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Phosphate Recovery from Aerobic Wastewater Bio-P Sludge through Precipitation Process: Understanding, Experimentation and Optimization

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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"*Education is an admirable thing, but it is well to remember from time to time that nothing that is worth knowing can be taught*."

Oscar Wilde
1854-1900

Abstract

Struvite precipitation process is one the most effective approaches for recovery of phosphorus in the form of a valuable product, which could be used as a fertilizer. Despite struvite added value as a product, its application at full scale is not very common worldwide due to its economic concern of requiring the addition of Mg and NaOH to the system. The process of struvite precipitation is generally applied to the dewatered sludge after anaerobic digestion where the concentration of phosphorus is sufficiently high. Although it could be possible to use the aerobic sludge taken from the activated sludge process in which phosphorus release is happening in the anaerobic stage and a luxury uptake occurs in the aerobic zone.

Lab-scale experimentation was carried out in this thesis on the process of struvite precipitation using the aerobic sludge taken from Nosedo WRRF, Milan, Italy. The impact of different reaction parameters has been studied on the process of struvite precipitation. Particular attention was paid to the effect of pH, $Mg:NH_4:P$ molar ratio and presence of calcium. The results showed that abundant amount of Mg and NH_4 are required for significant struvite precipitation. The analysis of precipitates using FTIR, XRD, TGA-MS, ICP-AES and Elemental analysis showed the presence of struvite in notable amounts for the experiments with 5:5:1 molar ratio at pH=8.5 and 9.0. in addition, the use of $Ca(OH)_2$ as an economic pH adjustment reagent showed a decent potential for obtaining an amorphous calcium phosphate (ACP) precipitates alternatively to the pure struvite.

Chemical equilibrium modeling and statistical optimization of the process of struvite precipitation were conducted using PHREEQC software and Response Surface Methodology (RSM) respectively with Saturation Index and P removal % as response variables. The results showed that struvite, ACP and calcite are three main solid phases that could precipitate in operating conditions of the experiments. It is also noted that the only parameter affecting significantly on the P removal was the pH while Ca:Mg and $NH_4:P$ were also significantly important for the struvite SI. It can be concluded that as the pH increases the P removal also increases but the possibility of struvite precipitation diminishes since the struvite SI is decreasing.

Pilot-scale study of the phosphate precipitation process was implemented using synthetic solution with the characteristics of aerobic sludge. The effect of pH and retention time of the reaction were studied. The pH of the reactor was controlled at two points using PID-Time Proportional control system. The result of the pH control was very satisfactory and kept the pH level sufficiently stable during the entire experimentation. The results demonstrated that P removal is not much dependent on the retention time and is decreasing rapidly with the start of the reaction and then reaches at the stable level where it does not improve anymore. It was also observed that RT of 60 minutes is enough for reaction completion but not for substantial crystal growth. The FTIR results showed the possibility of having a ACP-rich product. In addition, using sodium alginate demonstrated a potential for increasing struvite precipitation possibility by reducing calcium concentration by 20% and improving the Mg:Ca ratio.

Riassunto

Il processo di precipitazione della Struvite è uno dei metodi più efficaci per il recupero del fosforo (P) sotto forma di un prodotto di grande valore, che può essere usato come fertilizzante. Nonostante il valore aggiunto della struvite, la applicazione del processo di precipitazione su vasta scala non è molto comune a causa del costo dovuto alla necessaria aggiunta di Mg e NaOH. La precipitazione della struvite viene generalmente applicata al fango disidratato, in seguito alla digestione anaerobica, dove la concentrazione di fosforo è sufficientemente elevata. In alternativa è possibile utilizzare il fango aerobico prelevato dal processo a fanghi attivi, in cui avviene un rilascio di fosforo nella zona anaerobica e un "luxury uptake" nella zona aerobica.

In questa tesi è stata svolta una sperimentazione a scala di laboratorio sulla precipitazione della struvite utilizzando il fango aerobico prelevato dall'impianto di trattamento acque reflue di Nosedo (Milano, Italia). L'impatto di diversi parametri di reazione è stato studiato. Particolare attenzione è stata posta sull'effetto del pH, del rapporto molare Mg:NH_4:P, e della presenza di calcio. I risultati hanno mostrato che sono necessarie abbondanti quantità di Mg e NH_4 per la significativa precipitazione della struvite. L'analisi dei precipitati usando FTIR, XRD, TGA-MS, ICP-AES ed Elemental Analysis ha mostrato la presenza di struvite in quantità notevoli per gli esperimenti con rapporto molare 5:5:1 a pH = 8,5 e 9,0. Inoltre, l'uso di $Ca(OH)_2$ come reagente economico per l'aggiustamento del pH ha mostrato un discreto potenziale per ottenere precipitati ricchi di fosfato di calcio amorfo (ACP) alternativi alla struvite pura.

La modellizzazione dell'equilibrio chimico e l'ottimizzazione statistica del processo sono state condotte utilizzando rispettivamente il software PHREEQC e la RSM per due variabili; Struvite Saturation Index e P removal %. I risultati hanno mostrato che la struvite, il ACP e la calcite sono tre principali solidi che possono precipitare nelle condizioni operative degli esperimenti. Si è notato inoltre che l'unico parametro che influisce in modo significativo sulla rimozione del P è il pH, mentre i rapporti molari Ca:Mg e NH_4:P erano anche significativamente importanti per la SI. Si può concludere che all'aumentare del pH aumenta anche la rimozione del P, ma diminuisce la possibilità di precipitazione di struvite da quando la SI sta diminuendo.

Lo studio su scala pilota del processo è stato implementato utilizzando una soluzione sintetica con le caratteristiche del fango aerobico. Sono stati studiati l'effetto del pH e il tempo di ritenzione della reazione (RT). Il pH era controllato all'interno del reattore usando il sistema di controllo PID-Time Proportional. Il risultato è stato molto soddisfacente nel mantenere il pH stabile. I risultati hanno dimostrato che la rimozione del P non dipende significativamente dal tempo di ritenzione; il fosforo diminuisce rapidamente dall'inizio della reazione e raggiunge rapidamente un livello stabile. È stato anche osservato che un RT di 60 minuti è sufficiente per il completamento della reazione, ma non per una crescita cristallina sostanziale. I risultati della FTIR hanno mostrato la possibilità di ottenere un prodotto ricco di ACP. Inoltre, l'uso di alginato di sodio ha mostrato un potenziale per aumentare la possibilità di precipitare di struvite riducendo la concentrazione di calcio del 20% e migliorando il rapporto Mg:Ca.

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List of Abbreviations

◦c	Degree of Celsius
ACP	Amorphous Calcium Phosphate
AD	Anaerobic Digestion
Al	Aluminum
AlP	Aluminum Phosphate
ANOVA	Analysis of Variance
ATP	Adenosine Triphosphate
BBD	Box-Behnken Design
BES	Bio-Electrochemical System
Bio-P	Biological Phosphorus
BOD	Biological Oxygen Demand
BMPs	Best Management Practices
C	Carbon
Ca	Calcium
cap	Capita
CaP	Calcium Phosphate
CHS	Calciumsilicatehydrate
cm	Centimeter
DCP	Dicalcium Phosphate
DCPD	Dicalcium Phosphate Dihydrate
DO	Dissolved Oxygen
DTGA	Derivative Thermal Gravimetric Analysis
ε	Error
EBPR	Enhanced Biological Phosphorus Removal
EPA	Environmental Protection Agency
EU	European Union
Fe	Iron
FeP	Iron Phosphate
FO	Forward Osmosis
FOMBR	Forward Osmotic Membrane Bioreactor
FTIR	Fourier Transform Infrared Spectroscopy
g	gram
GWh	Giga Watt per hour
H	Hydrogen
HAP	Hydroxyapatite
hr	hour
IAP	Ion Activity Product
ICP-AES	Inductively Coupled Plasma- Atomic Emission Spectroscopy
IFDC	International Federation Development Center
IFA	International Fertilizer Agency
kg	Kilogram

K_d	Derivative Coefficient
K_i	Integral Coefficient
K_p	Proportional Coefficient
K_{sp}	Equilibrium Solubility Product
kWh	Kilo Watt per hour
L	Liter
m/z	Mass-to-Charge ratio
m^2	Squared Meter
MEC	Microbial Electrolysis Cell
MF	Microfiltration
MFC	Microbial Fuel Cell
mg	milli gram
Mg	Magnesium
MS	Mass Spectroscopy
Mt	Mega tonne
mW	milli Watt
N	Nitrogen
NF	Nanofiltration
nm	nanometer
OCP	Octacalcium Phosphate
OMBR	Osmotic Membrane Bioreactor
OP	Orthophosphate
P	Phosphorus
PAOs	Polyphosphate Accumulating Organisms
PHA	Polyhydroxyalkanoates
PID	Proportional Integral Derivative
PR	Phosphate Rock
P rem.	Phosphorus Removal
R/C	Resource to Consumption
RMSE	Root Mean Squared Error
RO	Reverse Osmosis
RSM	Response Surface Methodology
RT	Retention Time
SI	Saturation Index
SOD	Sediment Oxygen Demand
SP	Set Point
Std. Err.	Standard Error
T_d	Derivative Time
T_i	Integration Time
TCP	Tricalcium Phosphate
TGA	Thermal Gravimetric Analysis
TP	Total Phosphorus
TSP	Triple Superphosphate
UF	Ultrafiltration
UN	United Nations

USGS	United States Geological Survey
UV-Vis	Ultraviolet Visible
VFAs	Volatile Fatty Acids
WFD	Water Framework Directive
WRRF	Wastewater Resource Recovery Facility
XRD	X-ray Diffraction
yr	Year

Chapter 1

Introduction and Thesis Description

1. Introduction and Thesis Description

1.1. Scientific Background

Nutrients removal from water and wastewater streams has received many attentions during the past decades due to the problems that excessive amounts of nutrients cause to the aquatic environments. Eutrophication, which is the excessive growth of aquatic plants due to high levels of nutrients concentration, is a major concern. It leads to oxygen depletion that would put the life of all aquatic organisms at risk [1,2]. Therefore, high level of nutrients removal is necessary to avoid their environmental impacts. This could be a more critical problem in the so-called "sensitive areas" where more stringent wastewater treatment is required [3]. These areas, and particularly in the case of this thesis the entire Northern Italy, require high level of nutrients removal specially Nitrogen (N) and Phosphorus (P) due to the European Water Framework Directive [3] that defined low limits of nutrients in wastewater discharges.

Phosphorus, being an important element for all living organisms, will be depleted inevitably although this process is not imminent yet [4]. Phosphate rock, which is the main source of phosphorus, is not distributed evenly around the world. Around 73% of phosphate rock reserves are in Morocco and Western Sahara followed by China which represents only 5.4% [5]. In addition, a large amount of phosphate rock resources in the world that is around 300 billion tones, are not technically and economically available [6]. East Asia, Africa and North America are the biggest producers of phosphate rock with 42%, 21% and 14% respectively [7]. However, with the dramatic growth of the global population the demand for producing more food is rising. This leads to an increasing need for phosphorus-containing fertilizers in food production industry.

As a consequence of both environmental concern and resource depletion, there must be special attention on P removal and recovery technologies from wastewater.

Around 20 to 30 % of P is removed through conventional biological aerobic treatment. A rule of thumb for all biologists and environmental engineers is that the ratio of 100:5:1 for BOD:N:P (Biodegradable Oxygen Demand (BOD)) must be met. However, these removal rates are not sufficiently high for meeting the strict regulations in the sensitive areas and consequently some specific P removal process is required. The oldest approach for this aim, which is still being used substantially, is the process of chemical precipitation initially used in 1950s [8]. Usually, Iron (Fe), Aluminum (Al) or Calcium (Ca) salts are applied for achieving P removal producing a P-rich sludge which by the way due to its high metal content cannot be used directly in agriculture and needs further treatment. P removal with chemical precipitation could decrease the effluent P concentration to as low as 0.05 mg/l [9]. Biological phosphorus removal was discovered and then developed in the 1950s and 1960s [10,11,12]. It is based on the activity of some specific bacteria called Polyphosphate Accumulating Organisms (PAOs). The mechanism of bio-P removal process basically consists of two steps; a P release in the anaerobic zone followed by a luxury uptake of

P in the aerobic zone. Bio-P process can achieve 75 to 93% of phosphorus removal in the final effluent [12]. Although bio-P removal has some great advantages over chemical precipitation such as no need for chemicals and lower sludge production, its P-containing sludge cannot be landfilled under current regulations in Europe. Therefore, there is a need for implementation of some specific processes to recover P as a valuable product that can be used directly after treatment. EURAU, 2012 [13] estimated a potential P recovery of 300000 tons/year for the E.U., which corresponds to an economic value of around 300 million Euros.

Struvite precipitation is a common approach for P recovery that uses the chemical precipitation method with the aim of producing a valuable product to be used as a fertilizer. However, struvite is not the only way of phosphorus recovery since other compounds such as calcium phosphate could also precipitate in such process. Struvite is a white mineral with the chemical formula of $MgNH_4PO_4.6H_2O$ that in an alkaline environment with sufficient amount of constituent ions could precipitate easily. For many decades, struvite was considered as a major problem in wastewater treatment systems due to its precipitation in equipment such as pumps, valves, pipes etc. [14]. However, because of its low solubility in neutral and alkaline conditions (and therefore, slow release of nutrients in neutral/alkaline soils) and high nutrients content (N and P), it can be utilized as a fertilizer in the agricultural section. Therefore, there has been a growing attention towards its recovery from wastewater streams as a mean of recovering P in the form of a valuable product. The process of struvite precipitation could be affected by many factors and because of this its implementation and control to achieve an efficient P recovery has been always a challenge for researchers and engineers. The most important factor to consider is the pH of the solution. Struvite precipitation is working optimally in the pH range of 7-11 [15]. Molar ratio of the constituent ions ($Mg:NH_4:P$) could be another significant factor. However, one of the more challenging factors on the efficiency of the process is the presence of some competitive ions particularly Calcium (Ca). Calcium could react with the phosphate ion and form different calcium phosphate salts. Calcium phosphate compounds could also be used in the fertilizer industry although not as effective as struvite [16]. Calcium can also go through the reaction with carbonate (CO_3^{2-}) and precipitate as calcite ($CaCO_3$), especially in high pH levels. The precipitation of such minerals in the system, could significantly affect the purity of the final product. In addition, physical parameters such as retention time, agitation rate, the presence of seeding materials could be also important.

