvite crystallizers (i.e. settleability), and post-handling steps (filtration and drying).

The general trend in Fig. 6 shows that smaller particle size is accompanied by higher share of fine particles. This is because the nucleation rate scales with initial supersaturation and higher nucleation rate produces higher numbers of particles (Agrawal et al., 2018). The consumption of the remaining supersaturation for the growth of many particles leads to smaller particle size. However, lower initial supersaturations in the case of using seawater moderates the struvite nucleation rate, which consequently results in larger particles. The similar standard deviation values showed that homogeneity of the produced particles was not affected by seawater (data not shown).

The size of the produced particles by real reject water was significantly smaller than synthetic reject water (Fig. 6C). This could be associated with the presence of suspended solids in the real reject water which can increase the nucleation rate by acting as heterogenous nucleation sites or, with the presence of organic and inorganic impurities in the real reject water that might reduce the particle size by blocking the active growth sites and lowering the crystal growth rate (Koutsopoulos and Dalas, 2000; Van Der

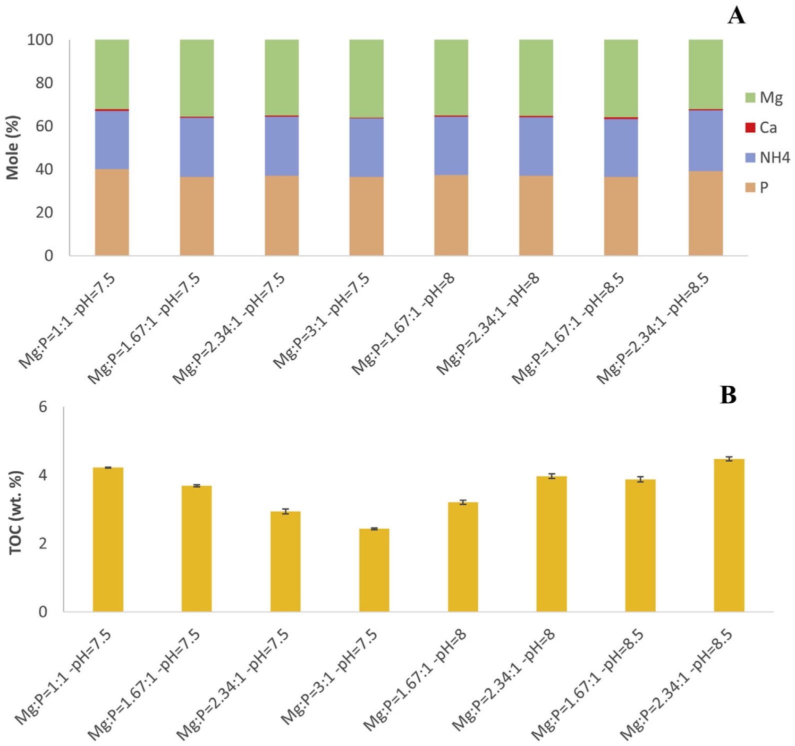

Fig. 4. (A) The measured mole percentage of major ions in final precipitate with real reject water, (B) The TOC content of unwashed product at different experimental conditions.

Houwen and Valsami-Jones, 2001). The size difference between particles precipitated by seawater and $MgCl_2$ is smaller for synthetic reject water, while bigger size difference for real reject water shows the dominant impact of organic and inorganic impurities. The larger particle sizes observed at 30 °C are associated with the effect of temperature on the nucleation and growth stages of crystallization (Fig. 6C). Increasing the temperature reduces the supersaturation and hence lowers the nucleation rate of struvite which results in larger particles as well as increasing the crystal growth rate.

4. Environmental footprint (LCA) and chemical costs

The reduction potential of the environmental footprint by using seawater as an alternative of commercial magnesium chloride has been evaluated using LCA. The data used in this evaluation originate from the laboratory experiments and discrepancy may occur with full-scale systems. The production infrastructures (facility and reactors) are expected to be very similar with the only difference being pumps and pipes necessary for the seawater extraction and transport. Yet, this assessment considers only the operational phase as the contribution of the infrastructure is considered negligible as stated in the literature (e.g. Lundin et al., 2000; Machado et al., 2007). The potential CO_2 eq. emissions associated with each alternative at each pH considered in this study are shown in Fig. 7. The results indicate that the use of seawater instead of synthetic magnesium chloride would allow to reduce the CO_2 eq. emissions in a range of 8–40%.

The results show that pH $\geq$ 9 has adverse effect on CO_2 eq. emissions. For instance, the Mg:P = 1.67:1 at pH = 7.5 and 8 with seawater has the minimum CO_2 eq. emissions while at the same conditions increasing the pH to 9.5 will increase the CO_2 eq. emissions by 67%. Fig. 8A shows, as an example, the contribution of each component used in the molar ratio of Mg:P = 1.67:1 using $MgCl_2$ at pH = 9.5 and Fig. 8B, shows the contribution when seawater is used for the same pH and Mg:P ratio. Similar distribution was observed for the other conditions evaluated in this study. These results indicate that the largest contribution to CO_2 eq. emissions is due to sodium hydroxide which has the highest CO_2 footprint per kg (2.16 kg CO_2 eq./kg NaOH) as it requires large electricity input. Sodium hydroxide is generated by the electrolysis of sodium chloride solution produced by mining salt deposits using high-pressure water to form a brine solution which is then pumped to the production facility (Garcia-Herrero et al., 2017). Traditionally, electrolysis has been carried out by the mercury amalgam or diaphragm cell processes, but the share of ion exchange membrane cell is growing for environmental and economic reasons (Garcia-Herrero et al., 2017). The main production route in the US is via the diaphragm cell while the mercury and membrane cells are more dominant in Europe. Sodium hydroxide used for the comparison presented in this study is modelled using the production mix model (mercury cell: 55.1%, diaphragm cell: 23.5% and membrane cell: 21.4%) available in Ecoinvent database. For the production mix an electricity consumption of 3.356 kWh/kg NaOH is calculated based on electricity input of 3.294 kWh/kg NaOH, 3.920 kWh/kg NaOH and 2.900 kWh/kg NaOH, for mercury cell,

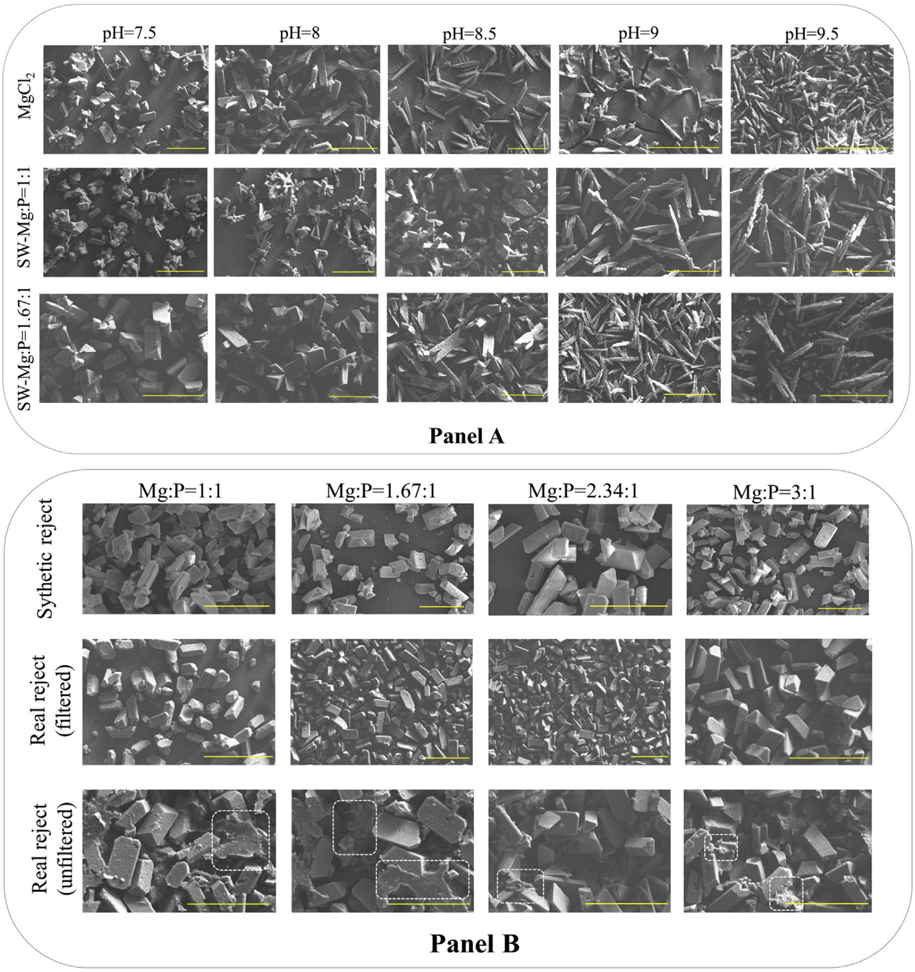

Fig. 5. The SEM image of obtained struvite crystals: Panel A) $MgCl_2$ and seawater with synthetic reject water, Panel B) seawater and real reject water at pH = 7.5 (the yellow scale bar is equivalent to 100 μm, the white rectangle shows the suspended solids in unfiltered reject water in a collected final product). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

diaphragm cell and membrane cell productions, respectively. Consequently, the electricity mix used for the production would have a large impact on the resulting CO_2 footprint and a production powered with renewable electricity should always be favored as well as membrane cell production.

The second largest contributor is the $MgCl_2$ which has a CO_2 footprint of 0.293 kg CO_2 eq./kg $MgCl_2$, while the transport and the electricity are minor contributors. Magnesium chloride used in this study is produced in Netherland with a total required energy of 1835 MJ/ton which is equivalent to 0.513 kWh/kg $MgCl_2$, $6H_2O$. Similarly, to sodium hydroxide, magnesium chloride salts are extracted from depth by applying water under high pressure. Salts are then dissolved to form a concentrated brine (>30% magnesium chloride) which is then pressed upwards. The brine is then purified by a series of processes and then heated to get a saturated solution of 47% magnesium chloride. This hot concentrated liquid is then transported to a water cooled rotating drum, where solid magnesium chloride flakes are formed (Nedmag, 2004).

The outcome of the comparison is very dependent on the input of sodium hydroxide and to smaller extent to magnesium sources. However, these results are very site specific as they depend on the type of production and electricity/energy mix. The reduction of CO_2 emissions implies optimizing the use of chemicals as the conditions requiring lower input of that chemical would have lower CO_2 emissions (Table S3), but also selecting the greenest available chemicals with respect to production and transport. Indeed, the type of technology (e.g. membrane cells for sodium hydroxide production) and renewable electricity/energy should always be favored to reduce the impact of those chemicals as long as the emissions associated with the transport (distance and type) to the struvite production site does not outweigh the benefits.