Most of the studies on phosphorus recovery have been conducted on anaerobic sludges. Nevertheless, as reported in Angela et al., 2011 [17], aerobic sludges could also have the potential for P recovery. In conventional biological aerobic treatments, the sludge usually has 2-3% of P content. However, in enhanced biological phosphorus removal (EBPR) systems, a significant P release is happening by the PAOs in the anaerobic zone, which is followed by a P luxury uptake in the aerobic stage. In this condition, the increased concentration of P could be a great potential for its recovery in the form of struvite or calcium phosphate compounds. Maurer et al., 1999 [18] investigated the possibility of chemical precipitation in an EBPR system and suggested that P precipitation and EBPR relate to each other and effective EPBR process could lead to higher P precipitation. The EBPR process has been studied for many years and has been implemented in many cases throughout the world. It has showed effective P removal performance [19] and it is relatively an economic and sustainable process. However, there are some important and challenging aspects to consider. To have a precise operation and control of the EBPR system, a very accurate process control system would be required, which includes mathematical models to implement a predictive control scheme [20]. Furthermore, the microbial populations involved in the process are highly site-specific and can have diverse set of characteristics depending on the treatment plant, which makes the calibration and validation of such models dependent on the specific set of data obtained for each plant. One other thing to note, is that biological sludge, per se, cannot be used directly as a ready-to-use fertilizer due to its organic P content, which cannot be used directly by the crops. Consequently, the application of P precipitation using the P-rich sludge produced during the anaerobic stage of an EBPR process could be an effective way of recovering P in a valuable way.

The Nosedo wastewater treatment plant that is the subject of this thesis, is located near the city of Milan, Italy and is serving the city with a capacity of 1 million p.e. Its annual sludge production is 50,000 tons/year with an estimated P content of around 1400 tons/year. The plant includes a nitrification/denitrification process with aerobic sludge stabilization. High dilution of the entering wastewater has made the plant to suffer from low organic strength. Consequently, its operational control becomes difficult. The plant does not have sludge treatment line and through an extended aeration process keeps the sludge production at minimum. In the pre-denitrification basins of the plant, the anaerobic conditions are often observed followed by a P uptake in the further aerobic stages. Therefore, a consistent EBPR condition can be regulated and optimized through appropriate modifications of flows and recycles thus making the situation suitable for P precipitation process.

This thesis is projected with the goal of studying the possibility of implementing P recovery through struvite precipitation process for the aerobic sludge of Nosedo wastewater treatment plant. Impact of different parameters on the process efficiency have also been studied throughout the project and the process has been modeled and optimized using chemical and statistical modeling tools. Finally, a pilot-scale installation of the process has been studied based on the lab-scale experimental results.

1.2. Objectives

The primary objective of this thesis is to investigate the process of struvite crystallization as an efficient method for P recovery in the form of a valuable ready-to-use fertilizer. This work tends

to study this process and the possibility of its implementation for a large wastewater treatment plant using the aeration sludge taken from the biological treatment stage.
The specific in-detail objectives of this thesis can be defined as following:

1. Studying the importance of phosphorus recovery and reviewing the state-of-art studies on different technologies available for achieving that.
2. Investigating the possibility of struvite precipitation from different types of sludge (anaerobic and aerobic).
3. Studying the chemistry and thermodynamics of struvite precipitation process and investigating the effect of different reaction parameters on the performance of the process.
4. Modeling and optimization of the struvite precipitation process from aerobic sludge firstly, to identify the significant parameters affecting the process and secondly, to achieve the optimum conditions under which high phosphorus recovery in the form of struvite can be obtained.
5. Developing a pilot plant for phosphorus recovery process from aerobic sludge and studying the impact of operating conditions on the process at pilot scale.

1.3. Novelty and Originality

Phosphorus recovery through precipitation process has been studied for many years. Most of these studies have focused on the dewatered sludge after the anaerobic digestion where the concentration of phosphorus is sufficiently high for achieving effective precipitation [8,21-25]. However, this specific type of sludge is not always available at WRRFs. Some WRRFs, such as the one in the subject of this study (NOSEDO WRRF), do not have the anaerobic sludge treatment facility. In this study, the possibility of implementing phosphorus recovery process for such a WRRF without anaerobic sludge treatment has been investigated. In this case, if the plant had the enhanced biological phosphorus removal line, it would be possible to use the sludge taken from the anaerobic stage of that. Nosedo WRRF, on the other hand has a conventional denitrification and nitrification/oxidation treatment line. Therefore, with an upgrade of the plant to include EBPR process, the phosphorus recovery could be implemented for that. In this study it is showed that the sludge taken from the oxidation pond of the Nosedo WRRF, after being under anaerobic condition for 1-2 days, could have up to 37-40 mg/l of phosphorus that is enough for phosphate precipitation process.

The most favorable product of phosphorus recovery process in most studies is struvite. In the case of anaerobic digestion sludge, adding Mg and adjusting the pH would facilitate the precipitation process of struvite. Contrary to that, the concentration of ammonium is not very high in the sludge taken from oxidation pond. Therefore, the NH_4 would also need to be added in order to achieve struvite precipitation. In addition, the concentration of calcium is relatively high in this sludge, making it a competitive ion for phosphate precipitation since it could easily react with phosphate ion and precipitate as different calcium phosphate compounds. The effects of pH, Mg:NH_4:P and presence of Ca are investigated in details for aerobic sludge to compare it with conventional anaerobic sludge that is being used for this recovery approach.

In this study, it is showed that producing struvite from aerobic sludge would not be economically efficient since high amount of Mg and NH_4 need to be added to the solution as well as NaOH for pH adjustment. Alternatively, the production of amorphous calcium phosphate (ACP) is economically feasible. An ACP-rich precipitate was obtained using NaOH for pH adjustment without any further chemical addition. NaOH still is an expensive chemical. Therefore, $Ca(OH)_2$ was used as a pH adjustment alternative which is considerably less expensive than NaOH. Interestingly, an ACP-rich precipitate could still be produced.

Modeling and optimization of the phosphate recovery process has also been studied before. Most of the studies are focused on the chemical equilibrium modeling using chemical speciation tools such as Visual MINTEQ or PHREEQC [26-28]. There are also a few studies using statistical tools (for example response surface methodology (RSM)) for optimization of the process [29-32]. Both approaches showed great potential for improving process efficiencies and optimizing the process parameters. However, there is a lack of any investigation on using a combination of both approaches. In nearly all the available studies, the response variables of the process are experimental phosphorus or ammonium removal percentages. In this study, a chemical equilibrium tool is used to model the equilibrium condition of the process and to calculate the struvite saturation index (SI) as an indicator of the possibility of struvite precipitation. Then this value is used as a response variable for RSM optimization. In this case, the SI could be a good indicator to see how efficient the process could be for phosphorus recovery in the form of struvite. This is more critical in the case of aerobic sludge which is highly influenced by the presence of calcium and the amount of struvite precipitation is not significantly high.

A pilot scale reactor is implemented in this study to investigate the phosphate recovery process in larger scales. In all the previous pilot scale studies for phosphorus recovery anaerobic sludge is used [33-37]. As the real aerobic sludge was not available for large pilot implementation at the time of the study, a synthetic solution was made based on the samples taken from the oxidation pond of the Nosedo WRRF. The pilot study used a PID-Time proportional control system for pH control using Arduino microcontroller. Although the idea of using such a control system for pH is not new, it has never been applied to the phosphorus recovery pilot reactors. The PID-Time proportional system showed great results while it is not very complex and not expensive to implement.

Struvite precipitation was highly affected by the presence of Ca as a competitive ion, and particularly by the competition of calcium phosphate compounds (mainly ACP) and calcite precipitation. It was observed that, to achieve significant struvite precipitation in tests with aerobic sludge, high amounts of Mg and NH_4 addition would be needed, which unfortunately would make the process economically inefficient. In addition, the cost of adding NaOH, needed for pH adjustment was also relatively high [38]. Moreover, the cost of struvite precipitation is also dependent on the initial phosphate concentration in wastewater and increases considerably with concentration below 200–300 mg/L [39,40]. In most of the reported experiments of this study, the final precipitates obtained were a mixture of struvite, ACP, and calcite, with the highest content for ACP. It was also determined through ICP and Elemental Analysis that precipitating aerobic sludge would lead to an ACP-rich precipitate. Although studies showed that calcium phosphate minerals could be utilized as fertilizers as well, these turned out not to be as efficient as pure struvite [15], as their P-available content in soils was lower than the latter but was still acceptable [41]. Calcium phosphate compounds are also difficult to settle [42,43]. In terms of effects on soil, the Ca:Mg molar ratio in final precipitates could impact its structure. Lower ratios imply higher struvite content in precipitates, and this would generally be considered a more favorable condition, depending on the specific soil characteristics of the application site. However, for some soils, a higher ratio would be considered more suitable, as it would improve their drainage properties [44]. Generally, the production cost of calcium phosphate fertilizers is lower than struvite fertilizers [45], since less added chemicals are needed. Therefore, an ACP-rich precipitate would significantly reduce the cost of fertilizer production, since ACP could still precipitate in significant amounts at very low values of Mg and NH_4 molar ratios. However, the use of ACP-rich precipitate as fertilizer would depend on specific regulations on fertilizer quality by local authorities. Heavy metal impurities in calcium phosphate fertilizers are generally higher than in struvite fertilizers [46], where they are usually below the limits for heavy metal content [47]. Nevertheless, this is a situation that ought to be verified on a case-by–case basis. Furthermore, in municipal WRRFs, P recovery by precipitation showed great potential of reducing the amounts of final excess sludge to be further treated, estimated at 8 to 31% [48,49]. However, due to the very limited studies available on phosphate precipitation from aerobic sludges, it is hard to compare their potential reduction to that achievable with anaerobic digestion dewatered sludge.

The study showed that there is a great potential in using aerobic sludge for recovering phosphorus in the form of struvite or calcium phosphate. Since aerobic sludge contains generally less P than its AD counterpart, the former has long remained outside the focus of attention as far as phosphorus recovery through precipitation processes is concerned. Nonetheless, this study showed that obtaining a precipitate that is rich in calcium phosphate (ACP) with small quantities of struvite from aerobic sludge liquor is highly feasible. Struvite precipitation, despite sporting many advantages, such as fertilizer recovery, and reducing nutrients pollution by simultaneous N and P removal, is usually not an economically sustainable full-scale approach, even for anaerobic sludges, as the current market price of recovered struvite is still relatively low compared to other P-containing fertilizers [50]. As illustrated before, process economics are even worse in the case of aerobic sludge struvite precipitation, due to the significant requirements of

Mg and NH_4 addition. Obtaining a calcium phosphate-rich product as final precipitate could be considered as a way to move forward in future studies and practice on phosphorus recovery. For many WRRFs, such as Nosedo, lacking AD sludge processing, this study highlights alternative possibilities to implement economically feasible phosphate recovery. Optimization of biological treatment processes in such WRRFs (i.e., full implementation of Bio-P processes) could lead to optimum anaerobic phosphorus release that would enhance the efficiency of phosphate precipitation from liquid sludge.

To sum up all the aspects of the study, the novelty of this thesis could be entitled as “an economic approach for phosphorus recovery from aerobic sludge of a WRRF without anaerobic sludge treatment facility” that showed a great potential also in a pilot scale reactor.

1.4. Thesis Description

This thesis is presented in a paper-based format. All the papers have been written by the first author Saba Daneshgar and have been reviewed by Prof. Andrea G. Capodaglio who was the supervisor of this Ph.D. program. All the experimental parts of the projects have been conducted by Saba Daneshgar in collaboration with Prof. Armando Buttafava. Chemical Modeling and statistical optimization of the struvite precipitation process have been studied during a six-month visiting research period that Saba Daneshgar has spent at Université Laval, Quebec, Canada in collaboration with Prof. Peter Vanrolleghem at his research group modelEAU.

Chapter 2 investigates the phosphorus scarcity issue and describes the current situation of phosphate rock (PR) consumption and production. It covers in-depth review of PR reserves and resources and how they are distributed unevenly around the world. It also gets through the future scenarios of the phosphorus situation and demonstrates its inevitable complete depletion. Then, it studies the phosphorus cycle and the intervention of human in this cycle. The natural phosphorus cycle as well as its mechanism in transferring phosphorus between different environments are explained thoroughly. The chapter shows the role of human in opening this cycle by discharging phosphorus containing materials in water bodies. It emphasizes on the importance of closing this cycle by implementing phosphorus removal and recovery technologies. It reviews state-of-art studies on different phosphorus removal and recovery technologies and explains some of them in details. Struvite precipitation is reviewed as one of the most important and widely used approaches. Membrane bioreactors and assimilation by algae are two recent and promising technologies for phosphorus recovery that are presented in this chapter. Finally, the chapter highlights some considerations related to energy-nutrients nexus and how important it is to consider minimum energy consumption along with nutrients recovery. It shows that apart from the mathematical modeling and optimization of the process to make it more energy-efficient, on-site energy generation is a promising and sustainable effort for recovering the energy from WRRFs. This literature review is presented in a paper titled "The Potential Phosphorus Crisis: Resource Conservation and Possible Escape Technologies: A Review".

Chapter 3 studies the use of a chemical equilibrium modeling software in order to predict the P removal percentage and equilibrium conditions of the process including saturation index values for possible solid phases precipitating in such a system. It presents the use of PHREEQC chemical equilibrium modeling tool. The model predicts the saturation index for Struvite, Amorphous Calcium Phosphate (ACP) and Calcite as the three-main precipitating solid phases in the operating condition of the experiments. It will also calculate the phosphorus removal percentage and the amount of phosphorus precipitated in the system based on the ion speciation results. It shows how powerful and helpful the chemical equilibrium modeling tool could be to predict the outcome of the process. The model shows a great ability to predict the SI and P removal of the system that could be useful for design and development of the process in pilot-scale which was a further important stage of the thesis. The results are written as a paper titled "Simulations and Laboratory Tests for Assessing Phosphorus Recovery Efficiency from Sewage Sludge".

In *Chapter 4*, an in-depth study of the struvite precipitation process has been explored demonstrating the experimental results of the process using different types of sludges; aerobic and anaerobic. An extensive analysis of precipitates using different analytical tools have been presented in this chapter to identify the solid phases precipitating during the process. The obtained precipitates were analyzed using Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA) combined with Quadrupolar Mass Spectroscopy (MS), X-ray Diffraction (XRD), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Elemental Analysis. First, the analysis has been conducted to confront the precipitation obtained from anaerobic sludge, oxidation pond sludge and denitrification pond sludge. Based on this analysis, the chapter showed that using aerobic sludge for struvite precipitation might be less effective than anaerobic sludge and will lead to precipitate more calcium phosphate compounds, but still could be a way to recover phosphorus as a valuable by-product. Then the chapter focuses on the aerobic sludge to investigate the conditions under which struvite precipitation is observed significantly. Finally, the possibility of using an economic pH adjustment reagent ($Ca(OH)_2$) has been studied that showed a great potential in achieving an ACP-rich precipitate instead of pure struvite that could still be used as an alternative fertilizer. The aim is to be able to recover phosphorus in a more economical way as a product that could be further used for other purposes since $Ca(OH)_2$ is less expensive than NaOH (45 Euro/tonne compared to 440 Euro/tonne of NaOH) [48,51,52] and in this case the ACP-rich product could be produced without Mg and NH_4 addition. This chapter has been portrayed as a paper with the title: "Impact of pH and ionic molar ratios on phosphorus forms precipitation and recovery from different wastewater sludges".

In the next step of the project, a modeling and optimization approach for the process of struvite precipitation from aerobic sludge has been studied in *Chapter 5*. This approach combines the use of chemical equilibrium modeling (described in *Chapter 3*) with a statistical optimization method called Response Surface Methodology (RSM). The aim of this study was to identify the significant parameters affecting the efficiency of the process including pH and different molar ratios between struvite constituent ions and calcium. Molar ratios of Ca:Mg and NH_4:P were considered as predictor variables as well as the pH. They have been used to fit a second order model for SI and P removal percentage, which were taken as the response variables of the model. The purpose of this study was to obtain the optimal conditions of these parameters so that highly efficient P recovery in the form of valuable products could be achieved. Ridge analysis has also been used to achieve the optimal condition by identifying the direction to move from the stationary point of the system that could lead to optimal values for predictors. The results have been demonstrated in the fourth paper called "Statistical Optimization of Struvite Precipitation from Wastewater Sludge by Combining Chemical Modeling and Response Surface Methodology (RSM)".

Lastly, a pilot-scale phosphate precipitation process using synthetic solution based on the characteristics of real aerobic sludge has been implemented to study the effectiveness of the process in larger scale. The experimental setup and operating conditions of the pilot were designed based on the previous works on the aerobic sludge that were described in *Chapter 4* and *Chapter 5*. A 200 L cone-shaped reactor has been implemented and the influent solution was fed to the reactor. pH of the influent was controlled using continuous NaOH solution added to the stream at the top of the reactor where solution enters to basify it. The system was also equipped with a PID-Time proportional pH control system to keep the level of pH at desired value inside the reactor (reaction zone) where acidification occurs due to the H^+ release from the crystallization reaction. The impact of pH and reaction retention time have been studied as two important parameters affecting the process of struvite precipitation. Three RT of 30, 60, and 120 have been studied at pH=8.5 and 9.0. P concentration was measured frequently during the experimentation. A sample of crystal suspension was also collected every time and then filtered and dried for FTIR analysis. The samples have also been checked qualitatively for enlargement of crystals during reaction. The preliminary results of pilot study are presented in *Chapter 6* titled: "Pilot-Scale Study of Phosphate Precipitation Process from Synthetic Aerobic Sludge".

As a future study, the project of pilot plant will be continued by conducting several experiments for different Mg:NH_4:P molar ratios at various pH levels and retention times. In addition, the possibility of using $Ca(OH)_2$ as an economic pH adjustment reagent will be studied in pilot-scale. It will be also complemented with an in-depth analysis of the obtained precipitates to prepare the results for a further submission of the paper.

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Chapter 2

The Potential Phosphorus Crisis: Resource Conservation and Possible Escape Technologies: A Review

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2. The Potential Phosphorus Crisis: Resource Conservation and Possible Escape Technologies: A Review

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Abstract

Phosphorus is an essential nutrient for every organism on the Earth, yet it is also a potential environmental pollutant, which may cause eutrophication of water bodies. Wastewater treatment plants worldwide are struggling to eliminate phosphorus from effluents, at great cost, yet current research suggests that the world may deplete the more available phosphorus reserves by around 2300. This, in addition to environmental concerns, evokes the need for new phosphorus recovery techniques to be developed, to meet future generations needs for renewable phosphorus supply. Many studies have been, and are, carried out on phosphorus recovery from wastewater and its sludge, due to their high phosphorus content. Chemical precipitation is the main process for achieving a phosphorus-containing mineral suitable for reuse as a fertilizer, such as struvite. This paper reviews the current status and future trends of phosphorus production and consumption, and summarizes current recovery technologies, discussing their possible integration into wastewater treatment processes, according to a more sustainable water-energy-nutrient nexus.

Keywords: phosphorus; scarcity; nitrogen; wastewater; eutrophication; recovery

2.1. Introduction

Phosphorus (P) is a non-metal in the 15th group of the periodic table or “nitrogen family” and is one of the most indispensable materials for everyday life, affecting each and every organism on Earth. The elemental form of phosphorus can be mainly found in two different physical forms; white (or yellow) phosphorus and red phosphorus. These two allotropes have miscellaneous physical and chemical characteristics. White phosphorus, which is widely in the form P_4, has considerably high reactivity, due to its tetrahedral structure causing ring strain. On the contrary red phosphorus is present as polymeric chains (P_n) and due to that, shows more stability [1]. Red phosphorus can be transformed into white phosphorus by heating it up to 300 °C in the absence of oxygen, or under direct exposure to sunlight. Phosphorus, however, is never found free in its elemental form in nature due to its high reactivity; instead, phosphorus-containing minerals (mainly as phosphate) are dispersed worldwide, predominantly in sedimentary rocks. P-containing minerals may store notable amounts of phosphate, usually 15–20%. This leads to a phosphate rock P content close to 2.7–3.7% by weight (phosphate minerals comprise approximately 18.5% P by weight), which is remarkable, considering that the typical sedimentary rock only contains about 0.2% P (*w*/*w*).

Phosphorus is a vital component of all living organisms, as it is a building substance of DNA and RNA (in form of phosphate ion PO_4^{3-}), plays essential roles in energy transfer through living cells as a component of adenosine triphosphate (ATP) and, as phospholipids, contributes to the formation of cell membranes. Besides that, a considerable amount of phosphorus is contained in living beings’ bodies, mainly in bones and teeth, mostly as calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ [2]. Around 650 g of phosphorus can be found in the average human body [3]; only its calcium content, apart from the four organic elements of oxygen, carbon, hydrogen and nitrogen, is higher than that.

Phosphorus has no stable gaseous form and, because of this, only appears in the atmosphere adsorbed on particulate matter, which is rapidly removed from the atmosphere by precipitation, either wet or dry, processes. Therefore, the amount of P present in the atmosphere at any time is low. However, studies on the presence of phosphine (PH_3) gas, which is known as a trace atmospheric gas constituent, were recently carried out [4]. Phosphine is a volatile, toxic gas that can be found around the globe at different, usually very low, concentrations. This is due to the fact that this compound can be oxidized very easily in air [5]. While it is believed that phosphine may have an important role in the biogeochemical phosphorus cycle [4], there is still a need for more extended studies on its origins and impacts on such cycle. In soils, however, phosphorus is widely present in different forms; soluble, mineral, adsorbed and organic. The soluble fraction represents a very low percentage of total P, but it is the only form (free orthophosphate ions PO_4^{3-}) that plants and crops can use for growth. Insoluble P, which consists of organic and mineral P, is instead the dominant P form in soils: the dominance of aluminum/iron phosphates and calcium phosphate forms limits its solubility in acid and alkaline soils, respectively. Phosphate forms excreted by living organisms are released in soils as organic phosphates. These are then broken down to inorganic fraction by microorganisms during a long mineralization process. Activity of these microorganisms is highly dependent on soil temperature and moisture content. Hence, being the amount of soluble P in soils quantitatively negligible, total phosphorus (TP) is almost solely dependent on its mineral, adsorbed and organic fractions. In aquatic environments, to relatively low concentrations of Al/Fe/Ca ions, P ions are much more available than in soils. Industrial wastes, detergents and domestic sewage are considerable sources of phosphate ions to waters, therefore high available amounts of phosphate ions, could stimulate growth of plants and phytoplankton in water bodies.

This paper summarizes the most recent information about phosphorus use trends and resources forecasting and discusses some of the proposed technologies for recovery of this essential element from wastewater.

2.2. Phosphorus Rock Reserves

Phosphorus is distributed around the world mostly in the form of minerals contained in sedimentary rocks (very little is of igneous origin); however, high-quality deposits that are de facto economically exploitable are not homogeneously available. Sedimentary deposits are formed from a combination of physical and chemical conditions associated with coastal upwelling zones, coupled with geological sea level changes. The rare combination of these conditions makes phosphate deposits unevenly distributed around the world. As a result, "*few prospects exist for new discoveries of phosphate rock*" [6]. This is consistent with the very few significant increases in known P reserves in the last century, and only in a few locations in the world [7], as shown in Figure 2.1.

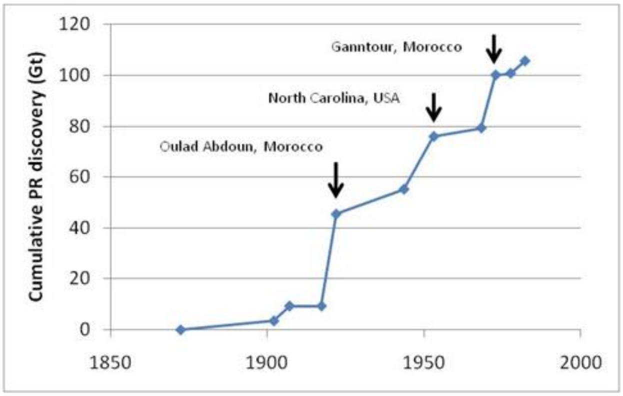

Figure 2.1. Discovery of phosphate rock reserves in the last century (based on [7]). The y-axis indicates the cumulative amount of P reserves discovered up to the year on x-axis.

The most common group of phosphorus-containing minerals is apatite. Apatite minerals are calcium phosphate compounds (5 calcium ions bonded to three phosphate ions) bonded to one of the F^-, Cl^- or OH^- ions, commonly known as fluorapatite, chlorapatite and hydroxyapatite. Among these, fluorapatite ($Ca_5(PO_4)_3F$) constitutes the largest amount of deposits of currently mined phosphate rocks. Phosphate rocks may contain some impurities, as well: of particular concern are cadmium and radionuclides including uranium and its decay products.

The application of phosphate-containing minerals can be categorized in two main streams: agricultural and nonagricultural. About 95% of all TP production around the world is utilized in the agricultural sector, mainly as fertilizers. Phosphorus and nitrogen are the two most important elements used in the inorganic fertilizers industry. In addition to fertilizers, P-containing minerals are also used in animal feed additives production.

In the nonagricultural sector, phosphorus is used in wide range of applications, from the food sector (as additives, i.e., polyphosphates) to actual industrial use, to preparation of household products. Soft drinks ingredients, detergents and cleansers, metal surface treatment and corrosion inhibition are just some examples of the many possible applications of this element. It is, however, important to emphasize that these constitute less than 5% of TP consumption in the world.

2.2.1. Current Phosphorus Production, Consumption and Resources

Phosphate rock as taken out of the ground, if it contains enough P to be considered as a usable source, is called ore. Ore is subjected to initial processing called beneficiation, which increases its purity: in a sedimentary phosphate ore, for example, beneficiation will remove much of the associated sand and clay. The resulting product is called phosphate rock (PR).

Traditionally, chemists used a weighting method for the determination of phosphorus content in fertilizers, in terms of P_2O_5. Nowadays, P content is still conventionally expressed in P_2O_5 equivalent: phosphate rock typically contains 30–32% P_2O_5 and, since P_2O_5 itself consists of 43.6% P, this range corresponds nominally to 13–14% P, by weight.

According to the International Fertilizer Association (IFA) [8] data, world total PR production in 2014 was around 197 Mt PR. Assuming a nominal 30% P_2O_5 content, this would correspond to about 26 Mt P, with the biggest share produced in East Asia (42%, mainly in China), followed by North Africa (Morocco) and North America (US), with 21% and 14% respectively. Figure 2.2 illustrates regional shares of PR production in 2014. In the late 1980s, a peak in PR mining was observed, due to an excessive fertilizers' use in the Soviet Union during those years, which was then followed by a considerable use decrease in the early 1990s (Figure 2.3). The latter occurred due to reduction of inorganic fertilizer use by developed countries, due to new awareness of phosphorus harmful effects on the environment, and especially to reduced fertilizers demand following the dissolution of the Soviet Bloc [9]. In the last decade, however, increased per-capita demand by developing countries due to dietary changes brought by increased generalized wealth, coupled with steady global population increase, has resulted in unprecedented levels of fertilizers production and consumption.