The chemical costs constitute an important fraction of the

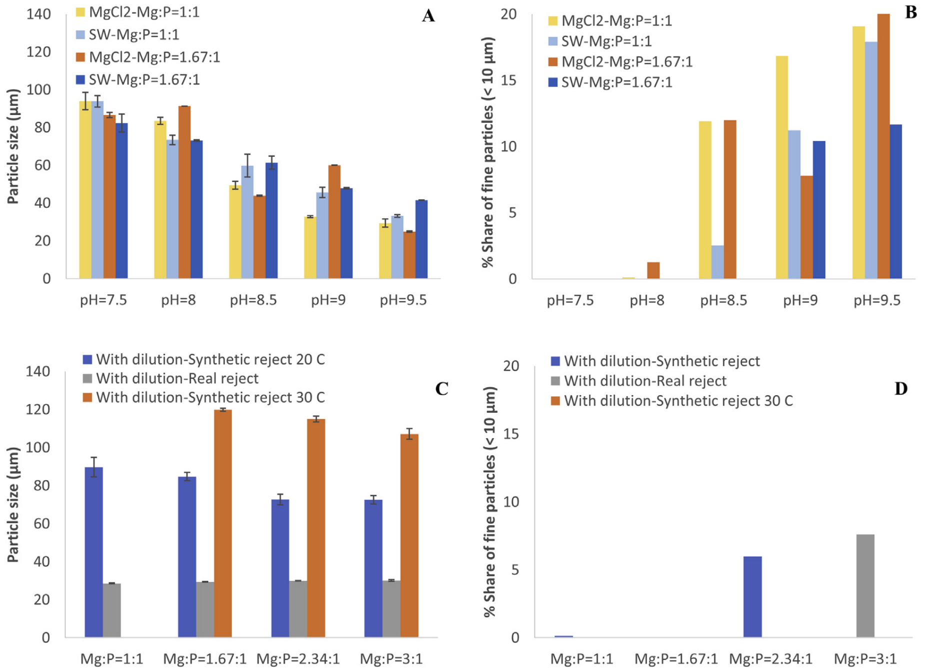

Fig. 6. A) The median particle size for $MgCl_2$ and seawater, B) the share of fine particles, C) the median particle size by seawater including dilution effect (pH = 7.5) and D) the share of fine particles by seawater including dilution effect (pH = 7.5).

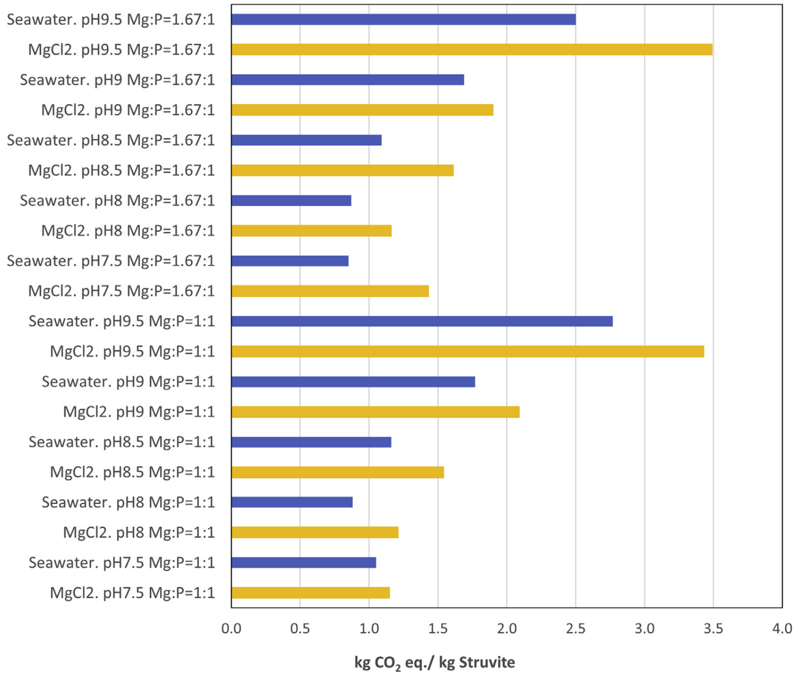

Fig. 7. The comparison of CO_2 eq. emissions determined by the LCA and the methodology CML2.

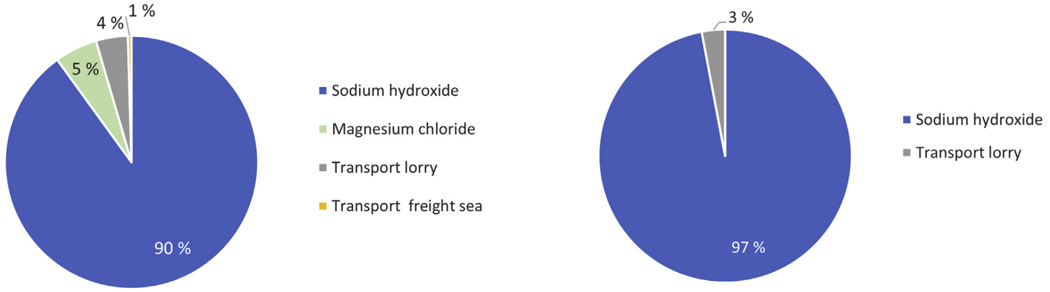

Fig. 8. The contribution of each input to the CO_2 eq. emissions for 1 kg of struvite with following conditions A) using $MgCl_2$, pH = 9.5 and Mg:P = 1.67:1, and B) using seawater, pH = 9.5 and Mg:P = 1.67:1.

operational costs. Magnesium source cost is a major part of the overall struvite production costs (50–70%) which is deterministic on payback time. The chemical cost calculations based on the experimental results in this study were performed for using $MgCl_2$ and seawater as magnesium sources (Fig. S9). The energy cost for pumping is the only associated cost with using seawater as Mg source which has been calculated according to Meneses et al. (2010) (Meneses et al., 2010). The results showed that increasing the pH when magnesium is the limiting factor is not cost-effective owing to low product yield with respect to high chemical consumption (i.e. Mg:P = 1:1 at pH $\geq$ 8.5). Further, the NaOH consumption for initial raise of pH increases exponentially by pH and the pH values higher than 8.5 are not cost effective. This is due to high buffer capacity of phosphate that implies addition of considerably higher amount of NaOH. In the current study the base requirement for adjustment of initial pH to 8.5 and 9.5 were respectively 2.2 and 7.7 times higher than base requirement for pH = 7.5.

Our calculations show that struvite production by seawater has clearly lower chemical costs than using $MgCl_2$ which can reduce the chemical costs by 30–50%. The combination of using seawater and pH values of 8 and 8.5 showed lower costs, and the lowest cost was obtained by using seawater at Mg:P = 1:1 at pH = 8. However, the Mg:Ca is a determining factor for minimum simultaneous precipitation of calcium phosphates, meaning Mg:P = 1.67:1 at pH = 8 can be considered as the optimum operational window in this case. The LCA analysis and calculation of chemical costs are based on lab-scale experimental results in this study and presented for comparison between $MgCl_2$ and seawater, while an inclusive analysis applicable for full-scale requires data of main metrics in relevant scale (i.e. operational and maintenance costs, savings, revenue and period of analysis).

5. Conclusion

The presented study demonstrated both the potential of seawater as an alternative magnesium source for struvite production and the optimization of operational conditions for enhancing phosphorus recovery and product quality. The minimal reduction of phosphorus recovery ($\approx$1–6%) by using seawater compared to $MgCl_2$ indicates seawater can be an adequate magnesium source for struvite production. The Mg:Ca and N:P molar ratios and reaction pH were important factors to control the simultaneous precipitation of calcium phosphates. It was concluded that the simultaneous precipitation of other compounds would not significantly compromise the struvite purity in the final product. The particle size of the final crystals was highly dependent on supersaturation and pH has a prominent impact on supersaturation as the median particle size was reduced by 40–70% at the pH values higher than 8. The presence of soluble organic compounds in the real reject water reduced the median particle size by 50–70%. The presence of suspended solids, in this study, had no notable impact on the phosphorus recovery, but it reduced the final product quality by making it more difficult to separate the final product from the suspended solids. The increase of temperature from 20 °C to 30 °C reduced the phosphorus recovery (11–28%) but produced slightly bigger crystals. The LCA analysis in this study showed that optimization of reaction conditions (Mg:P and pH) is an effective approach to minimize the CO_2 eq. emissions of struvite production. It was shown that using seawater instead of $MgCl_2$ will improve the environmental and financial sustainability of the struvite production process by reducing the CO_2 footprint by 8–40% and the chemical costs by 30–50%. The results show that the concept of using untreated seawater as an alternative magnesium source for struvite precipitation is feasible both technically and economically. Owing to the controlled conditions and the lab-scale experiments in this study, investigation in larger scales is recommended for verification of the results and demonstration of benefits in full-scale application.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.115572.

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Supplementary data (Paper IV)

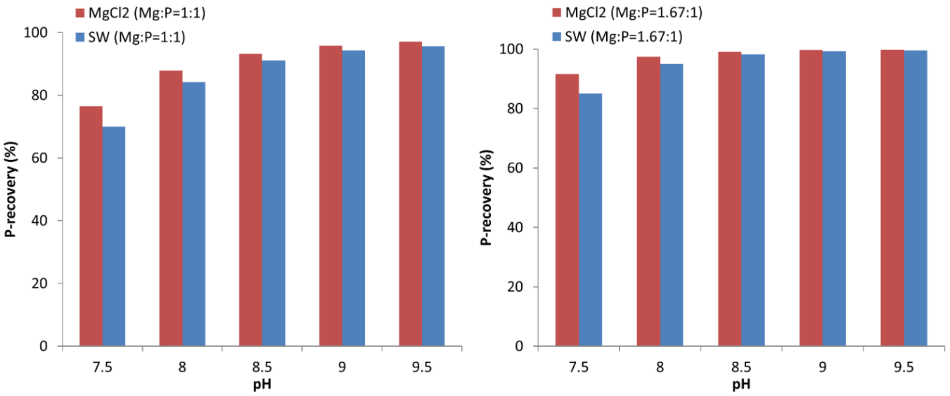


Figure S1: The equilibrium (theoretical) P-recovery based on struvite calculated by Visual MINTEQ

Table S1: The supersaturated phases according to thermodynamic modeling by Visual MINTEQ 3.1. (Note: the compounds shown with * are only supersaturated in the experiments with real reject water)

Calcium-bearing compounds	**Magnesium-bearing compounds**
$CaMg(CO_3)_2$ (dolomite)	$MgNH_4PO_4.6H_2O$ (struvite)
$Ca_5(PO_4)_3(OH)$ (hydroxyapatite)	$Mg_3(PO_4)_2$ (magnesium phosphate)
$Ca_3(PO_4)_2$ (am1)	$CaMg(CO_3)_2$ (dolomite)
$Ca_3(PO_4)_2$ (am2)	$MgCO_3$ (magnesium carbonate) *
$Ca_3(PO_4)_2$ (beta)	
$Ca_4H(PO_4)_3\cdot 3H_2O$	
$CaHPO_4$	
$CaHPO_4\cdot 2H_2O$	
$CaCO_3$ (calcium carbonate) *	

Table S2: The initial ion concentrations at different Mg:P molar ratios with dilution effect of seawater

Mg:P (Molar ratio)	**SW vol. (mL)**	**Dilution (%)**	**Initial PO_4-P (mgL^{-1})**	**Initial NH_4-N (mgL^{-1})**	**Initial Mg (mgL^{-1})**
1:1	77.7	7.7	126.4	695.7	99.2
1.67:1	123.4	12.3	120.1	661.2	157.5
2.34:1	164.7	16.4	114.5	630.0	210.2
3:1	201.8	20.1	109.4	602.1	257.5

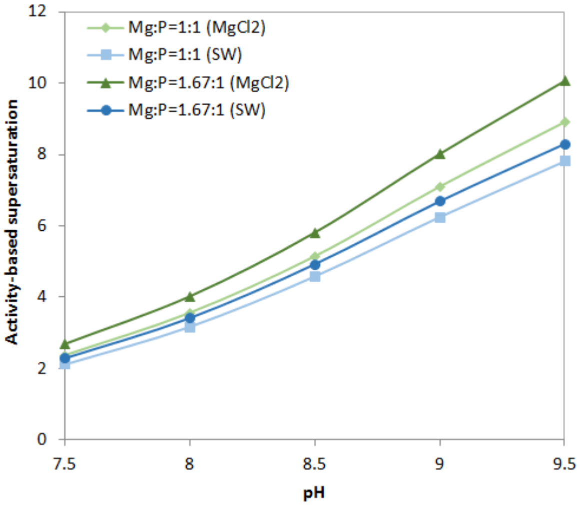


Figure S2: The activity-based supersaturation calculated by Visual MINTEQ software