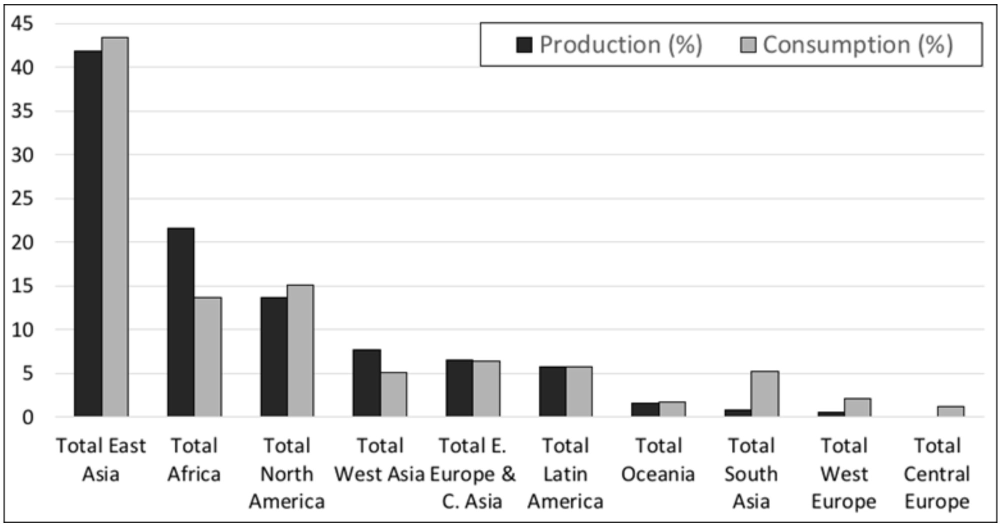

Figure 2.2.Global P production and consumption shares (based on [8]).

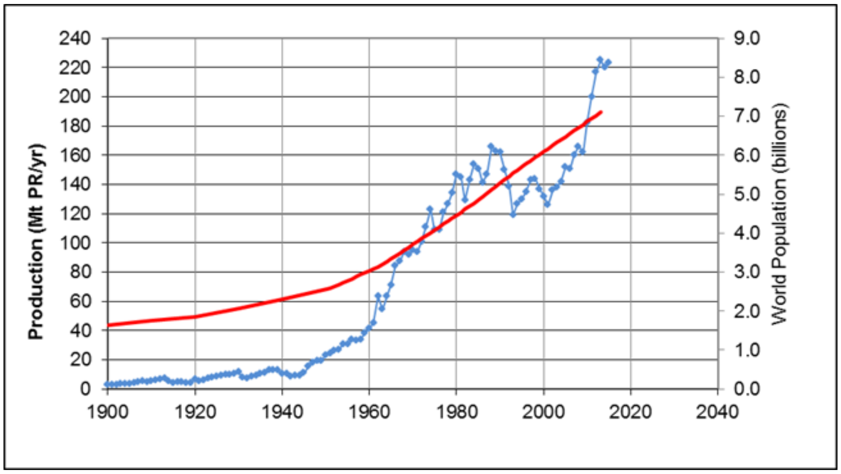

Figure 2.3. Global production of phosphate rock (blue) coupled with world population (red) in time [10].

World total phosphate rock reserves in 2014 (Table 2.1) were reported as 68,776 Mt (about 9000 Mt as P), of which 73% (50,000 Mt) just in Morocco and Western Sahara [11]. China currently holds the second biggest global reserves at 3700 Mt PR, which however represent only 5.4% of the world total. Figure 2.4 shows the geographical distribution of phosphate rock reserves [11]. Although total global phosphate resources are estimated at more than 300 billion tonnes, a great part of these are not available for extraction under current economic and technological conditions. For instance, deposits comparable to present Moroccan reserves have been detected in the continental shelves of the Atlantic and Pacific Oceans [12]; however, at the moment there is no economically profitable method for ocean mining, and the exploitation of these deposits remains prohibitive for reasonable consideration.

Table 2.1. PR production and reserves as beneficiated PR, 2014 data (based on [11]).

Source	**Production**		**Reserves**		**R/C**
	(Mt/yr)	**(%)**	**(Mt)**	**(%)**	**(yrs)**
Morocco & Western Sahara	30	13	50,000	73	1667
China	100	45	3,700	5.4	37
United States	25.3	12	1,100	1.6	40
MENA-M/WS*	25.7	12	8,166	12	318
Rest of the world	37.2	17	5,810	8	156
World total	218		68,776		315
As P**	28.6		9,005		

Mt = megatonnes = million metric tonnes = Tg. * Middle East and North Africa not including Morocco and Western Sahara. ** Assuming PR is 30% P_2O_5. NOTE: USGS data differ from IFA estimates [8] about total world PR production, however, data shown herein are internally consistent (i.e., are related to the same set).

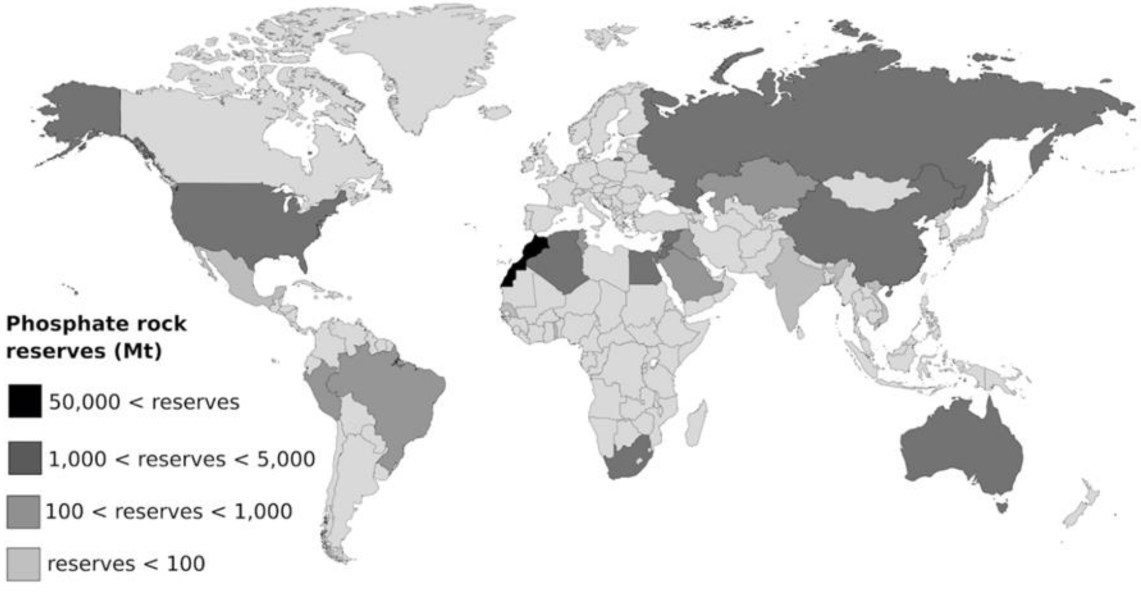

Figure 2.4. Geographical distribution of the world's known PR reserves (based on [11]).

North Africa, based on high production from its huge amount of reserves, has the highest export of phosphate worldwide, representing nearly 53% of all imports by other regions [8]. North America, in spite of a high production rate and a still considerable amount of reserves, is highly dependent on imports, due to the declining internal availability of PR and the Country's high consumption rate. Also, East Asian Countries, despite substantial amounts of PR production, have high consumption rates due to high population, which leads the region to import. Worldwide, however, Europe is the region most dependent on imports, which represent 86% of its total demand [8] since local production is very low. The uneven global distribution of reserves, production control and population growth could therefore potentially induce critical and unprecedented international tensions, when the perception of the "announced" P crisis will hit the public.

2.2.2. Future Trends

Phosphate rock is a finite, irreplaceable, nonrenewable resource [13]. The future trend of PR production and consumption and, consequently, the question of whether (and when) it will be totally depleted in the future, is currently one of the most controversial issues among researchers. As global population is expected to grow drastically, demand for phosphorus will increase due to the unavoidable need to produce more food. Nevertheless, there is still a huge amount of phosphate resources unexploited because of the lack of feasible and not over-expensive methods to extract them. Generally, there are two main views which address the issue of phosphorus scarcity [14].

The first view claims that the rate of consumption will eventually regulate the rate of reserve depletion, leading to a fairly static reserve situation. Forecasting approaches based on this assumption are the "ratio of reserves to consumption" (R/C ratio) to estimate the "lifetime" of available reserves. This of course assumes that both numerator and denominator are static, both of which are highly unlikely assumptions. Nevertheless, applying the R/C ratio could be useful as a general indication of *when* concern about resources could be warranted.

Before 2010 the R/C ratio for global phosphorus was estimated at just over a century [15]. However, in that year the International Fertilizer Development Center (IFDC) published revised estimates that were much larger than the previous [16]. According to some researchers, this "expansion" of reserve estimates does not have a strongly proven basis [17], nevertheless it has been accepted by most global institutions concerned. Accounting for the new estimates, the R/C ratio stands now at almost 300 years, a slightly reassuring figure. It might however be considered that any foreseen timeline for depletion, short of a very, very long time should be worrisome, and suggests that, at the very least, present wasteful use should be controlled, and actions for recovery researched and implemented.

Interestingly, the expanded estimate of global PR reserves is based largely on a paper published by the Morocco Phosphate Company, (OCP SA) [18]. It is, however, also interesting to note that, in 2006, the president and CEO of the same company stated: "*With the anticipated requirements for phosphate for agricultural and industrial uses, the world is likely to run out in the near future of low-cost recoverable phosphate rock*" [19].

Another forecasting approach, with underlying assumptions similar to the former, consists of the application of the Hubbert Curve [13]. This is based on the assumption that PR production will follow a Gaussian distribution, peaking when half of the reserves are consumed. This point is called "peak phosphorus". Cordell et al. [20] predicted that peak phosphorus would occur around year 2035. When the revised reserve numbers were included, the peak was extended only to around 2070. The peak phosphorus concept has been criticized from several points of view. Mew [21], pointed out that the Hubbert Curve is intended to be applied to resources, such as oil, for which there are other feasible alternatives. Thus, the method may be considered to be useful for modeling production from an individual source (such as one country), for which other countries may serve as alternative sources. Its application to global production, whether for phosphorus or oil, has never been scientifically validated. Vaccari and Strigul [22] show that the Hubbert curve worked when applied to USA PR production, but that the peak could not have been accurately "predicted" until after it had occurred! As Mew points out, these criticisms do not contradict the need to start a global discussion on how humanity could "*use the finite resources of phosphate that exist, in the most efficient way possible*." On the other side, the second approach criticizes the first one in some aspects. Primarily, it points out that this only considers PR proven reserves, and not other possible resources in estimating available phosphorus. Scholz and Wellmer [23] point out that resources that are unexploitable under current economic and technological conditions may become available in the future. While this cannot be denied *a priori*, it could also be said that, dealing with an irreplaceable and essential resource, it would be at least prudent to act on the basis of current conditions and available knowledge.

Both sides of the debate, however, recognize that phosphorus scarcity is not only dependent on just the rate of resources depletion. Other factors such as potential geopolitical instability of supplier countries, market price, time and effort it takes to extract phosphate rock, all of which lead PR to have highly variable value in the global society, are of great importance.

The historical trends of PR production should become clearer examining global production trends (Figure 2.3), from which the per capita production illustrated in Figure 2.5 can be derived. Some of the interesting historical events that become evident from Figure 2.5 are:

(1) There was a large per-capita PR increase after World War II through the 1970s, which could be attributed to the "green revolution" of the time;

(2) These high levels stabilized from 1975 to 1991 at an average of 30.1 kg PR per capita, per year;

(3) This was followed by a 24% reduction for reasons described in Section 2.1, to about 22.8 kg PR/cap/yr from 1993 to 2006;

(4) In the last decade, the per capita consumption recovered to about 31.0 kg PR/cap/yr. This may be due to improved diet in historically undernourished regions, and due to an increased amount of meat in the diet of nations such as China that have experienced rapid economic development.

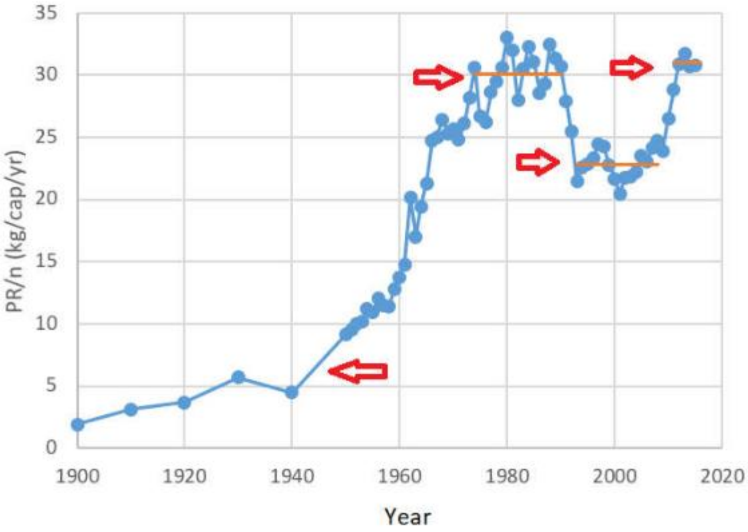

Figure 2.5. Historical trend for per capita phosphate rock production (based on [10]).

The world's population has been increasing approximately according to a linear trend for the last 50 years, adding between 70 and 87 million people per year onto the globe. Since 1997, the rate has been more stable, between 77 and 81 million people per year. Nevertheless, the UN estimates the annual population growth rate to decline steadily from this point forward. If the current level of per capita PR production rate is applied to the median UN population projection, the current reserves would last until the year 2315. However, if population growth rate continues to stay similar to the current rate (as forecasted in the UN "high" population estimate), they would only last until 2170.

There are reasons to be concerned about the short-term vulnerability of phosphorus supply, as well. Some of the major producers have an R/C ratio of only a few decades (Table 2.1). Specifically, two of the top three producers, China and the US, have an R/C ratio of less than 30 years. Thus, both can be expected to be running low of P in a similar time frame, when they will have to compete with each other for other sources, which are likely to include Morocco. Several investigators have looked at this situation on a country-by-country basis. Walan et al. [24] predicts that "exports will depend heavily on Morocco in the future." Cooper et al. [25] predicted that "*70% of global production is currently produced from reserves which will be depleted within 100 years*," and that "*Morocco, with nearly 77% of global reserves, will need to increase production by 700% by 2075 in order to meet most of this deficit*." The situation looks dangerously similar to that in which the world found itself at the inception of the first oil crisis, with the difference that also China is now a major economic and military powerhouse.