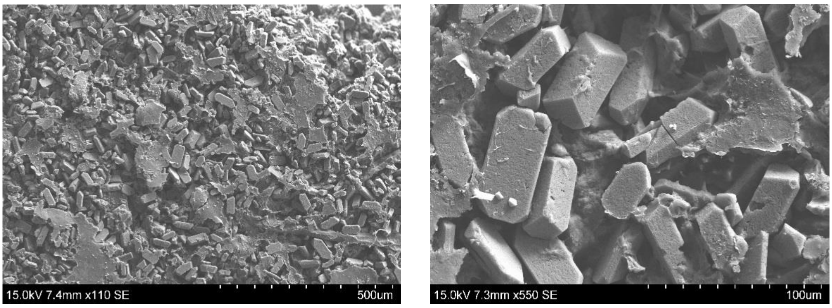
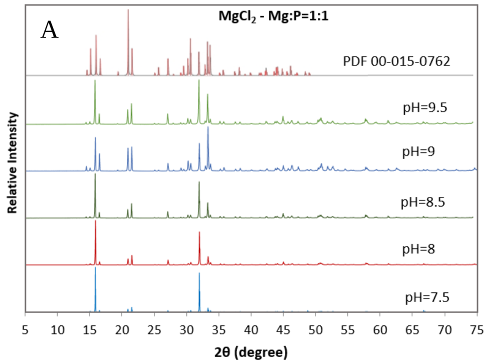
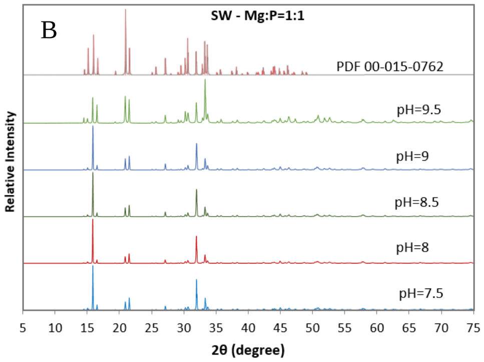
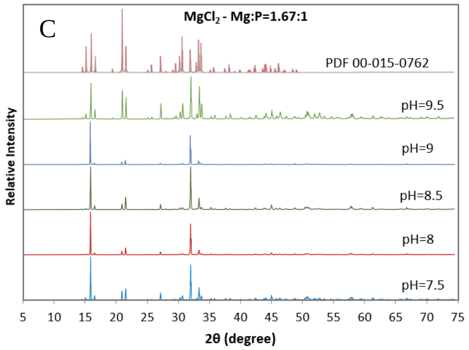
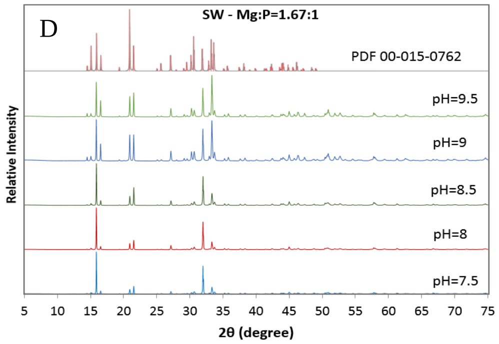


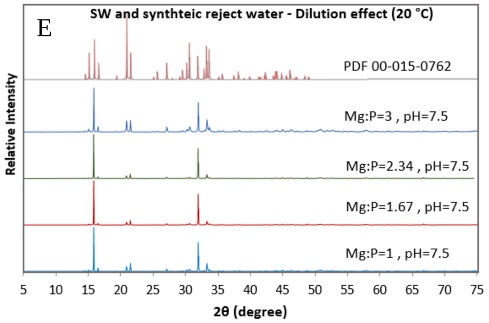
Figure S3: The struvite particles mixed with suspended solids in real reject water

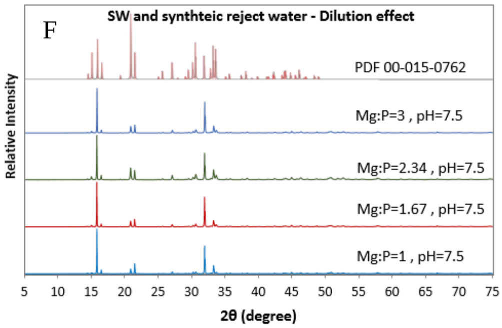

A
MgCl$_2$ - Mg:P=1:1
PDF 00-015-0762
pH=9.5
pH=9
pH=8.5
pH=8
pH=7.5
Relative Intensity
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
2θ (degree)


B
SW - Mg:P=1:1
PDF 00-015-0762
pH=9.5
pH=9
pH=8.5
pH=8
pH=7.5
Relative Intensity
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
2θ (degree)


C
MgCl$_2$ - Mg:P=1.67:1
PDF 00-015-0762
pH=9.5
pH=9
pH=8.5
pH=8
pH=7.5
Relative Intensity
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
2θ (degree)


D
SW - Mg:P=1.67:1
PDF 00-015-0762
pH=9.5
pH=9
pH=8.5
pH=8
pH=7.5
Relative Intensity
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
2θ (degree)


E
SW and synthteic reject water - Dilution effect (20 °C)
PDF 00-015-0762
Mg:P=3 , pH=7.5
Mg:P=2.34 , pH=7.5
Mg:P=1.67 , pH=7.5
Mg:P=1 , pH=7.5
Relative Intensity
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
2θ (degree)


F
SW and synthteic reject water - Dilution effect
PDF 00-015-0762
Mg:P=3 , pH=7.5
Mg:P=2.34 , pH=7.5
Mg:P=1.67 , pH=7.5
Mg:P=1 , pH=7.5
Relative Intensity
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
2θ (degree)

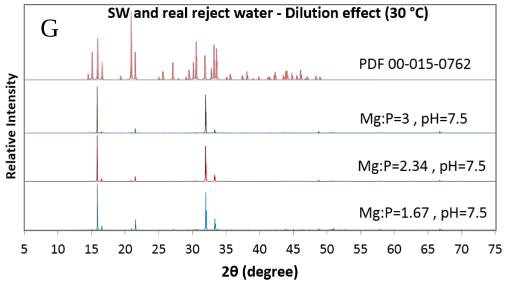


Figure S4: The XRD spectra of obtained precipitates with MgCl2 and seawater (A, B): Mg:P=1, (C,D): Mg:P=1.67, (E): with dilution effect synthetic reject water, (F): with dilution effect real reject water, (G) with dilution effect synthetic reject water at 30 °C

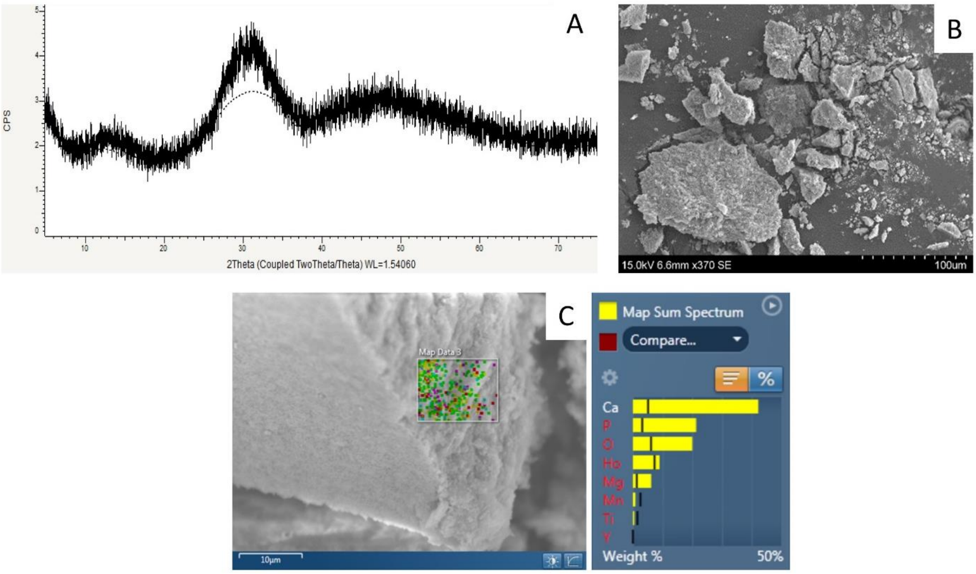


Figure S5: A) XRD spectra of precipitated amorphous phase by using seawater in absence of ammonium at Mg:P=1:1, pH=8.5, B) SEM image of precipitated phase, C) SEM-EDX of a part of precipitated phase

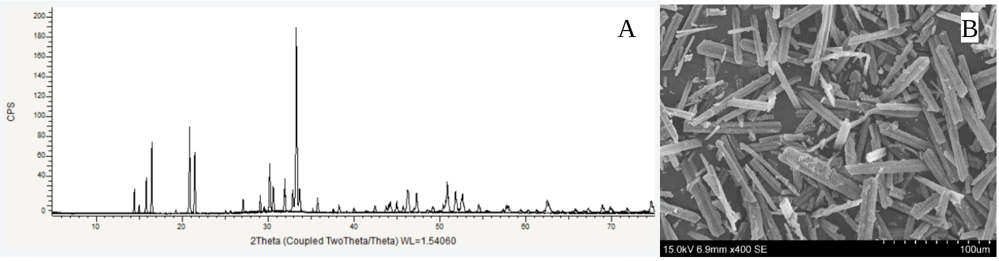


Figure S6: A) XRD spectra of precipitated phase by using seawater in presence of ammonium (Mg:N:P=1:1:1, pH=8.5), B) SEM image of precipitated phase

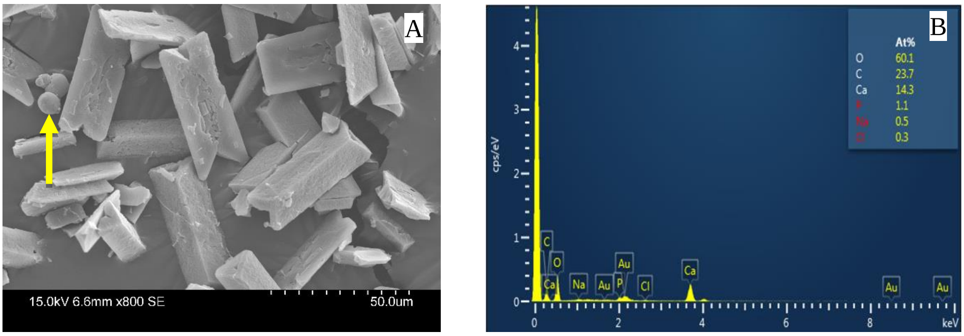


Figure S7: A) The trace amount of calcium carbonate observed in the experiment with real filtered reject water Mg:P=2.34:1 at pH=8.5, B) The elemental identification by SEM-EDX analysis