The data indicate that a crisis in phosphorus resources is not yet imminent. Nevertheless, P scarcity, whether it occurs decades or in centuries from now, would be catastrophic for humanity. Although all future scenarios involve substantial assumptions, these could go either way: the catastrophe could be forestalled, or the situation could become even worse. This risk suggests that society should begin now to modify current wasteful practices concerning management of P resources, especially given that many of these practices result in environmental problems that affect us still today.

2.3. Phosphorus Cycle

Potential interventions to conserve known phosphorus resources require an understanding of the P flow through modern agricultural ecosystem. As P cannot be found in the atmosphere, due to the lack of stable gaseous forms, its cycle involves mainly transfer of this element between rocks, water, soil, sediments and organisms.

In the natural phosphorus cycle (Figure 2.6), rocks release phosphate ions and other minerals due to weathering, these are then distributed into soil and water. In soils, phosphate is absorbed by plants, and subsequently uptaken by animals consuming the latter. Through the process of animal excretion (and decomposition of dead animals and plants), phosphate returns to the soil. Natural terrestrial ecosystems tend to recycle phosphorus many times before it washes out of the local environment. For example, Leopold [26] reports that an atom of phosphorus can be cycled locally about 47 times before being lost. Even after finding its way to aquatic water bodies, phosphorus may recycle between the water column and sediments repeatedly.

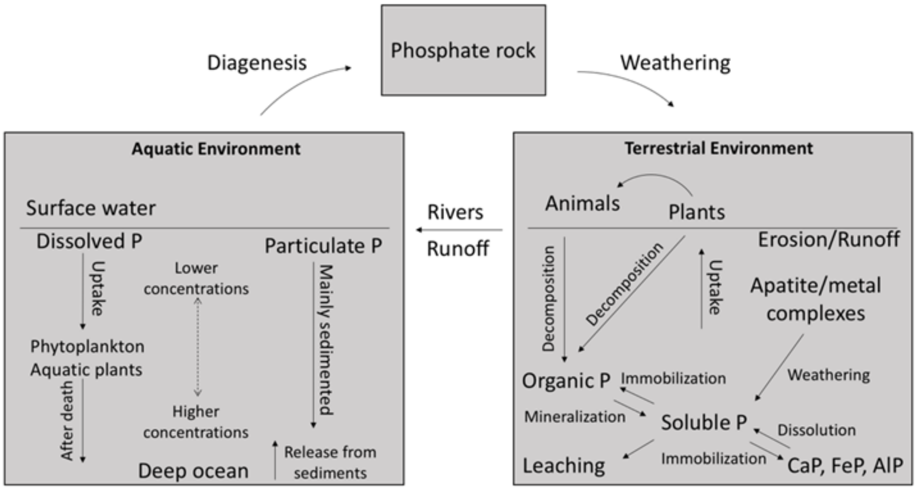

Figure 2.6. Natural phosphorus cycle in aquatic and terrestrial environments (based on [27,28]).

Eventually, phosphorus-containing substances flow to the ocean via rivers, estuaries and coastal waters. Other sources to the ocean include hydrothermal inputs and low-temperature reactions between sea waters and sea-floor. The phosphorus delivered into the oceans can be categorized in two forms; dissolved and particulate. Particulate phosphorus, due to high pH of seawater and its buffering property, is barely soluble and is found mostly sedimented on the bottom of the oceans and seas. Hence, it does not participate in the active phosphorus cycle until it is returned to the land by tectonic forces.

Dissolved phosphorus, once released into the oceans, is immediately absorbed by phytoplankton and aquatic plants, and therefore its concentration near the water surface is approximately zero. When phytoplankton and other organisms die, they sink transporting nutrients into deeper strata. Some may be sequestered in sediments, but a portion of them returns to the surface by upwelling currents along continental margins, where this phenomenon is favored by prevailing winds, creating as a consequence well-known fishery area, such as those off the western coast of South America and North Africa. It also results in higher P concentrations in coastal sediments, which would, in geologic time, lead to the formation of new, high-concentration phosphate rock (the existing formations are approximately ten to hundred million years old). Sedimented oceanic phosphorus may form again deep phosphate rocks during the process of diagenesis. This process is significantly slow, with a time scale of the order 10^8–10^9 years [28,29]: based on these considerations, the phosphorus cycle can be considered one of the slowest biogeochemical cycles among all elements.

2.3.1. Streamlining the Human P Cycle

Humans intervene in the phosphorus cycle by many ways. The anthropogenic phosphorus cycle resembles the natural one (Figure 2.7), except it uses only the higher concentration mineral phosphorus deposits (phosphate rock) more intensively. The total anthropogenic flux of phosphorus is about three times the natural flux, that is about 29 against 10 Mt/yr [9] and, in this accelerated cycle, only a negligible fraction of the phosphorus is recycled. In addition, the anthropogenic cycle, mainly targeted to the production of food for human consumption, significantly “leaks” phosphorus along the way, resulting in the fact that only about 16% of the mined phosphorus is consumed by humans, in the end. The most significant leaks are erosion and leaching from cropland, improper disposal of animal waste, and production of food waste, all of which could have negative environmental impacts. Targeted efforts at reducing P wastage could therefore potentially increase the duration of existing reserves by a factor of about 8.

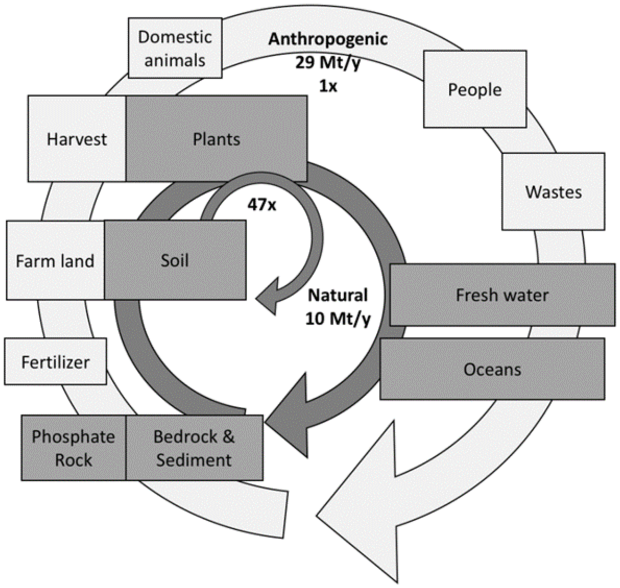

Figure 2.7. The natural and anthropogenic (agricultural) phosphorus cycles.

Reduction of food waste may have the potential to conserve significant amounts of phosphorus. Reducing losses from agricultural land could be equally important, but more difficult to achieve, as this is usually attempted by implementing voluntary Best Management Practices (BMPs), which are mainly aimed at the control of nutrients and pollutants (pesticides) leaching to surface waters. Losses via animal waste could be reduced either by reducing the incidence of meat consumption in human diet, or by more effectively recycling animal waste. Recycling could be applied at other parts of the cycle, such as from crop waste, harvest waste, food waste, and human waste.

Recycling of human wastes will be specifically discussed below. However, it should be understood that since only about 16% [11] of mined phosphorus is actually consumed in the human diet, even if 100% recycling of human waste could be attained, this would only reduce our dependence on mined phosphorus by 16%, as all the previous forms of environmental P leaching would not have been addressed. Nevertheless, even such a relatively small recovery and recycling of phosphorus could be an important intervention in the realm of global P consumption. Figure 2.8 shows the effect of human intervention on open phosphorus cycle (a) and how this cycle can be closed by applying phosphorus recovery processes for wastewater and sewage sludge (b).

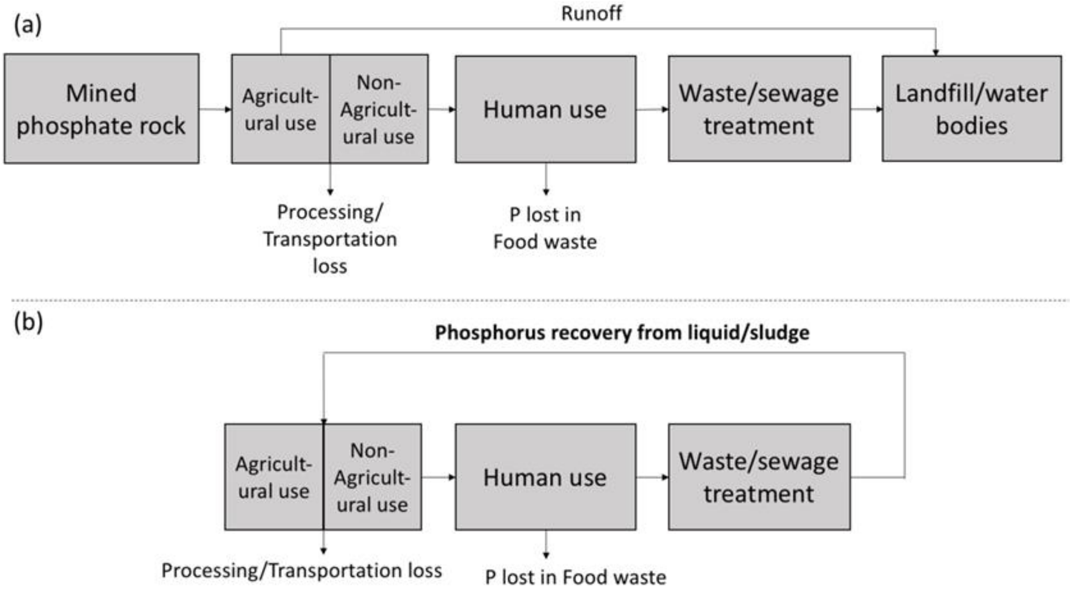

Figure 2.8. (a) Open phosphorus cycle, (b) Closed phosphorus cycle with recovery process (based on [3,30]).

2.4. Environmental Effects of Phosphorus Pollution

Mankind, breaking the natural phosphorus cycle, is releasing more phosphorus-containing wastes into the rivers and seas. The acceleration of natural cycle has already caused disastrous problems in aquatic and marine ecosystems, represented in primis by the eutrophication phenomenon.

In the presence of a high enough amount of phosphorus in surface waters, nitrogen will in fact temporarily become a limiting agent for aquatic plants and algae growth. In this case, nitrogen-fixing organisms such as bluegreen bacteria will start to overdevelop to bring back the system into an equilibrium with the increased amount of available P. Accumulated, internal water body loadings could maintain excessive phosphorus levels even after external pollution sources had been eliminated [31-33].

The produced, dead biomass often accumulates in the sediment of freshwater bodies, contributing in the long term to sediment oxygen demand, depleting oxygen content in the water column. In addition, large quantities of suspended photosynthetic biomass could cause large daily swings of dissolved oxygen (DO) and pH (linked to dissolved CO_2). In marine environments subject to nutrient runoff from coastal lands, biomass may settle into deeper layers, resulting in fast oxygen depletion (hypoxia) and acidification due to dissolved CO_2. All these effects are indicated under the term eutrophication and are considered a water quality degradation (pollution) issue that can induce additional negative ecological impacts. For this reason, at present, much effort is being devoted to the removal of N & P from wastewater discharges, especially in low exchange water bodies [34-36], as foreseen by current environmental protection regulations (in the EU, the Water Framework Directive, WFD). Such removal can occur both with physicochemical and biological processes [37,38] however, is it costly and perhaps not completely necessary in view of the new paradigms on wastewater management, stressing resource recovery according to circular economy principles [39-41].

In most cases, this is due to excessively high concentration of phosphorus in water bodies. "Harmful algal bloom" may also produce toxic, or taste-and-odor compounds, in drinking water sources.

Photosynthetic reactions remove carbonates from water. Potentially, alkalinity shifts to hydroxide form, raising the solution pH. For example, water with alkalinity of 100 mg/L $CaCO_3$ would theoretically have a pH of 11.3 if all carbonates were removed. In real systems, this may be buffered to a certain degree due to exchange of CO_2 with the atmosphere. During the night the opposite happens, as CO_2 is generated by algal respiration, lowering the pH. Such potentially significant pH swings could be detrimental to indigenous biota and may cause leaching of heavy metals from the sediments. In addition, high pH would cause ammonium to convert to the ammonia form, more toxic to fish.

In oceans (as well as in deep, stratified lakes) photosynthesis and respiration reactions are to some extent spatially separated. Photosynthesis occurs within the surface water layers, where light can penetrate. Phytoplankton then sinks where its degradation consumes oxygen and reduces pH. The low oxygen condition is known as hypoxia, and more popularly as "dead zone" if oxygen levels are low enough to stress or eliminate fisheries. Additionally, if deep waters are occasionally brought to the surface due to coastal upwelling, then the resulting low pH conditions can inhibit growth of organisms such as mollusks and crustaceans that form shells incorporating calcium carbonate.

2.4.1. Phosphorus Removal

The P issue is clearly a double-edged problem: it concerns both phosphorus potential resource depletion, and environmental pollution. As mentioned above, there are several interventions that could conserve phosphorus, reduce its discharge to the environment, or both. The focus henceforth should be on technologies and approaches allowing for recovery of phosphorus from wastewater and its byproducts.

Raw wastewater contains somewhere in the range of 4.0–16.0 mg P/L. About 20–30% of this is removed during conventional biological aerobic treatment without any use of specific P-removal processes though anabolic uptake (i.e., the incorporation of P in new cellular material). This would leave a nominal 3.0 to 12.0 mg P/L in treated effluents. However, due to recent environmental regulations, this removal rate is often not sufficient. Based on the European Water Framework Directive [42], P concentrations released in the environment from wastewater treatment facilities located in sensitive areas (i.e., those where discharge of excessive nutrients could originate severe basinwise water quality impairments—including eutrophication) have been identified as 1 or 2 mg/L depending on the facility's capacity.

The first phosphorus removal processes date back to the late 1950s when companies started to achieve this goal by using the only known method, chemical precipitation, which is still used substantially today. In chemical precipitation, P is removed by adding chemicals such as iron, aluminum or calcium salts to the wastewater. The salts precipitate as insoluble hydroxides, phosphorus is removed by a combination of co-precipitation and adsorption to the metal hydroxides. If combined with filtration, chemical methods can achieve effluent concentrations as low as about 0.05 mg P/L [43]; however, the precipitated P is bound in a sludge that necessitates of complex and expensive operations to make it recoverable and reusable.

From the mid-1960s researchers discovered that under certain conditions activated sludge can absorb phosphorus in excess of their needs [44]. Biological phosphorus removal was discovered and gradually introduced into common practice. If the wastewater contains a sufficient quantity of readily biodegradable organic matter, fermentation in an anaerobic zone produces volatile fatty acids (VFAs). A specific group of bacteria known as polyphosphate accumulating organisms (PAOs) uses the energy stored in intracellular polyphosphates to take up VFAs and convert them into intracellular organic storage compounds called polyhydroxyalkanoates (PHAs). Intracellular polyphosphates release orthophosphate (OP) into the mixed liquor, and P concentration increases within. An aerated zone downstream contains sufficient oxygen for the organisms to use PHAs for its energy requirements; at this point, PAOs take advantage of this 'substrate bounty' condition to regenerate their stores of polyphosphate, removing OP from solution in excess of actual requirements (this is in fact called excess, or 'luxury' uptake). Phosphorus in solution falls to low levels, below 1.0 mg P/L [44]. The organisms are then separated from the effluent and returned to the anaerobic zone, and the low-P solution is released as effluent. Biological phosphorus removal can consistently achieve nowadays, with properly managed processes, 75 to 93% reduction of effluent phosphorus.

Although biological processes may not remove P to levels as low as chemical processes, they have some advantages: there is no need of chemicals, the amount of sludge produced is lower than for chemical precipitation, and the biosolids that are produced are easier to utilize than chemical sludge.

These phosphorus-contained sludges were, and sometimes still are, transferred to landfills; however, this is forbidden by current legislation Europe-wide. Given the discussion in this paper, it would seem reasonable to modify processing technologies and direct these sludges to a recovery of phosphorus (and energy) in the form of products such as struvite ($NH_4MgPO_4 \cdot 6H_2O$), a mineral which can be utilized for fertilizer production.

2.5. Phosphorus Recovery

The most important difference between phosphorus removal and phosphorus recovery processes is that the former aims at obtaining phosphorus-free effluents from wastewater treatment plants (WRRFs), while the latter is focusing on phosphorus-containing by-products, which can then be reused for another purpose.

Phosphorus recovery technologies are mainly applied to industrial and urban wastewater, while there are few methods available for the livestock manure due to lack of suitable markets for processed manure, and the ready availability of low-cost alternatives (e.g., disposal) [45]. In the first case, recovery of phosphorus can be implemented in different stages of treatment, from the liquid to the sludge phase, and also from sludge post-treatment, such as incinerated sludge ash. Recovery rate from a liquid phase can reach up to a maximum of 40–50%, while in the sludge phase higher recovery rates of close to 90% can be achieved [46]. Figure 2.8 shows different possible locations for phosphorus recovery processes within a wastewater treatment plant. Table 2.2 shows a classification of commercially available technologies organized by type of waste treated and by type of technology.

Table 2.2. Known processes for phosphorus recovery from wastewater and sewage sludge (based on [50]).

Sludge type	Process name	Method	Products	Operational scale
Sludge liquor	P-ROC	Adsorption	CaP, CaP on CSH	Semi-industrial
	RECYPHOS	Adsorption	FeP	Semi-industrial
	PHOSIEDI	Adsorption	CaP	Lab scale
	PHOSTRIP	Precipitation	CaP	Full scale
	PRISA	Precipitation	Struvite	Semi-industrial
	CRYSTALACTOR	Pellets	CaP, struvite	Full scale
	PEARL	Pellets	Struvite	Full scale
Digested sludge	BERLINER VERFAHREN	Without leaching	Struvite	Full scale
	FIX-PHOS	Without leaching	CaP on CSH	Lab scale
	SEABORNE	With leaching	Struvite	Full scale
	STUTTGARTER VERFAHREN	With leaching	Struvite	Full scale
	LOPROX/PHOXAN	With leaching	Phosphoric acid	Full scale
	CAMBI	With leaching	FeP, AlP, CaP	Lab scale/ Full scale
	AQUA RECI	With leaching	FeP, AlP, CaP	Lab scale/ Full scale
	K REPO	With leaching	FeP	-
	SEPHOS	With leaching	AlP, CaP	Lab scale
	SESAL-PHOS	With leaching	CaP	Lab scale
	P ASCH	With leaching	Struvite	Semi-industrial
	BIOLEACHING	With leaching	Struvite	Lab scale
	BIO CON	With leaching	Phosphoric acid	Semi-industrial
Sludge ash	MEPHREC	Thermal treatment	CaP	Semi-industrial
	ASH DEC	Thermal treatment	Fertilizer	Semi-industrial

	THERMPHOS	Thermal treatment	Elemental phosphorus	Industrial process
	PHOSPHORUS INDUSTRY	Thermal treatment	Fertilizer	Industrial process

As accumulated polyphosphates accumulated in bacterial cells performing an enhanced biological phosphorus removal (EBPR) process can be released under anaerobic conditions, phosphorus can be recovered in a relatively efficient way from the supernatant of the side-stream recycled to the activated sludge process, the effluent after secondary sedimentation, or from the dewatering process after anaerobic digestion of sludge (location L1, L2, L3 in Figure 2.9). Recovery of phosphorus from wastewater streams is commonly achieved by precipitation/crystallization processes. Typically, the product of this process is in the form of calcium phosphate or magnesium ammonium phosphate hexahydrate (struvite), the latter a suitable mineral for fertilizer use. Struvite crystallization is one of the current leading technologies for P recovery, described in detail below. Recovery from the solid phase can also be achieved from the primary sludge, excess sludge after secondary sedimentation, the raw sludge before anaerobic digestion and the sludge before and after dewatering (locations S1–S5 in Figure 2.9). Crystals of struvite and calcium phosphate may also be obtained from sewage sludge or sludge ash with alternative processes: as an example, it is possible to recover P from sludge ash after incineration (location A in Figure 2.9), and this is actually the technology in which the most concentrated form of phosphorus will be obtained; 4–11% by weight comparable to phosphate rock with about 13% phosphorus content [47-49]. Phosphorus can be recovered from ashes by acid extraction or bioleaching. The phosphorus in the sludge ash can also be recovered in a fairly pure form as phosphoric acid or as white phosphorus using high-temperature thermal treatment processes [49].

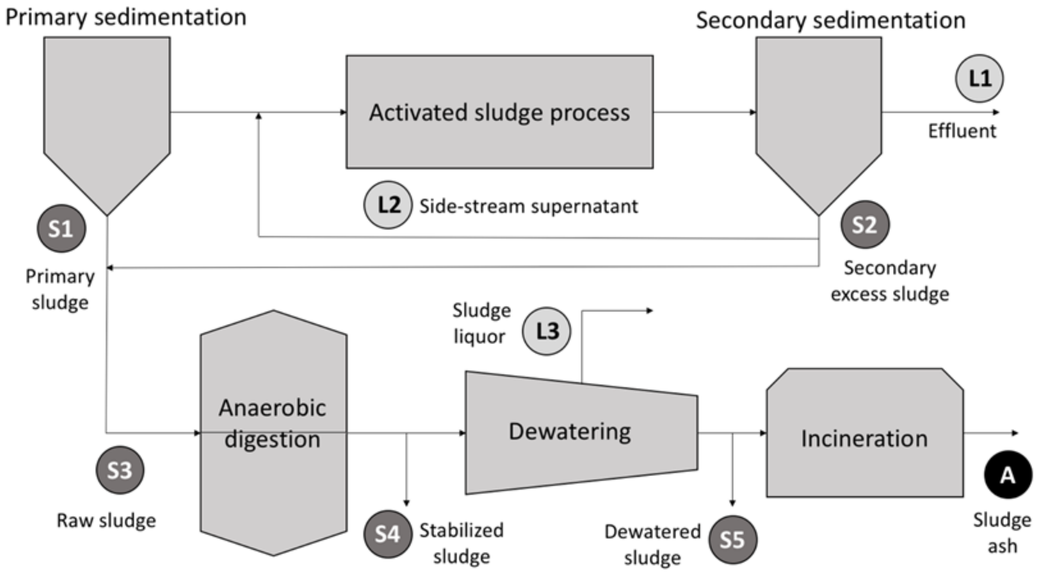

Figure 2.9. Possible phosphorus recovery locations in a conventional WRRF, S: Sludge phase, L: Liquid phase, A: sludge Ash (based on [30,46]).

2.5.1. Struvite Crystallization

Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4{\cdot}6H_2O$), or struvite, is a white mineral that can be naturally formed under certain conditions in sewer systems and WRRF conduits. In WRRFs it is often considered a nuisance, due to its potential for uncontrolled precipitation in undesired locations, such as in pipes, where it could form severe clogging [51]. This occurs typically in those parts of a WRRF where there is localized turbulence, for instance in pumps, aerators and pipes, due to pressure decrease and consequent release of dissolved CO_2. This will increase pH levels and, consequently, enhance chances of its formation [52]. Removal of struvite incrustations under these circumstances is quite expensive. Incidentally, it should be noted that struvite also precipitates in alkaline urine, forming one type of the kidney stones that may affect about 15% of the human population at one point in each individuals' life.

Struvite, however, can also be formed under controlled conditions in crystallization reactors, in which it is removed as small, fairly pure pellets. Low solubility, low metal content and the presence of both nitrogen and magnesium, which are also basic nutrient elements, make struvite suitable as a slow-release fertilizer.

The process of struvite crystallization is based on the following stoichiometric equations:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \quad (1)$$

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + H^+ \quad (2)$$

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + 2H^+ \quad (3)$$

In the pH range of struvite precipitation (pH 7–11) the reaction of HPO_4^{2-} is the dominant one [53]. Key factors in struvite formation are pH, magnesium concentration and presence of other competing ions, such as calcium, in the original solution. In most cases, the limiting agent in wastewater streams is magnesium, therefore it should be added to the process in the form of $MgCl_2$, $Mg(OH)_2$ or MgO to ensure its stoichiometric concentration. In addition to stoichiometry, an appropriate level of pH needs to be verified and, for this, addition of sodium hydroxide to the solution is the most common approach. Using added MgO or $Mg(OH)_2$ as a source of magnesium could also provide sufficient pH adjustment to the solution (due to the oxides' alkalinity) but their low level of solubility should also be considered as a drawback. The final product obtained, struvite, can be further used directly as a fertilizer (if it meets the requirements as certified fertilizer, based on EU criteria), otherwise it can be further processed by the fertilizer industry to overcome such limitations.

Struvite solubility product is in the range of 9.4–13.26 [54] and it can be precipitated within pH range 7–11 [53]. Increase in pH will decrease struvite solubility and hence enhance its precipitation potential [53]. One of the key obstacles on the way of precipitation is the presence of other competitive ions, particularly calcium (Ca^{2+}). This can lead to impurities in the final precipitate in the form of calcium phosphate salts. Studies suggest that in order to achieve effective precipitation the Ca^{2+}: Mg^{2+}ratio should be <1 [55] unless there is abundant concentration of ammonium in solution [56]. Many studies have been conducted on the effect of calcium co-precipitation on the process efficiency [55,57-59].

One of the advantages of struvite crystallization is that it can simultaneously remove phosphorus and nitrogen, in fact, this mineral typically contains 12% P and 5% N, by mass. A high efficiency of 80–90% can be achieved for soluble phosphorus recovery in the process. Struvite crystallization is mainly effective for waste streams with low solids content and relatively high phosphorus concentration ($P\text{-}PO_4 > 50$ mg/L). The hydraulic retention time of the process is usually less than 60 min, but high solid retention times (usually more than 10 days) are needed to allow sufficient crystal growth to achieve larger, well separated stones.

The crystallization process performance can be improved by introducing seed materials to the system [60,61]. The presence of seed materials such as white quartz sand and granite chips (with low solubility in alkaline conditions) improves crystals reaction rate and reduces reaction time. They also improve the nucleation process (crystal birth) of struvite if having sufficiently large surface area [60]. Struvite itself has been studied for application as a seed material, in order to improve the efficiency of the crystallization process [60,62,63]. Shih et al. [64] showed that under optimal operational conditions (e.g., pH and constituent ion molar ratios) and with proper dosage and size of seed material, up to 95.8% P recovery could be achieved. Nevertheless, using seed material may have its own drawbacks: implementation costs, phosphate ion selectivity, efficient settling, and separation are some of the challenges to overcome [60].

2.5.2. P Recovery by Assimilation

Adsorption and assimilation of phosphate by algae is another promising method for P-recovery from wastewater [65-67]. Photosynthetic algae use CO_2 and nutrients (NH_4^+, NO_3^- and PO_4^{3-}) for their growth, while producing oxygen. This is then utilized by heterotrophic bacteria for their metabolism thus producing NH_4^+, NO_3^- and PO_4^{3-} [60]. Algae have been applied in the aerobic ponds of wastewater treatment plants to deal with organic carbon and pathogenic pollutants removal [67-69]; however, their phosphorus removal was generally low [70], the main reason being that aerobic ponds are not optimized for biomass production [67]. Algal assimilation, nonetheless, could have a great potential for P-uptake under optimized conditions, as algal dry biomass can contain up to 3.3% P by weight [71]. El Hamouri [72] reported 63% P-removal by an algal pond. Light intensity, influent P concentration, pH, aeration, mixing rate and temperature are important factors for achieving high P recovery by algal biomass [60-67]. Microalgae are most widely used in these wastewater treatment systems. Harvesting of algae at the end of the treatment could be achieved by filtration, sedimentation or centrifugation: although, there are some successful examples of algae harvesting at the pilot scale, large-scale application of such systems is still challenging [60-69].

The big advantage of P recovery by algal assimilation is the value of the produced biomass. The harvested algal biomass can be used in different industries including slow-release fertilizers, animal food production, pharmaceuticals, food processing, etc. and can be a feedstock for liquid biofuels production, due to high lipids content [73].