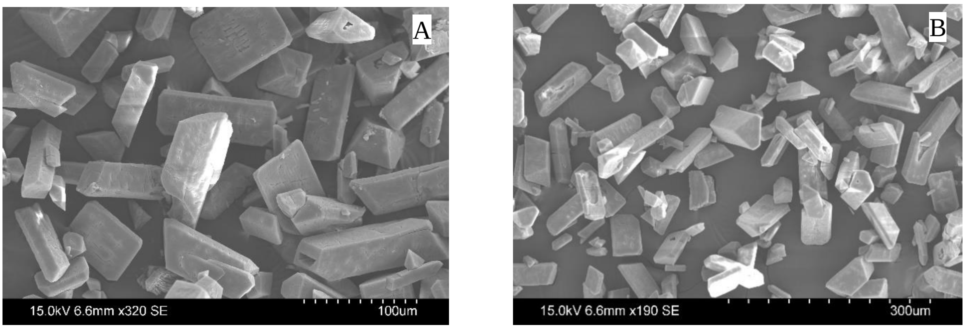


Figure S8: The SEM image of the obtained struvite crystal at pH=7.5 and 30 C A) Mg:P=1.67:1 and B) Mg:P=3:1

Table S3: The input values for LCA analysis in this study

Inputs per kg of produced struvite										
	pH=7.5		**pH=8**		**pH=8.5**		**pH=9**		**pH=9.5**	
$MgCl_2$ alternative	*$MgCl_2$ (kg)*	*NaOH (kg)*	*$MgCl_2$ (kg)*	*NaOH (kg)*	*$MgCl_2$ (kg)*	*NaOH (kg)*	*$MgCl_2$ (kg)*	*NaOH (kg)*	*$MgCl_2$ (kg)*	*NaOH (kg)*
Mg:P=1:1	0.52	0.42	0.45	0.46	0.42	0.61	0.41	0.86	0.40	1.45
Mg:P=1.67:1	0.72	0.51	0.67	0.38	0.65	0.60	0.65	0.73	0.65	1.44
Transport kgkm	-	-	-	-	-	-	-	-	-	-
Mg:P=1:1	105	83	90	92	85	122	83	171	81	291
Mg:P=1.67:1	144	102	134	76	131	121	130	147	130	288
Seawater alternative	*SW volume (L)*	*NaOH (kg)*	*SW volume (L)*	*NaOH (kg)*	*SW volume (L)*	*NaOH (kg)*	*SW volume (L)*	*NaOH (kg)*	*SW volume (L)*	*NaOH (kg)*
Mg:P=1:1	0.13	0.47	0.09	0.39	0.08	0.51	0.08	0.78	0.08	1.23
Mg:P=1.67:1	0.15	0.38	0.14	0.39	0.13	0.48	0.13	0.75	0.13	1.11
kWh pumping seawater*	-	-	-	-	-	-	-	-	-	-
Mg:P=1:1	3.3E-05	-	2.4E-05	-	2.2E-05	-	2.1E-05	-	2.1E-05	-
Mg:P=1.67:1	4.0E-05		3.6E-05		3.4E-05		3.4E-05		3.4E-05	
Transport kgkm	-	-	-	-	-	-	-	-	-	-
Mg:P=1:1	-	94	-	79	-	102	-	157	-	246
Mg:P=1.67:1	-	76	-	77	-	97	-	150	-	222

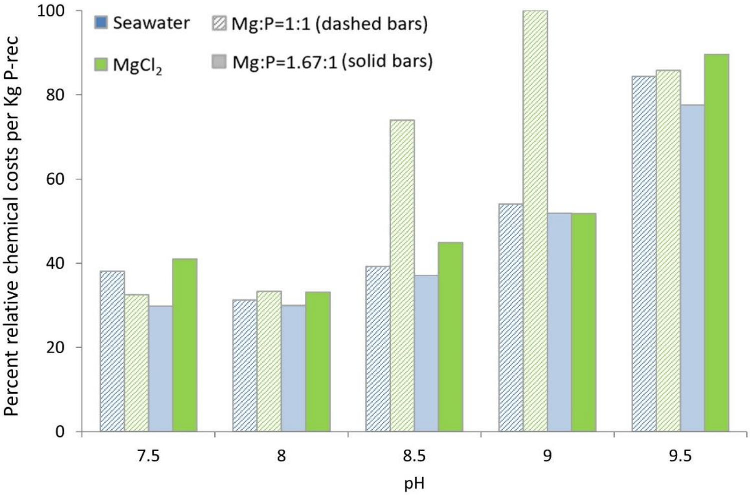


Figure S9: The relative chemical costs per kg of the recovered P by using MgCl$_2$ and seawater at different operational conditions

Paper 5

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Crystallization kinetics and growth of struvite crystals by seawater versus magnesium chloride as magnesium source: towards enhancing sustainability and economics of struvite crystallization

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HIGHLIGHTS

- Higher Mg:P molar ratios improve the struvite crystallization kinetics by seawater.
- PH is the most significant supersaturation regulator for struvite crystal growth.
- Mg:P > 0.2 and N:P > 6 were beneficial for the struvite crystal growth.
- High N:P molar ratio significantly improves the struvite growth by seawater.
- Struvite seeding minimizes the simultaneous precipitation of calcium phosphates.

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ABSTRACT

The recycling of nutrients from wastewater and their recovery in the form of valuable products is an effective strategy to accelerate the circular economy concept. Phosphorus recovery from wastewater by struvite crystallization ($MgNH_4PO_4 \cdot 6H_2O$) is one of the most applied techniques to compensate for the increasing demand and to slow down the depletion rate of phosphate rocks. Using low-cost magnesium sources, such as seawater, improves the financial sustainability of struvite production. In this study, the potential of seawater for struvite crystallization versus the commonly used magnesium source, $MgCl_2$, was tested by crystal growth and kinetic experiments. The impact of ammonium concentration, magnesium concentration and pH on the growth kinetics of struvite in synthetic and real reject water were studied. The results showed that simultaneous precipitation of calcium phosphate was insignificant when using seawater, while presence of struvite seeds diminished it further. Among the supersaturation regulators, pH had the most significant effect on the struvite growth with both $MgCl_2$ and seawater, while high N:P molar ratios further improved the struvite crystal growth by seawater. The N:P molar ratios higher than 6 and Mg:P molar ratios higher than 0.2 are recommended to improve the crystal growth kinetics. It was concluded that seawater is a promising alternative magnesium source and the control of supersaturation regulators (i.e., Mg:P, N:P and pH) is an effective strategy to control the reaction kinetics and product properties.

1. Introduction

The new generations of wastewater treatment plants need to target several developments including improving effluent quality, cutting greenhouse gas emissions and recovering energy and valuable resources. The contribution to the global phosphorus load from domestic sewage to water recipients should be reduced. This is because in many areas of the world either there is not enough water to assimilate the phosphorous or the pollution load is so huge that the water systems can not assimilate everything. In addition, the recovery and recycling of phosphorus from wastewater is gaining momentum in many countries due to vital importance of phosphorus in fertilizer industry and adaption of the circular economy strategies. Further acceleration of phosphorus recovery can be achieved by improving the economic drivers and

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environmental legislations (Shaddel et al., 2019c). Therefore, the improvement of financial sustainability by reducing the operational costs is a strong financial driver for the nutrient recovery technologies. The recovery of phosphorus, among all available resources in wastewater, is a prominent action as it can reduce the conventional mining and moderate the expected future shortage of phosphate rocks used to produce phosphorus fertilizers (Shaddel et al., 2019c).

The preferred method for phosphorus recovery mainly depends on the infrastructure of the existing wastewater treatment plant. However, struvite crystallization is one of the main methods used to recover phosphorous from wastewater due to the physical and chemical properties of struvite mineral ($MgNH_4PO_4 \cdot 6H_2O$)(Li et al., 2019). Struvite forms large diameter crystalline aggregates and show good settling and dewatering properties, as well as low incorporation of heavy metals or pathogenic contaminations, which makes it a good candidate for phosphorus removal and recovery (Shaddel et al., 2019a; Uysal et al., 2010). Struvite is comprised of primary (nitrogen and phosphorus) and secondary (magnesium) macronutrients and has low solubility in water, which results in reduced runoff and improved plant uptake. The crystallization of phosphorus as struvite by addition of an adequate amount of magnesium to the sidestreams that are rich in NH_4^+ and PO_4^{3-} has been recognized as an efficient means of solving operational challenges and recycling the phosphorus to conserve and protect natural resources (Li et al., 2019). However, the use of pure magnesium sources such as magnesium salts (i.e. $MgCl_2$ and $MgSO_4$) may stress the total sustainability and economic feasibility of the process (Shaddel et al., 2019a). The cost of struvite production is mainly influenced by chemical costs, especially the cost of magnesium source which can contribute up to 75% of overall costs (Hövelmann and Putnis, 2016). Therefore, using low-cost magnesium sources for struvite production is an effective approach to improve the economics of struvite crystallization while ensuring the quality of final product.

A cost reduction of 18–81% for struvite production was reported by using a low-cost magnesium source (Gunay et al., 2008; Lahav et al., 2013). Various low-cost magnesium sources have been studied for struvite production including bittern (a by-product in salt industry) (Ye et al., 2011), wood ash (Sakthivel et al., 2012), pretreated seawater, and seawater concentrate (nanofiltration, reverse osmosis) (Kim et al., 2016; Lahav et al., 2013). The high heavy metal content in the wood ash and limited access to bittern in many areas have made them less advantageous compared to seawater (Sakthivel et al., 2012). Using seawater in the form of a concentrate can reduce the intake volume, but it does not improve the molar ratio of magnesium with respect to other ions. The removal of interfering ions by pretreatment of seawater is an alternative, however, it increases costs and complexity of the process. On the other hand, raw seawater (untreated seawater) is an environmentally friendly and cost effective alternative, as well as being technically feasible since magnesium is the second most abundant cation in seawater ($\approx$1300 mg/L). The availability of an alternative magnesium source in local context is also important, thus, it should be noted that for plants located away from the seashore, using seawater may not be as profitable due to increasing power costs of pumping for long distances, as well as investment and maintenance costs. Additional ions unavoidably will be added to the treatment system, although it is expected that the adverse effect of these ions would not be significant. This is because sidestreams constitute $\approx$1% of the overall flowrate to the plant and likely the influence of salt content from seawater to the main stream is marginal (Lahav et al., 2013; Matsumiya et al., 2000). Further, it is reported that phosphate accumulating organisms (PAO) can be adopted to seawater and functioning in seawater conditions is as stable as in freshwater conditions (de Graaff et al., 2020).

The potential of seawater for offsetting operating costs for struvite production is demonstrated (Nur et al., 2018; Quist-Jensen et al., 2016; Rubio-Rincón et al., 2014), although much less is unveiled on reaction kinetics and crystal growth with seawater. The crystal growth information is essential for the design and optimization of struvite crystallization to fully realize plant specific benefits. The challenges associated with using seawater for struvite production should be addressed both theoretically and practically. The presence of additional ions, specially calcium, can affect the kinetics of struvite crystallization. Higher calcium concentrations can lead to complexation of calcium and phosphate species ($CaHPO_4$ (aq), $CaPO_4^-$) and reduce the activity of precursor ions in the reaction medium, or even result in simultaneous precipitation of calcium phosphate minerals.

The supersaturation regulation has been recognized as an effective strategy to optimize the phosphorus recovery and struvite properties (Shaddel et al., 2019b). However, further investigations are required to optimize the conditions for struvite crystallization by seawater. This is because the supersaturation regulation is possible by both adjustment of precursor concentrations and reaction pH. Several ions (i.e. sodium, chloride, calcium, and sulfate) will inevitably be added into the system with the use of seawater, therefore, simultaneous precipitation of various compounds (i.e. calcium phosphates, calcium carbonate) should be considered and minimized to improve the quality of the produced struvite. Moreover, the struvite crystals experience different degrees of supersaturation during their crystal growth period, while the crystal growth kinetics in the low supersaturation regions were mainly overlooked. Generally, there is surplus of ammonium in sidestreams of anaerobic digestion, and while the phosphorus recovery should be maximized, the magnesium addition should be minimized due to associated costs.

A comprehensive understanding of struvite crystal growth with seawater still requires further systematic evaluation. Therefore, the main objective of this work is to assess the crystal growth kinetics of struvite crystallization by seawater as a sustainable alternative magnesium source. A systematic and comparative approach is employed in the experimental design by comparing the crystal growth rates and particle properties of struvite precipitated with seawater and $MgCl_2$ under varying operational conditions. The effects of reject type (i.e., synthetic and real reject), ammonium and magnesium concentrations and pH on struvite crystal growth were studied.

The results of this study can be used for the development of struvite crystallizers by using seawater in industrial scale. Further, this study provides a better understanding to modify full-scale installations with an understanding of the true benefits, challenges and operating strategies in struvite production by using seawater.

2. Materials and methods

2.1. Materials

The chemical reagents were purchased from Merck with analytical grade including sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$), ammonium chloride (NH_4Cl), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and sodium hydroxide (NaOH). Milli-Q water (18.2 MΩ cm) was used for all purposes. The struvite seeds with a purity of ≥98 wt% were obtained from Alfa Aesar and sieved to 125-63 μm to be used in seeded experiments. Seeds were composed of 39% phosphate, 10% magnesium, 7% ammonium and 44% crystal water by mass. The scanning electron microscopy (SEM) (Hitachi S–3400 N) image and the particle size distribution for the seed particles are presented in Figs. S1 and S2. The surface area of the seeds was determined by multiple point BET (Brunauer–Emmett–Teller) from N_2 adsorption and desorption isotherms at 77 K, after degassing at 40 °C for 72 h prior to analyses (Fig. S3). The BET surface area was 374.9 ± 3.4 m^2/g with the cumulative pore volume (17-3000 Å) of 0.357 cm^3/g and pore size of 30.53 Å based on BJH (Barrett– Joyner–Halenda) method (Figs. S3 and S4) (Heraldy et al., 2017; Hövelmann et al., 2019; Stone, 1958).

The seawater was obtained from Trondheim fjord (an inlet of the Norwegian Sea) where it was pumped from a depth of 70 m and 800 m away from land. The seawater passed through a sand filter of ~70 μm and then kept in the fridge (1-4 °C) during the experimental period. Table 1 presents the properties of seawater.

2.2. Preparation of solutions

The real reject water was obtained from dewatering of waste biological sludge of a wastewater treatment plant with biological phosphorus removal. The characterization of real reject is presented in Table 2 by determination of solids in wastewater according to Standard Methods 209 (American Public Health, 1960). Synthetic reject water, composed only of ammonium and phosphate at the same concentrations, was prepared from stock solutions with dissolution of the corresponding crystalline solids ($NaH_2PO_4 \cdot 2H_2O$ and NH_4Cl).

2.3. Methods

All experiments were carried out using a lab-scale crystallization system, composed of a 1 L glass reactor, stirred with a combined mixer controlled by a mechanical stirrer operated at 150 rpm. The combined mixer composed of a common shaft with a Teflon two-blade propeller in the middle and a four-blade propeller (45°) at the end to ensure proper mixing of the crystals (Fig. 1). This mixer configuration reduced the dependency of complete mixing on high rpm values (i.e., high G-values) and allowed for using a low stirring speed, which minimizes the possibility of secondary nucleation due to crystal breakage (Fig. 1). Temperature was regulated by a water bath and maintained at 20 ± 0.5 °C for all experiments. Nitrogen, presaturated with water, was constantly preserved on top of the solutions throughout the crystallization reactions to prevent intrusion of atmospheric carbon dioxide.

The unseeded experiments were carried out by preparation of supersaturated solutions with respect to struvite via addition of $MgCl_2$ solution or seawater to the reject solution. The reactions were let to proceed for 60 min under constant pH. For this purpose, pH was continuously monitored by a combined glass electrode connected to EasyDirect™ pH Software (Metrohm), and 1 M NaOH was added manually to compensate for pH decrease accompanying the crystal formation.

Table 2
The characterization of the real reject water.

Parameter	Value	Standard deviation (%)
Tot-P (mM)	4.78	±1.63
PO_4–P (mM)	4.42	±1.34
NH_4–N (mM)	53.85	±1.34
Na^+ (mM)	15.10	±2.11
K^+ (mM)	0.88	±1.84
Ca^{2+} (mM)	1.36	±4.15
Mg^{2+} (mM)	1.71	±2.40
Initial pH	7.00	±0.01
TSS (%)	2.05	±0.18
VSS (%)	0.62	±0.06
Total COD (mgL^{-1})	1838	±6.21
Soluble COD (mgL^{-1})	468	±5.73

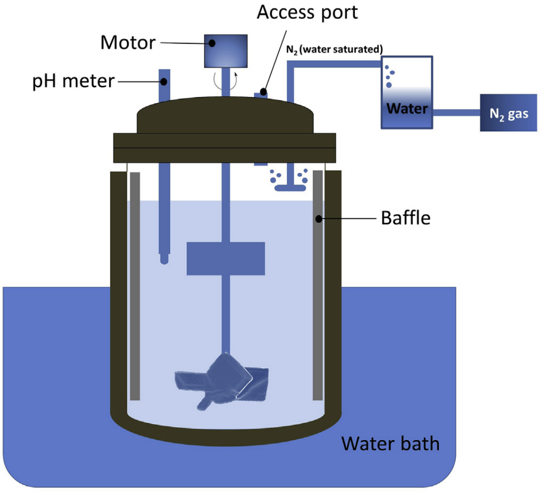

Fig. 1. The schematic representation of the reactor setup.

For the seeded growth experiments, metastable solutions supersaturated with respect to struvite were prepared (Table 3) and growth was initiated by addition of 0.7 g of struvite seeds at a constant stirring speed (150 rpm) and temperature (20 ± 0.5 °C) at pH = 7.5. The seed amount and mixing intensity were optimized in

Table 1
The seawater properties and composition.

Parameter	Values	Standard deviation (%)	Molar conc. (mM)	Mol./Mol. (**Mg^{2+}**)
pH	7.90	±1.0	–	–
Conductivity (mS/cm)	31.60	±0.3	–	–
Alkalinity (mM)	1.66	±1.0	–	–
Na^+ (mgL^{-1})	10570	±1.7	459.77	8.76
Mg^{2+} (mgL^{-1})	1276	±2.6	52.49	1.00
Ca^{2+} (mgL^{-1})	447	±6.9	11.15	0.21
K^+ (mgL^{-1})	393	±4.5	10.00	0.19
Cl^- (mgL^{-1})	19325	±6.4	545.00	10.38
SO_4^{2-} (mgL^{-1})	2740	±1.5	28.52	0.54
NO_3^-(mgL^{-1})	160	±4.0	2.60	0.05
Br^- (mgL^{-1})	67	±0.3	0.83	0.02
F^- (mgL^{-1})	1.30	±0.3	0.06	–

Table 3
The experimental conditions for struvite crystal growth at pH 7.5 and 20 °C.

Target	ExP.	Mg^{2+} (mM)	NH_4^+ (mM)	PO_4–P (mM)	Mg-source	Initial S_a
NH_4-concentration	1	0.93	26.55	4.43	$MgCl_2$	1.30
	2	0.93	40.39	4.43	$MgCl_2$	1.43
	3	0.93	53.10	4.43	$MgCl_2$	1.51
	4	0.93	26.55	4.43	SW	1.25
	5	0.93	40.39	4.43	SW	1.38
	6	0.93	53.10	4.43	SW	1.46
Mg-concentration	7	0.89	26.55	4.43	$MgCl_2$	1.28
	8	1.55	26.55	4.43	$MgCl_2$	1.52
	9	2.21	26.55	4.43	$MgCl_2$	1.69
	10	0.89	26.55	4.43	SW	1.25
	11	1.55	26.55	4.43	SW	1.43
	12	2.21	26.55	4.43	SW	1.55
pH	13	2.21	26.55	4.43	SW, pH = 7.5	1.60
	14	2.21	26.55	4.43	SW, pH = 7.7	1.90
	15	2.21	26.55	4.43	SW, pH = 7.9	2.23

preliminary experiments to avoid additional nucleation and mass transfer to be the limiting factor during the crystal growth, respectively. During the seeded growth experiments, the reaction pH was monitored continuously, and samples were withdrawn for ion analysis at determined time points. All experiments in this study were performed in triplicate.

The vacuum filtration through a 0.2 μm pore size filter (polypropylene membranes) was used to collect the precipitates at the end of each experiment. The powder X-ray diffraction (XRD) (D8 Advance DaVinci, Bruker AXS GmBH) was used for solid phase characterization in the range of 5–75° with a step size of 0.013° and a step time of 0.67 s. The obtained data were analyzed by DIFRACC.SUITE EVA software (Bruker) and the International Centre for Diffraction Data database (ICDD PDF-4 + 2018). The SEM analyses were performed on samples sputtered with gold on carbon tape. The particle size analyzer with laser diffraction (Beckman Coulter LS230) was used to measure and analyze the particle size distribution. The presented particle sizes were obtained by dynamic light scattering technique and derived based on sphericity of particles, so they should be interpreted as nominal size of crystals for the comparison of the results. The elemental composition of final precipitates was measured by complete dissolution of product in 1 M HNO_3 and the ion concentrations were measured by ion chromatography (940 Professional IC Vario, Metrohm). The experimental and theoretical results of percent phosphorus recovery are calculated by using Eq. (1):

$$\text{P} - \text{recovery}\ \% = \left(\frac{\text{P}_{\text{initial}} - \text{P}_{\text{final}}}{\text{P}_{\text{initial}}}\right) \times 100\% \qquad (1)$$

An ion exchange chromatograph (940 Professional IC Vario, Metrohm) with an autosampler (813 compact) was used for characterization of seawater and wastewater. The samples were filtered by 0.45 μm pore size filter (polypropylene membranes) before analysis with ion exchange chromatograph. It should be noted that determination of ion concentrations in seawater with ion chromatography technique is challenging since some of the ions such as sodium and chloride are present in very high concentrations, while certain metals are in such minute quantities (Table 1). The phosphate ion concentrations were determined via spectrophotometry (Hach DR Lange, 1900). Standard Methods 209 (American Public Health, American Water Works, 1960) was used for the determination of solids including total suspended solids (TSS) and volatile suspended solids (VSS).

2.3.1. *Crystal growth model*

In this study, the crystal growth rates were measured with seeded batch experiments by monitoring the changes in solution supersaturation (i.e. ion concentrations). This method allows for the determination of overall growth rates without distinguishing between different sizes or individual faces of struvite crystals. The growth rate can be calculated by using Eq. (2) where $\frac{dC}{dt}$ denotes the concentration change of precursor ions due to crystal growth with respect to time and A is the surface area of the seeds (Mullin, 2001). The depletion of magnesium concentration as a function of time was followed to calculate and compare the growth rates of struvite crystals in seeded growth experiments at varying conditions.

$$\text{R} = \frac{1}{A}\cdot\frac{dC}{dt} \qquad (2)$$

The crystal growth experiments were performed at pH = 7.5 and 20 °C under different operational conditions to investigate the effect of seawater as magnesium source versus $MgCl_2$ and the effects of Mg^{2+} and NH_4^+ concentration. The reported studies on struvite crystal growth at varieties of pH values have been performed at ion concentrations (i.e. Mg^{2+}, PO_4^{3-}, and NH_4^+) much lower than typical concentration at full-scale (Wei et al., 2017). However, in this study the ion concentrations are similar to typical values of dewatering sidestream of anaerobically digested sludge of a full-scale wastewater treatment plant using enhanced biological phosphorus removal (EBPR). The effects of constituent ion concentrations were studied at pH = 7.5 since additional nucleation to seed growth was observed at pH values higher than pH = 7.5.