2.5.3. Membrane Technologies

Phosphorus recovery using membrane technologies is relatively new, and still in a development phase. Membrane media have great potential in increasing concentrations of constituent ions in a solution for further precipitation of (for example) struvite and calcium phosphate compounds [60]. Reverse osmosis (RO), forward osmosis (FO), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and possibly a combination thereof could be used for simultaneous wastewater treatment and nutrient recovery. Generally, membrane technologies allow to obtain concentrated streams that could be subsequently subjected to a precipitation process for P recovery. Mg^{2+} and Ca^{2+} sources and pH adjustment methods would be required to achieve the initial conditions for the precipitation process, while the performance of these systems could be affected by several parameters. Influent quality, hydraulic load, salinity, membrane fouling (organic, inorganic, or biological fouling) are the most important ones [60,74].

Osmotic membrane bioreactors (OMBRs) are a novel approach for P recovery using membrane technologies [75,76]. The process is an integration of osmotically-driven membranes and biological treatment, which has been used recently for phosphorus recovery mainly in the form of amorphous calcium phosphate (ACP, $Ca_3(PO_4)_2{\cdot}xH_2O$) [75]. OMBR uses a non-porous osmotically-driven membrane instead of conventional porous MF or UF membranes under hydraulic pressure driving force [74,77]: the use of osmotically-driven membranes, such as FO membranes, has the advantage of an enhanced rejection, reduced fouling and lower costs [60,74].

Qiu and Ting [75] showed that >95% P could be recovered through this system. The system's performance, however, can be highly affected by salinity [75,78] and it has to be taken into consideration to achieve high efficiency. Integration of MF with FOMBR was studied by Qiu et al. [79], achieving >90% P recovery. Luo et al. [80] investigated an OMBR-RO system in combination with an MF for recovering P in the form of Ca-P compounds, obtaining 15–20 wt% P-containing precipitates. Ninety percent P recovery was achieved by Thing et al. [81] using a NF system and Hou et al. [82] obtained a remarkable 99% recovery by application of a NF and FO combination.

In spite of having demonstrated great efficiency and high P recovery rates, membrane systems have been developed solely at the laboratory scale. The feasibility of continuous operation of these membranes is still a challenge [60], since membrane performance will significantly decrease with deposit accumulation (fouling), requiring frequent cleaning and showing gradual loss of performance. High operational costs for the overall process (cleaning, maintenance and chemicals for precipitation) are still high, which make membrane technologies difficult to implement at large scale at the moment [60,74,76] although few studies could be found with effective results in pilot scale [83].

2.6. Considerations on the Energy-Nutrient Nexus in WRRFs

Wastewater treatment plants are essential facilities for the protection of the environment and public health; however, they are among the greatest public consumers of energy and resources in developed countries. It is in fact estimated that WRRFs are the single, most energy-intensive public operation in most towns of the developed world; up to 3–4% of the total electric consumption in the US has been related to the water cycle, including WRRFs [84]. In Australia, where most treatment plants are based on conventional activated sludge process, including aerobic sludge digestion with no energy recovery (no onsite biogas production), electric energy use for running these systems may total 80 kWh/capita-year [85]. In Europe, estimated optimized energy requirements (under current mainstream technology) are in the range 25–30 kWh/capita-year [86]. In addition, WRRFs also need large amounts of process materials (chemicals) during their lifespan. Recovery of materials and energy with appropriate technologies could therefore be a desirable, additional requirement for future, sustainable

WRRFs. By recovering N & P contained in wastewater, an equivalent amount of external fossil-fuel energy, which would be required for the production of equal amounts of fertilizing elements N and P by industrial processes, would effectively be saved, corresponding to 19.3 kWh/kg N (extracted by the Haber-Bosch process), and 2.11 kWh/kg P (processed from PR) [87]. Hence, supposing that just 50% of all human-consumed P worldwide (3.84 Mt P/year, excluding upflow losses) could be usefully recovered (1.92 Mt P/yr), this would translate both into direct recovery of an equal amount of limited P resources, and in the avoided consumption of about 4000 GWh of energy, roughly the same consumed in 1 month in the entire Switzerland.

Therefore, from a sustainability point of view, it is not enough to summarize the aim of a WRRF referring solely to nutrients recovery. Minimum energy consumption is of significant importance in order to meet sustainable development objectives. One of the possible approaches is to improve the efficiency of plants by implementing adequate control systems, replacing old inefficient equipment and performing energy conservation analyses of plants [88]. Mathematical models are of great interest for optimization of current systems [89,90] which can be a helpful tool for reducing energy consumption and maximizing resource recovery (in particular N and P). A good example of such approach can be found in Vaneeckhaute et al. [91] that developed a generic nutrient recovery model library in order to optimize nutrient (N, P) and energy recovery of treatment facilities with a focus on fertilizer quality and quantity. Batstone et al. [92] showed that there is a serious need of improvement on current physicochemical models for them to be applied for nutrients recovery purposes.

More progress was achieved in the last decade; however, in terms of on-site energy generation in WRRFs. On-site generation is the most favorable approach in order to move towards WRRF sustainability as the generated energy can be directly used by the plant itself, and by other facilities as well [93-95].

Bio-electrochemical systems (BES) including microbial fuel cells (MFC) and microbial electrolysis cells (MEC) are relatively new approaches for on-site energy generation and nutrients recovery. These have been investigated since approximately a decade; however, applications are limited to pilot scale due to high capital costs and technological limitations. Studies on nutrient recovery using BESs have been mostly focused on removal of nitrogen, with few studies on their potential for phosphorus recovery. The latter show, nevertheless, great prospects on the P recovery issue [96]. MFC systems that directly convert the chemical energy of the wastewater into electricity by means of microorganisms through the conventional oxidation/reduction process have been tested, with no or limited large scale applications [97,98]. MEC systems, on the contrary, could generate methane or hydrogen by applying an electric current to the organic materials. Power generation by MFC systems are typically between 10 to 100 mW/m^2 [99,100]. Hydrogen recovery using MEC systems has not been studied thoroughly and consequently there are no practical application for that so far.

In spite of problems and challenges of MFC and MEC systems application at the full-scale for on-site energy generation, they have shown potential of being beneficial. Sewage treatment using MFC systems in European Union could save up to 1 M tonne/year, and a considerable amount of sludge disposal costs [101,102]. Bio-electrochemical systems could also be implemented for the integration of energy and nutrients recovery: there have been, in fact, interesting studies on the possibility of phosphorus recovery in the form of struvite by MFC systems [92,103]. Studies suggest that phosphorus could be removed up to 82% by MFC systems, 40% of which it could be recovered as struvite [104]. Fischer et al. [103] used a three-stage single chamber MFC for phosphorus recovery, achieving 78% recovery in the form of struvite. MECs have also been used to that end: with a single-chamber MEC Cusick and Logan [105] were able to produce struvite at a rate of 0.3–0.9 g/m^2-hour. You et al. [106] investigated a two chamber MEC to achieve 97% phosphorus recovery by struvite precipitation. Despite the good results obtained by these systems on treatment efficiency; however, their main remaining drawback is the high capital cost per unit of energy produced [60,107].

2.7. Conclusions

Although phosphorus resources are apparently abundant, they are not unlimited by any means. It can be reasonably anticipated that future generations may at some point find these resources to reflect a much more critical situation than the one currently perceived. It is clear that current agricultural practices waste a large amount of these resources, since only 16% of the total are effective for their planned use. Not only this is critical towards long-term sustainability of this element, but these wasteful practices also result in high levels of pollution that harm water supplies, fisheries and ecosystems balance even today. Taken together, these concerns should produce a strong moral and economic incentive to conserve phosphorus. Recovery from wastewater streams is one approach that could contribute to the improvement of current practices. Some proposed technologies were illustrated in the paper; notwithstanding the current limitations of some of them, it could be expected that they may, in a few years, reach a level of industrial maturity for full-scale application.

2.8. References

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Chapter 3

Simulations and Laboratory Tests for Assessing Phosphorus Recovery Efficiency from Sewage Sludge

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3. Simulations and Laboratory Tests for Assessing Phosphorus Recovery Efficiency from Sewage Sludge

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Abstract

Phosphorus is a potential environmental pollutant, which could lead to the eutrophication of water bodies. For this reason, wastewater treatment plants worldwide are often designed and operated to eliminate phosphorous from effluents, at substantial cost. At the same time, phosphorus is an essential nutrient for agriculture and, consequently, human life. Data seem to suggest that the world will run out of phosphorus by around 2300, in the best-case scenario, although even shorter estimates exist. This situation evokes the need for more efficient phosphorus recovery technologies, in order to meet current water quality requirements and—at the same time—critical future phosphorous needs. Chemical precipitation is the main process for achieving a phosphorus-containing mineral suitable for reuse as a fertilizer, where Struvite is an example of such a product. In this study chemical equilibrium of struvite precipitation was simulated using US Geological Survey (USGS)' PHREEQC model, and results were compared to laboratory precipitation tests to evaluate struvite recovery efficiency under various conditions. pH had the most significant effect on the results and P recovery of >90% was achieved at pH = 9.5. Simulations indicated that struvite precipitation is affected by the presence of Amorphous Calcium Phosphate (ACP) and calcite in the final product of the process. The model showed great potential for predicting equilibrium conditions and could be very helpful for future optimization of the process.

Keywords: mineral phosphorous; scarcity; wastewater; precipitation modeling; struvite

3.1. Introduction

Potential environmental effects of phosphorous in surface waters are well known: the most important is eutrophication, that is, the excessive growth of aquatic plants, algae and photosynthetic bacteria such as cyanobacteria (often incorrectly called blue-green algae), most often controlled by the high concentration of this nutrient in a water body. In addition to the aesthetic damage, eutrophying organisms may produce toxic or taste-and-odor compounds into sources of drinking water, requiring additional treatment [1]. Dead photosynthetic biomass will settle, leading to accumulation of organic matter and phosphorus storage into sediments, which could contribute to future sediment oxygen demand (SOD), or cycle between water column and sediments in a phenomenon known as internal loading, which could maintain excessive phosphorus levels in a water body even after external pollution sources have been eliminated [2-4]. Large daily swings in dissolved oxygen (DO) concentrations and pH (due to complementary swings in dissolved carbon dioxide concentrations) could also be due to excessive amounts of floating photosynthetic biomass. Lakes are the water bodies most frequently affected by this phenomenon [5-8]. In aquatic environments, based on relatively low concentrations of Al, Fe and Ca ions, P is much more available than in soils, where the soluble fraction represents a very small part of total P (TP), but is the only form of phosphorus (free orthophosphate ions PO_4^{3-}) that plants are able to assimilate for growth. Since this amount is quantitatively negligible, TP in soils consists almost solely of the adsorbed and organic fractions of the mineral. Where mandated, removal of N & P from wastewater discharges can occur both with physicochemical and biological processes [9,10]. This process is costly, and perhaps not completely necessary in view of the new paradigms on wastewater management, stressing resources recovery principles [11-13]. In this study, chemical equilibrium modeling of struvite precipitation was conducted to evaluate its behavior in the presence of constituent ions, the presence of Ca^{2+} as a competitive ion and variable pH and compared to laboratory experiments.

3.2. The Phosphorus Resources Issue

In a recent paper, Daneshgar et al. [14] summarized and commented on the most recent information about P use trends and resources forecasting. About 95% of all phosphorous production in the world is used in the agricultural sector, mainly in fertilizers: aside from P, only nitrogen has such an important role in the inorganic fertilizers industry. Almost the totality of Phosphate is taken out of the ground as ore, which, after processing to remove impurities (sand, clay etc.) is called phosphate rock (PR). PR typically contains 13–14% P by weight.

World total PR production in 2014 was around 197 Mt, which, assuming nominal contents, would correspond to about 26 Mt P [15]. World total PR reserves in 2014 (Table 3.1) were reported as 68,776 Mt (about 9000 Mt as P) with a 73% share stored in geological deposits located in Morocco and Western Sahara. Estimated total global phosphate resources, on the other hand, are more than 300 billion tonnes [16], the great part of which are not suitable for extraction under current economic and technological conditions, since they are located in the continental shelves of the Atlantic and Pacific Oceans, with no economically profitable method for their exploitation. It should be noted that, in addition to the specific issues examined in this paper, the high geographical concentration of these resources is also liable to create issues related to the security of their supply in case of sudden sociopolitical changes.

Table 3.1. PR production and reserves as beneficiated PR, 2014 data ([14]).

Source	**Production**		**Reserves**		**R/C**
	(Mt/yr)	**(%)**	**(Mt)**	**(%)**	**(yrs)**
Morocco & Western Sahara	30	13	50,000	73	1667
China	100	45	3,700	5.4	37
United States	25.3	12	1,100	1.6	40
MENA-M/WS*	25.7	12	8,166	12	318
Rest of the world	37.2	17	5,810	8	156
World total	218		68,776		315
As P**	28.6		9,005		

Mt = megatonnes = million metric tonnes = Tg** Assuming PR is 30% P_2O_5.
* Middle East and North Africa not including Morocco and Western Sahara.

Phosphate rock seems thus to be a finite, irreplaceable, nonrenewable resource. The question is therefore whether (and when) it will be totally depleted in the future, although overall data indicate that a crisis in phosphorus resources is not yet imminent. According to some researchers from the International Fertilizer Development Center (IFDC) the current ratio of “serves to consumption” stands now at almost 300 years [17], however, if population growth rate continues at the current rate (as forecasted in the UN “high” population estimate), they could only last until 2170 [18].

P scarcity, whether decades or centuries from now, would be catastrophic. Such a risk suggests that mankind should begin immediately to modify current wasteful practices concerning phosphorus resources management, especially since many of these practices result in environmental problems seriously affecting us today. Humanity, in fact, intervenes in the global P cycle in many disrupting ways: the anthropogenic P cycle, while resembling the natural one (Figure 3.1), induces a more intense use of this resource, with a flux that is about three times the natural one [19], and a negligible fraction actually recycled. In addition, the cycle, mainly targeted to the production of food for human/animal consumption, shows significant “leaks” of material (e.g., erosion and leaching from cropland, improper animal waste disposal, food waste, etc.) along the way, resulting in only about 16% of the original quantities being put to effective use. Efforts at reducing P wastage could potentially increase the duration of existing reserves by a factor of up to six.