3. Results and discussion

3.1. *Unseeded experiments*

The optimum selection of magnesium concentration and pH are two key parameters in the matrix of regulating parameters to maximize the P-recovery at lowest costs. However, maintaining product quality is more significant when using seawater compared to pure Mg-based chemicals. The full-scale struvite crystallization reactors are working based on the growth of available struvite seeds, while secondary nucleation is necessary to generate new particles after harvesting the struvite from the reactor. In other words, the overall phosphorus recovery and the final product properties are a result of generation of new particles (i.e. secondary nucleation) and the growth of available crystals. Therefore, a series of unseeded experiments (Fig. 2) were performed to investigate the efficiency of seawater for P-recovery and the quality of the obtained precipitate. The detailed results of the unseeded experiments are presented in a dedicated paper, and briefly summarized here

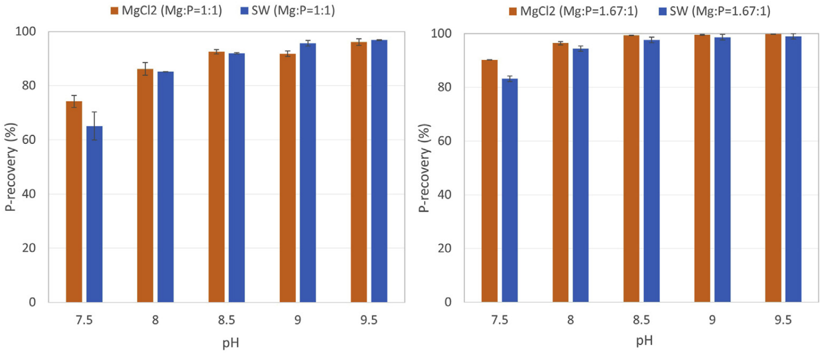

Fig. 2. The measured P-recovery in unseeded crystallization experiments with synthetic reject water by using seawater and $MgCl_2$ (adapted from Shaddel et al., 2020).

(Shaddel et al., 2020). The results showed that final P-recovery mainly depends on the Mg:P molar ratio and the reaction pH (Fig. 1). Further, it was shown that satisfactory P-recovery efficiency (65-99%) can be achieved by using seawater for struvite crystallization. This confirms the potential of seawater for struvite production, although slight reduction in phosphorus recovery was observed (≈ 1-6%) when seawater was used compared to $MgCl_2$ salt as the magnesium source. The bigger difference in P-recovery at lower pH values (i.e. pH = 7.5) was mainly due to the strong effect of decreasing supersaturation with seawater on the kinetics of the precipitation reaction. The higher ionic strength due to introduction of additional ions in seawater in the reactor lowers the ionic activity product and supersaturation with respect to struvite, so maintaining higher pH is necessary to compensate for this effect. However, under the current experimental conditions increasing pH above 8.5 is not advantageous as it has minimal improving effect. The quality of the final product was also investigated by XRD analysis and complete dissolution of the final precipitates. The presence of struvite as the main phase in the final precipitate was confirmed, although insignificant amounts of calcium carbonate (<1%) and trace amounts of sodium and potassium (<0.1%) were also detected in the re-dissolved samples precipitated from real reject water. Maintaining a high N:P molar ratio in the reaction solution was shown to be critical to precipitate struvite in competition with other potential phases (Shaddel et al., 2020). Overall, it was concluded that appropriate product properties by using seawater for struvite crystallization is achievable in addition to comparable P-recovery efficiency with respect to $MgCl_2$.

Further, crystallization kinetics and crystal growth data are important in the design and operation of struvite crystallizers as the reaction kinetics is decisive in the determination of retention time and the reactor volume. Therefore, the kinetics of struvite crystallization by seawater and $MgCl_2$ were studied under the similar operational conditions, which enables us to compare the impact of seawater in struvite crystallization versus $MgCl_2$.

3.2. Seeded growth experiments

The struvite reactor design and overall optimization of economy and process efficiency require crystal growth and reaction kinetic data. The reaction kinetic data can be used to optimize the hydraulic reaction time (HRT) and phosphorus recovery efficiency. Therefore, the seeded growth experiments were performed to evaluate the crystal growth and reaction kinetics by seawater and $MgCl_2$.

3.2.1. Effect of Ca^{2+} ions

An important aspect to be considered while using seawater as the magnesium source for struvite crystallization is its calcium content. During struvite crystallization, calcium ions, when present in the solution, can potentially compete with magnesium ions to react with phosphate species both for complexation and simultaneous precipitation. However, the interfering effect of calcium ions on struvite precipitation strongly depends on operational conditions, where both strong interference (Jaffer et al., 2002) and insignificant effects (Krähenbühl et al., 2016; Le Corre, 2006) on struvite crystallization were reported in the literature. Moreover, formation of calcium phosphates in the early stages of crystallization (1-30 min) followed by their dissolution in later stages has been reported at high ammonium (>300 mg/L) and phosphate (>100 mg/L) concentrations. In the crystal growth experiments of this study, the calcium concentration was stable during the crystal growth, indicating that simultaneous precipitation of calcium phosphate phases did not occur. The prevention of the possible formation of calcium-bearing precipitates can be explained by the presence of struvite seeds, high ammonium concentration and the applied Mg:P molar ratio in these experiments. The ammonium concentration is one of the determining factors that can enhance struvite precipitation in the presence of calcium. This is explained by inhibition of the initial step of precursor-controlled reaction or as a result of Mg^{2+} ions blocking the surface growth sites of Ca-phosphates and slowing down the growth rate of calcium precipitates (Golubev et al., 1999; Gunnars et al., 2004). An increase of N:P molar ratio increases the buffer capacity of solutions and precipitation kinetics of struvite, which makes it kinetically more favorable with respect to potential calcium phosphates at similar conditions (Crutchik and Garrido, 2011). Enhanced buffer capacity of the solutions results in lowering the required pH for nucleation of struvite, which in turn favors the precipitation of P as struvite and improves the product purity by reducing the share of other compounds (i.e. calcium phosphates) (Capdevielle et al., 2013). The calcium interference was insignificant in crystal growth experiments, although the ammonium and magnesium concentrations as well as pH are among key parameters affecting the growth kinetics of struvite crystal. Therefore, the effect of ammonium and magnesium concentration on struvite crystal growth by $MgCl_2$ and seawater was further studied, and the results are presented in the following sections.

3.2.2. Effect of NH_4^+ concentration

The particular processes in wastewater treatment plants, feed and seasonal variations often create changes in the composition of the input material to the crystallizer. Further, the sidestreams after dewatering of EBPR sludge are rich in phosphorus, while the anaerobic digestion of sludge produces surplus of ammonium with respect to phosphate and magnesium. Therefore, the ammonium concentration (N:P molar ratio) can be regulated by adjusting the share of pre-digestion and post-digestion sidestreams to the crystallizer (Shaddel et al., 2019a). The N:P > 6 is beneficial to maximize the recovery efficiency and purity of struvite (Vaneeckhaute et al., 2017). Therefore, the N:P molar ratio was varied as N:P = 12:1, 9:1 and 6:1.

All the reaction conditions were kept constant except the ammonium concentration to investigate the role of ammonium on the struvite growth kinetics (Table 3). The consumption rate of magnesium ion in Fig. 3 reflects the kinetics of crystal growth. The results showed that the crystal growth and kinetics of struvite crystallization increases at higher ammonium concentration. The kinetics of crystal growth with seawater was ≈5-20% slower with respect to $MgCl_2$. The presence of additional ions in the seawater reduces the activity of precursors which consequently reduced the crystal growth kinetics. The thermodynamic modeling by Visual MINTEQ software showed that under the operational conditions in this study magnesium activity was reduced due to the formation of $MgSO_4$ (aq) and $MgCl^+$ complexes (7.8% of total concentration), and ammonium activity was slightly lowered by the formation of $NH_4SO_4^-$ (0.16% of total concentration) in the crystal growth experiments by seawater.

In general, the rate of supersaturation consumption in the experiments with $MgCl_2$ as the magnesium source is higher than seawater (Fig. S5). Higher ammonium concentrations enhanced the rate of magnesium consumption for both $MgCl_2$ and seawater. Considering the supersaturation consumption during the growth period, the N:P molar ratio higher than 6 is beneficial for struvite crystal growth. However, the sole increase of N:P molar ration higher than 6 will not significantly improve the kinetics of struvite crystallization if the other constituent ions are limited (i.e. Mg and P). In other words, if the N:P molar ratio is higher than 6, the increase of Mg:P molar ratio or pH is a more efficient strategy to enhance the struvite crystal growth. The improving effect of higher ammonium concentrations on the magnesium consumption was more significant in the experiments by using seawater as magnesium source. Therefore, higher ammonium concentration (i.e., N:P) is beneficial for struvite crystal growth and in practice during the periods with higher ammonium in the influent, the magnesium addition and pH should be accordingly adjusted to reduce the overall operational cost.

3.2.3. *Effect of Mg^{2+} concentration*

Although seawater is a readily available source of magnesium, the magnesium dosing should be optimized to maximize the phosphorus recovery efficiency and the crystal growth kinetics and to avoid overdosing of seawater. The overdosing of magnesium beyond the process needs increases the risk of uncontrolled struvite precipitation in other process stages and in the case of seawater, it results in unwanted residual ions in the system. Therefore, the impact of magnesium concentration on the kinetics of struvite crystallization for both $MgCl_2$ and seawater was investigated.

Fig. 4 presents the consumption rate of magnesium and Fig. S6 the consumption rate of supersaturation for the crystal growth experiments by $MgCl_2$ and seawater. The results showed that the major part of the supersaturation (≈60%) was consumed in the first 10 min of the growth experiments and in average the kinetics of crystal growth with seawater was ≈10-24% slower with respect to $MgCl_2$. As mentioned previously, when seawater is used, additional ions are also introduced in the reaction medium, which results in a higher ionic strength. The effect of high ionic strength on crystal growth kinetics is twofold. Increasing ionic strength can lead to a reduction in the double-layer thickness around the crystals and hence enhance the mass transfer of monomers to the crystal surface (Stubičar et al., 1993; Tai et al., 2006). Yet, the activity of the

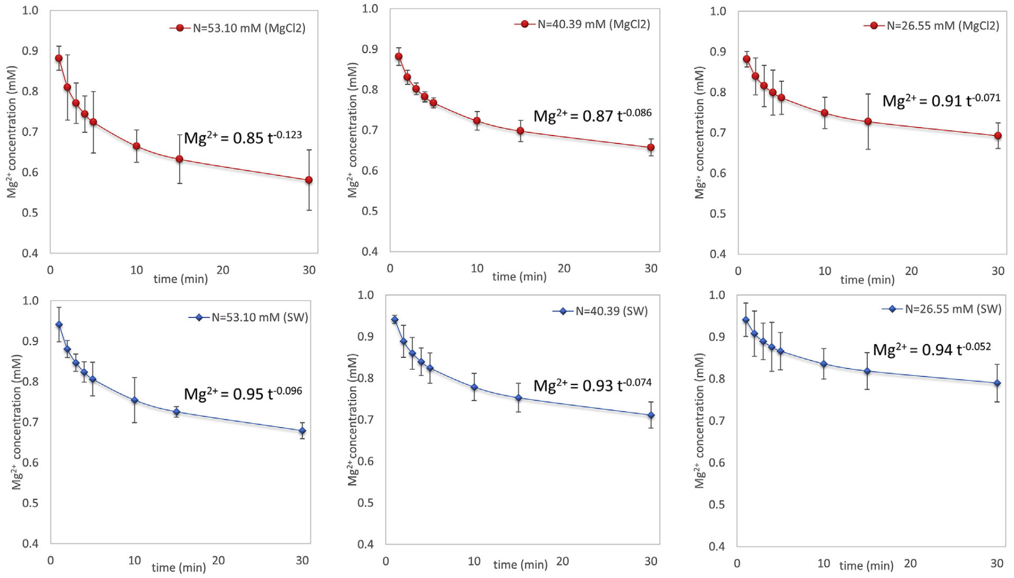

Fig. 3. The magnesium consumption as a function of time at an initial magnesium concentration of 0.925 mM and varying ammonium concentrations (a) 53.10, (b) 40.39, and (c) 26.55 mM with using $MgCl_2$ or seawater (SW) as the magnesium source.

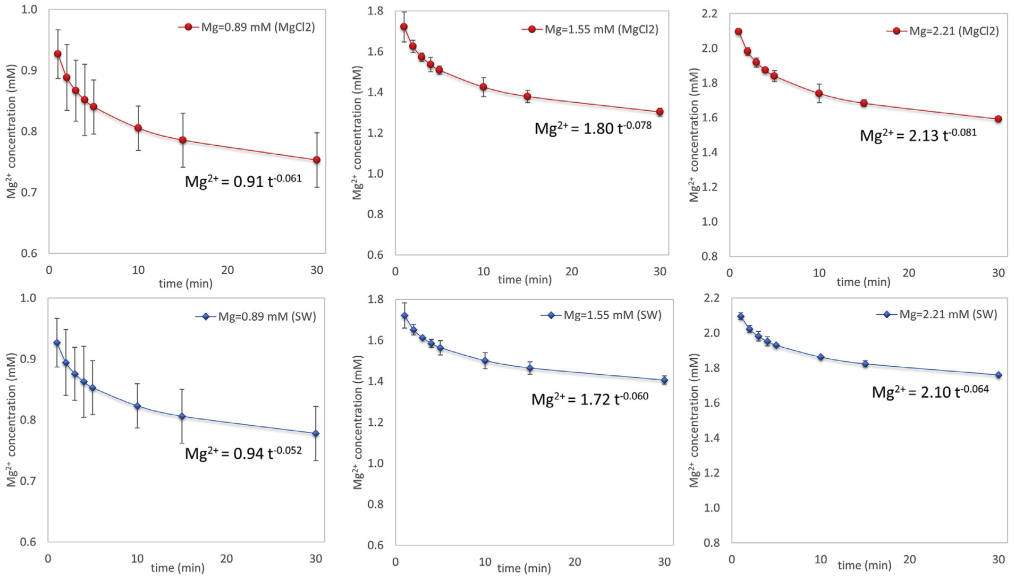

Fig. 4. The magnesium consumption as a function of time at an initial ammonium concentration of 26.55 mM and varying magnesium concentrations (a) 0.89, (b) 1.55, and (c) 2.21 mM with using $MgCl_2$ or seawater (SW) as the magnesium source.

precursor ions of struvite reduces with high ionic strength due to ion complexation by foreign ions in seawater. The overall decrease in the struvite growth rates with seawater indicated the second effect to be more pronounced on the reaction kinetics.

The $Mg^{2+} = 0.89$ mM resulted in slower growth kinetics than other experimental conditions and it can be considered as the lower cutoff for the consumption of magnesium, where extending the reaction time at lower magnesium concentrations than this value is not effective. The reaction kinetics is determining in the operation of struvite crystallizer since slow reaction kinetics will increase the operational costs associated with mixing and pumping which will further affect the economic sustainability of the process.

3.2.4. *Effect of pH*

The regulation of Mg:Ca molar ratio is an effective strategy to improve the reaction kinetics while maintaining the purity of struvite in crystallization by using seawater as the magnesium source. The original Mg:Ca molar ratio in seawater is higher than 4 (Table 1) and it is important to use this privilege during the period of crystal growth by regulation of growth kinetics. It was reported that under relevant ion concentration in the municipal wastewater the kinetics of struvite precipitation is faster than calcium phosphate precipitation (Lahav et al., 2013), which is advantageous in the case of struvite crystallization by seawater. Therefore, the reaction pH should be adjusted to an optimum value that results in: i) maximum phosphorus recovery efficiency, ii) proper reaction kinetics and iii) at the same time does not trigger the precipitation of calcium phosphates after consumption of magnesium by struvite crystallization (Shih et al., 2017). The effect of pH was studied by using real reject water rather than synthetic reject water that was used in previous sections. The increase of pH beyond pH = 7.5 in synthetic reject water triggered particle nucleation, which was identified by a pH reduction before addition of the seeds. However, the real reject water was stable at pH values higher than 7.5.

The results of magnesium consumption kinetics in Fig. 5 shows that magnesium consumption rate at pH = 7.5 was increased by ≈ 32 and 45% at pH = 7.7 and 7.9, respectively. The higher magnesium consumption rate is the result of higher initial supersaturation at higher pH values, which provides higher driving force for crystal growth. The practical implication of these findings can be used for the adjustment of the hydraulic retention time (HRT) with respect to magnesium consumption in full-scale. It is important to regulate the HRT based on the kinetics of magnesium consumption rate both for reduction of operational costs and for keeping the Mg:Ca molar ratio at a level that minimizes the simultaneous

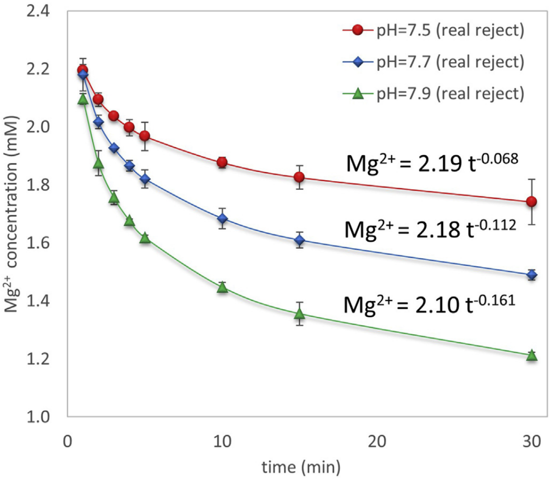

Fig. 5. The magnesium consumption at NH4–N = 26.55 mM and different pH values in crystal growth experiments with seawater and real reject water.

precipitation of calcium phosphates. In general, the pH regulation is an effective strategy to adjust the solution supersaturation since pH is a more effective variable than precursor concentrations and struvite solubility on supersaturation.

3.3. *Product properties*

The XRD analyses of the products (Fig. S7) after growth reactions with seawater showed that struvite was the main precipitated phase. Previous studies showed that Mg:Ca>1 can avoid the formation of crystalline calcium phosphates and the co-precipitated CaP phase with struvite has primarily amorphous structure, which cannot be clearly detected by XRD analysis (Lee et al., 2013). Moreover, small crystalline size and low crystallinity can prevent those phases to be detected by XRD measurements. Therefore, samples taken after crystal growth reactions were completely dissolved and analyzed also with ion chromatography. As it was expected due to the stable calcium concentration during the crystal growth, the final precipitate was further confirmed to be pure struvite. This showed that insignificant simultaneous precipitation of calcium compounds in unseeded experiments was not detected and the seeding under current experimental conditions further improved the product quality.

The particle size distribution of struvite seeds before and in the end of the crystal growth experiments (media size of the seeds = 106.2 μm) were measured to determine the increase of the particle size under different reaction conditions. Fig. S2 presents the particle size distribution of the original seeds before the growth experiments and Fig. 6 in the end of crystal growth experiments. The median size for the experiments with $MgCl_2$ is generally bigger than experiments with seawater (≈3.5%), in accordance with the observed growth rates. It was shown that this difference is more pronounced at lower initial supersaturations and higher ammonium concentrations was beneficial to improve the growth at low supersaturation. However, in the case of $Mg^{2+} = 0.89$ (Mg:P = 0.2) the growth was limited by low magnesium concentration. The lower ion activities and complexation of struvite constituent ion reduces the crystal growth rate and the final size of the crystals.

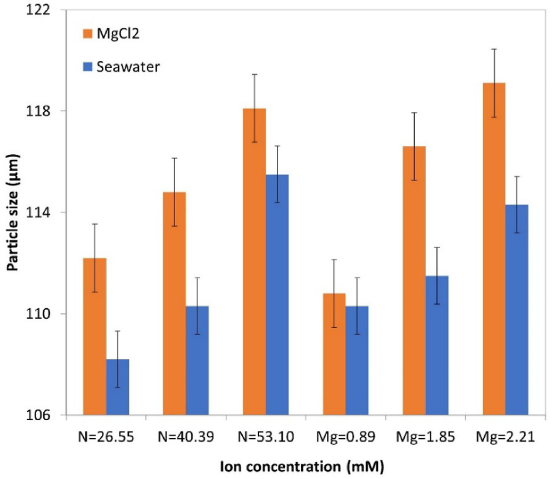

Fig. 6. The median size of particles after 60 min growth experiments (Seed $_{\text{median size}}$ = 106.2 μm).

4. Conclusion

The crystal growth and kinetic experiments for struvite crystallization under different experimental conditions showed the potential of seawater as an alternative magnesium source. The simultaneous precipitation of calcium phosphate, under the experimental conditions in this study, was not a major obstacle for struvite crystallization using seawater. The insignificant precipitation of calcium phosphate in unseeded experiments was further diminished in the presence of struvite seeds. The slower crystal growth kinetics with seawater was mainly due to extra ions added to the reactor which resulted in reduction of ion activities and available supersaturation for crystal growth. However, it was shown that at higher Mg:P and N:P molar ratios the struvite growth kinetics is comparable for both seawater and $MgCl_2$. Among the supersaturation regulators, pH has the most dominant effect on crystal growth kinetics, where the magnesium consumption rate at pH = 7.5 was increased by 32 and 45% at pH = 7.7 and 7.9, respectively. Further, high N:P molar ratio enhanced the struvite crystal growth by seawater as the magnesium consumption rate at N:P = 12 was 20% and 40% higher than N:P = 9 and N:P = 6, respectively. The results showed that for the reject water composition used in this study, the molar ratio of N:P > 6 improves the crystal growth kinetics while the growth kinetics would be limited at a molar ratio of Mg:P < 0.2. The result of this study can be used for the design of a struvite crystallizer by using seawater. Further, the presented results for the low supersaturation window of struvite crystal growth are useful for the optimization of reactor volume and hydraulic retention time which further affects the operation costs.

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Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Sina Shaddel: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Tonje Grini:** Data curation, Investigation, Writing - review & editing. **Jens-Petter Andreassen:** Supervision, Methodology, Writing - review & editing. **Stein W. Østerhus:** Funding acquisition, Supervision, Writing - review & editing. **Seniz Ucar:** Conceptualization, Methodology, Validation, Writing - review & editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.126968.

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Supplementary data (Paper V)

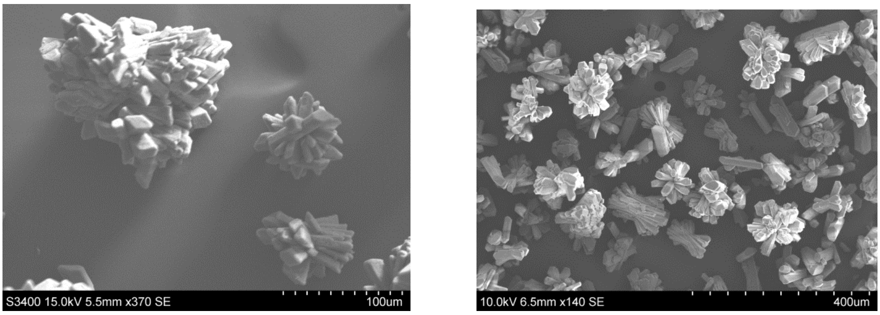

Figure S1: The SEM images of seed crystals A) before the crystal growth experiments and B) after crystal growth experiment (note the difference in scale bar)

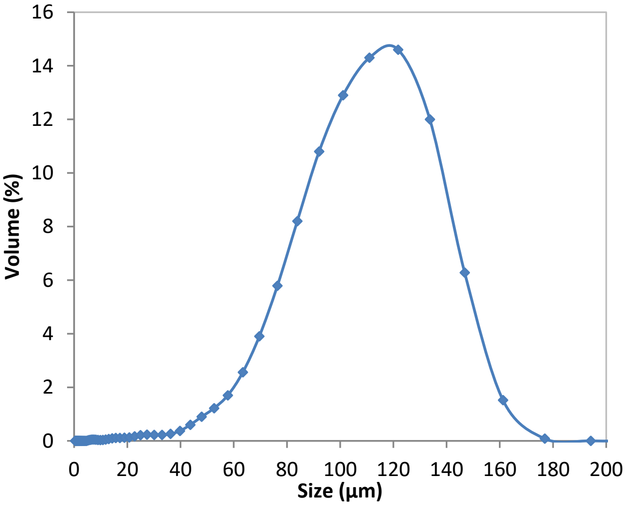

Figure S2: The particle size distribution for the struvite seeds (median size =106.2 µm)

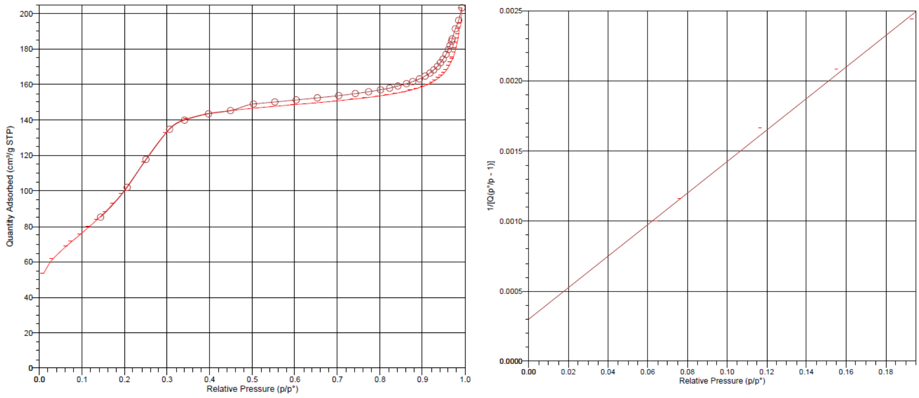

Figure S3: The Isotherm linear plot and BET surface area plot of struvite seeds

BET test: previous studies reported that micro- (pore width <2 nm) and mesopores (pore width=2-50 nm) of struvite contribute to the total surface area (Heraldy et al., 2017). However, the BET test was conducted at a low relative pressure range (0.0099-0.99) to minimize the effects of those on the calculated surface area. Similar high values of specific surface area for struvite are previously reported in the literature (Hövelmann et al., 2019). Moreover, the type IV isotherm characteristics of mesoporous materials with a C-type hysteresis loop of the de Boer classification can be seen in the nitrogen adsorption-desorption isotherms of struvite crystals (Stone, 1958) (Figure S3). This corresponds to a wedge-shaped pores with struvite surface, which can be observed in the SEM image of struvite seed crystals (Figure S4) (Wei et al., 2017).

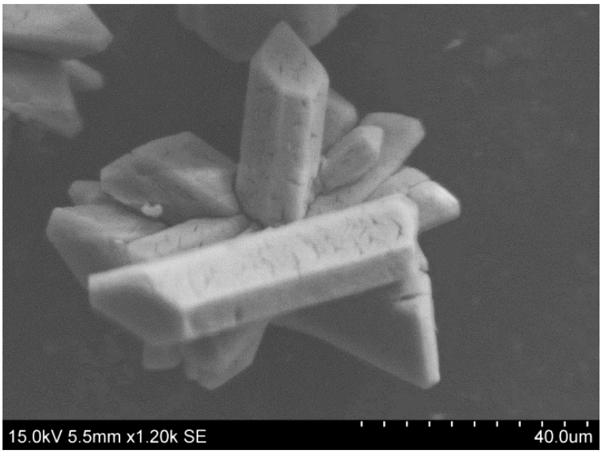

Figure S4: The wedge-shaped pores on struvite surface

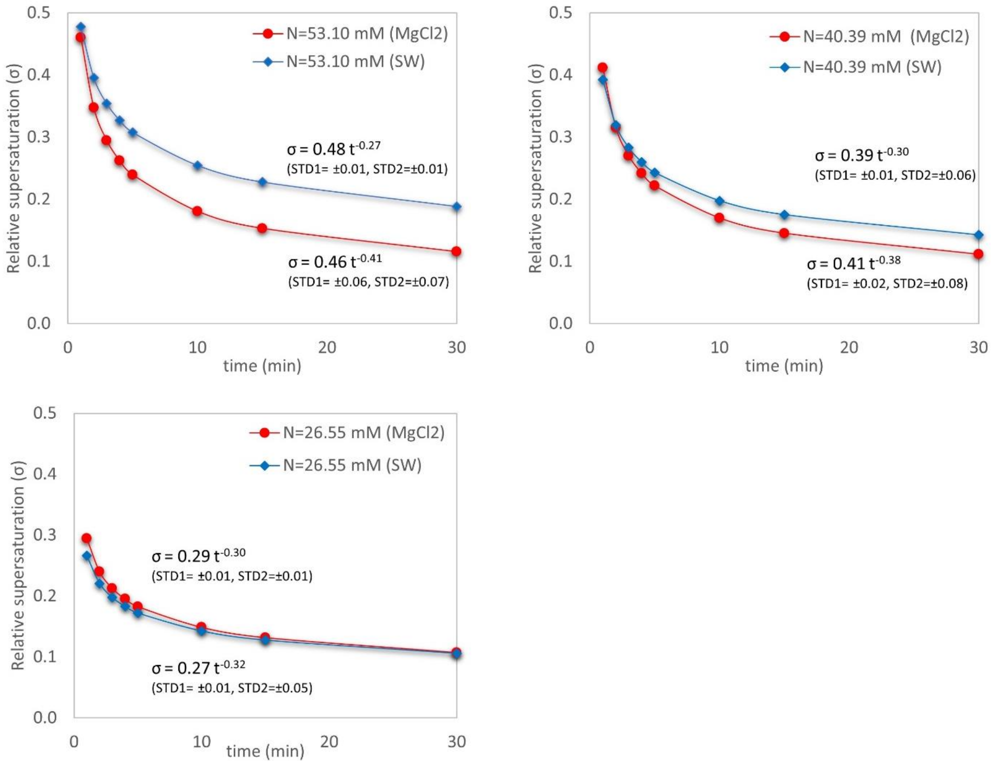

Figure S5: The supersaturation consumption as a function of time at an initial magnesium concentration of 0.925 mM and varying ammonium concentrations (a) 53.10, (b) 40.39, and (c) 26.55 mM (STD1: standard deviation value for the multiplier, STD2: standard deviation value for the power)

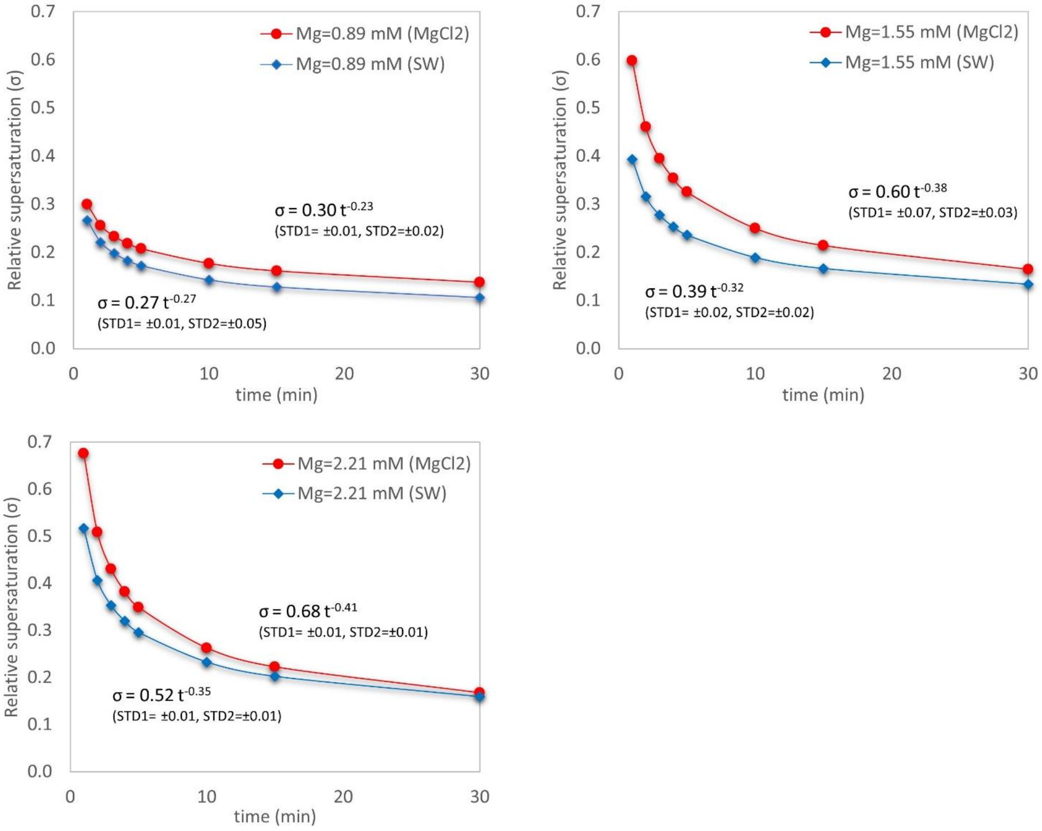

Figure S6: The supersaturation consumption as a function of time at an initial ammonium concentration of 26.55 mM and varying magnesium concentrations (a) 0.89, (b) 1.55, and (c) 2.21 mM (STD1: standard deviation value for the multiplier, STD2: standard deviation value for the power)

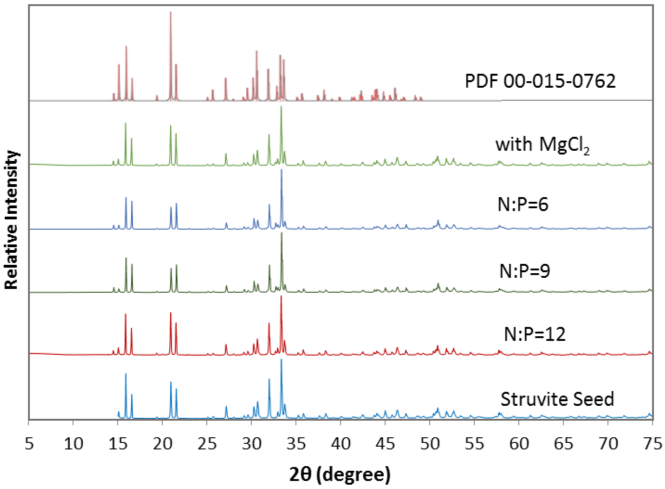

Figure S7: The XRD spectra of struvite crystals after seeded growth experiments by using seawater at varying N:P molar ratio and $MgCl_2$ at N:P=12 at

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