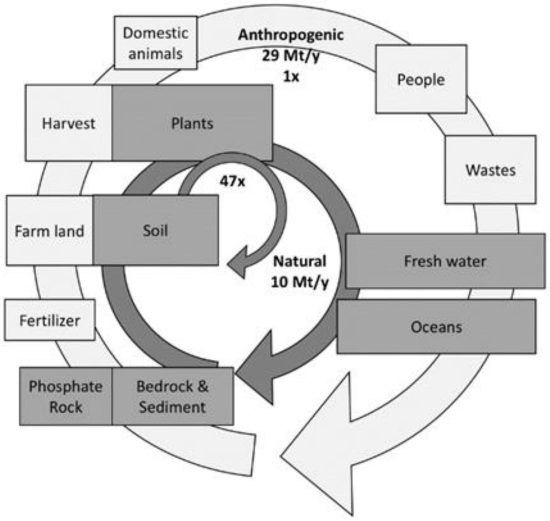

Figure 3.1. The natural and anthropogenic (agricultural) phosphorus cycles.

Phosphorous Waste Reduction and Recovery

The issue is clearly double-edged: it concerns P resources depletion and environmental pollution due to its excessive dispersion in the environment. As mentioned, there are a number of interventions that could conserve phosphorus, reduce its dispersion, or both. Reduction of food waste could potentially help in conserving it in significant amounts. Reducing losses from agricultural land would also be an important goal, though more difficult to implement, as this is currently mandated to voluntary Best Management Practices (BMPs) aimed at the control of nutrients leaching into surface waters. Losses via animal waste could be reduced either by reducing the incidence of meat consumption in the human diet, or by more effective recycling strategies for animal waste. Recycle could be applied to other parts of the cycle, such as crop waste, harvest waste, food waste, and human (bodily) waste.

Recycling the P fraction contained in human wastes will affect, however, only about 16% of mined phosphorus, even if 100% recycling of this stream could be achieved. Raw wastewater contains somewhere in the range of 4.0–16.0 mg P/L. About 20–30% of this is removed during conventional biological treatment, which would leave a nominal 3.0 to 12.0 mg P/L in treated effluents. Enhanced chemical precipitation, combined with filtration, could achieve effluent concentrations as low as about 0.05 mg P/L [20], resulting, however, in a form of precipitated P bound in a sludge that would necessitate complex post-treatment to make it recoverable and reusable. It would therefore seem reasonable to modify processing technologies and direct these sludges to P (and energy) recovery in the form of products such as struvite ($NH_4MgPO_4{\cdot}6H_2O$), a mineral which can be utilized for fertilizer production.

3.3. Phosphorus Recovery Technologies

The most important difference between P-removal and P-recovery processes is that the former aim at obtaining phosphorus-free wastewater treatment plant (WRRF) effluents, while the latter is focusing on creating P-containing by-products, which can then be reused for other purposes, mainly in the fertilizers' industry. P-recovery technologies are mainly applied to industrial and urban wastewater, while there are few available methods applicable to livestock manure [21,22]. Recovery rate from liquid phase wastes can reach up to a maximum of 40–50% (with respect to the wastewater influent), while in sludge phase rates close to 90% could be achieved [21]. Figure 3.2 shows different possible locations for P-recovery processes within a wastewater treatment plant. Table 3.2 summarizes commercially available technologies, organized by type of waste treated and technology.

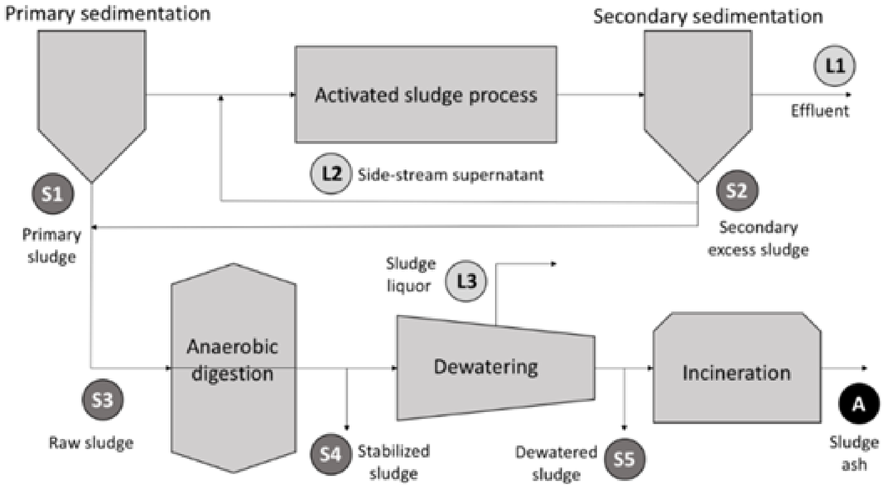

Figure 3.2. Possible phosphorus recovery locations in a conventional wastewater treatment plant (WRRF) (based on [21,23]).

Table 3.3. Some commercially available technologies for P recovery (from [14])

Sludge type	Process name	Method	Products	Operational scale
Sludge liquor	P-ROC	Adsorption	CaP, CaP on CSH	Semi-industrial
	RECYPHOS	Adsorption	FeP	Semi-industrial
	PHOSIEDI	Adsorption	CaP	Lab scale
	PHOSTRIP	Precipitation	CaP	Full scale
	PRISA	Precipitation	Struvite	Semi-industrial
	CRYSTALACTOR	Pellets	CaP, struvite	Full scale
	PEARL	Pellets	Struvite	Full scale
Digested sludge	BERLINER VERFAHREN	Without leaching	Struvite	Full scale
	FIX-PHOS	Without leaching	CaP on CSH	Lab scale
	SEABORNE	With leaching	Struvite	Full scale

	STUTTGARTER VERFAHREN	With leaching	Struvite	Full scale
	LOPROX/PHOXAN	With leaching	Phosphoric acid	Full scale
	CAMBI	With leaching	FeP, AlP, CaP	Lab scale/ Full scale
	AQUA RECI	With leaching	FeP, AlP, CaP	Lab scale/ Full scale
	K REPO	With leaching	FeP	-
	SEPHOS	With leaching	AlP, CaP	Lab scale
	SESAL-PHOS	With leaching	CaP	Lab scale
	P ASCH	With leaching	Struvite	Semi-industrial
	BIOLEACHING	With leaching	Struvite	Lab scale
	BIO CON	With leaching	Phosphoric acid	Semi-industrial
Sludge ash	MEPHREC	Thermal treatment	CaP	Semi-industrial
	ASH DEC	Thermal treatment	Fertilizer	Semi-industrial
	THERMPHOS	Thermal treatment	Elemental phosphorus	Industrial process
	PHOSPHORUS INDUSTRY	Thermal treatment	Fertilizer	Industrial process

Accumulated polyphosphates in bacterial cells performing an Enhanced Biological Phosphorous Removal (EBPR) process can be released under anaerobic conditions, so phosphorus could be recovered from the supernatant of the side-stream recycle to the activated sludge process (L2), the effluent after sedimentation (L1), or from the dewatering process after sludge digestion (L3). P recovery from wastewater streams may be achieved by precipitation/crystallization processes: struvite (magnesium ammonium phosphate hexahydrate) crystallization is one of the current leading technologies for P recovery. Recovery from the solid phase could also be achieved from primary sludge (S1), excess secondary sludge (S2), the raw sludge prior to anaerobic digestion (S3) and sludge before and after dewatering (S4, S5). Struvite and calcium phosphate may also be alternatively obtained from sewage sludge or sludge ash: as an example, it is possible to recover P from incinerated sludge ash (A, in Figure 3.2). This is actually the technology that will yield the most concentrated form of phosphorus: 4–11% by weight, comparable to PR (about 13% P) [24].

Chemical precipitation methods and in particular, the struvite precipitation process, are variably efficient methods for recovery of P from wastewater. Precipitation may produce a high-quality mineral that could be further used as a fertilizer, and generally has low metal content compared to raw sludge. However, some disadvantages in this method are present as well. The process may need substantial amounts of Mg^{2+}added to the system, since this element is usually present at insufficient concentrations in typical wastewater streams [25,26], and that would significantly increase costs. In addition, also the cost of added NaOH, necessary to control the pH level, may be considerably high [26]. Although struvite would have an added value as a fertilizer product, the offset in costs may not be yet high enough to justify process implementation at large scale, under current conditions [26]. At the moment, in fact, there are only a handful of full-scale plants worldwide using this technology. Furthermore, obtaining pure struvite as a final product could still be a challenge, as shown by the experimental results of this study, and specific regulations must be met for a struvite product to be used as a fertilizer. Struvite could in fact still contain some unwanted contaminations due to the presence of heavy metals, pathogens and pharmaceutical residues [27,28,29].

Other technologies that could be applied to P recovery have also been proposed recently. Assimilation is an example, consisting of the adsorption of phosphate by algae. Usually, microalgae are good candidates for this process, applied through an old technology, such as the so-called aerobic pond. However, due to the non-optimized biomass production in aerobic ponds, P recovery rate with this method is limited, and maxima of up to around 60% of P recovery could be achieved in practice [30]. A major advantage of the assimilation concept, however, is the production of high-value biomass that can be further used in different industries (biofactories/biorefineries) [31].

Lately, the use of membrane technology was proposed as another method for P recovery. This could be used in combination with chemical precipitation, since membrane media might promote precipitation by concentrating the necessary ions in their retentate [32]. Osmotic membrane bioreactors (OMBRs), in particular, are part of a newly developed technology that could be applied to P recovery. While so far it has been applied mostly for P recovery in the form of Amorphous Calcium Phosphate (ACP) [28], this method has a potential for P recovery up to 95% [33]. Recovered ACP appears to have potential as a fertilizer source without further chemical processing, such as the acid treatment typically used to process phosphate rock. Plants fertilized with recovered ACP showed P uptake responses almost as good as for triple superphosphate (TSP, one of the first P-based fertilizers widely used in the 20th century, [$Ca(H_2PO_4)_2 \cdot H_2O$], now less popular in use than other fertilizers). As systems' performance may be affected by many environmental factors such as salinity, membrane fouling, hydraulic load, and so on [34], their assessment is still under progress.

Struvite Crystallization

Struvite can form under controlled conditions in crystallization reactors, from where it is removed as small, fairly pure pellets. It might also take place spontaneously in different locations of a wastewater treatment facility with undesired consequences (i.e., clogging of pumps, pipes and valves) [35]. The initial concentration of P determines whether struvite formation is possible, due to its limited solubility product. The process of crystallization is based on the following stoichiometric equation:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O \downarrow \tag{1}$$

However, phosphate in solution could also be present in HPO_4^{2-} and $H_2PO_4^-$ forms that can contribute to struvite formation according to Equations (2) and (3):

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O \downarrow + H^+ \quad (2)$$
$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O \downarrow +2H^+ \quad (3)$$

In practice, Equation (2) is dominant in the favorable pH range 7–11 for struvite formation [36]. Solution's pH influences P forms and dominant crystal type. Struvite crystal are possible at the above pH value range, otherwise, at a higher values $Mg_3(PO_4)_2$ or $Mg(OH)_2$ could be formed. All reactions, and in particular the reaction of HPO_4^{2-}, should be taken into account while examining struvite precipitation. Important factors affecting this process are pH, concentrations of mineral constituents and presence of competitive ions, most notably Ca^{2+} that could reduce the size of struvite, modify crystal growth, or delay the nucleation rate and the growth rate of crystals [37].

The mechanism of crystallization can be divided into three steps: nucleation (formation of small crystals of struvite), crystal growth (development of the small sized crystal into larger ones), and aggregation (a number of crystals come together and forming clusters) [38]. Studies on the kinetics of struvite precipitation suggested that the three steps above can all be formulated empirically as a function of supersaturation ratio of struvite [38]. This is basically the ionic activity product (*IAP*) of constituent ions in the solution, over its equilibrium solubility product or K_{sp}. A solution is supersaturated when ionic concentration is above its equilibrium level, and consequently struvite precipitation may occur to bring back the system into equilibrium conditions. Equation (4) formulates the "Saturation Index (*SI*)" concept, which is the logarithm of a system's supersaturation ratio [39]:

$$IAP = \{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\} \quad (4)$$
$$SI = \log(\frac{IAP}{K_{sp}}) \quad (5)$$

Struvite solubility product is in the range of 9.4–13.26 [40], and it can precipitate in the pH range of 7–11 [41]. An increase in pH will decrease struvite solubility. One of the key obstacles on the way of obtaining pure struvite precipitation is the presence of competitive ions, and particularly calcium (Ca^{2+}), which could lead to the presence of impurities in the final precipitates (calcium phosphate salts).

3.4. Materials and Methods

For this study, sludge samples were collected from the Nosedo (Milan, Italy) wastewater treatment plant (WRRF), the largest in northern Italy (with average daily flow rate of 432,000 m^3) , and the main one among those serving the city of Milan, with capacity of 1 million p.e. and an annual sludge production of 50,000 tons/year. The estimated phosphorus content of this sludge is at least 1400 tons/yr. The Nosedo facility has suffered from a chronic organic underloading condition since the beginning of its operation, due to excessive dilution of the incoming wastewater, originated by infiltration/inflow phenomena of ground (high piezometric levels) and surface (sewage collectors undercross in several points local streams) waters in the combined sewer collectors. It has four parallel process lines, with nitrification and denitrification/oxidation tanks. The facility does not have an anaerobic sludge treatment line but relies on an extended aeration process to limit its production.

Samples were taken from one of the activated sludge system oxidation tanks, where a higher P concentration is normally observed, due to its release after being under anaerobic condition for 1-2 days, therefore creating higher potential for struvite precipitation. Table 3.3 summarizes the main characteristics of the samples in terms of relevant ionic content for struvite crystallization.

Table 3.3. Wastewater filtrate sludge characteristics.

Ion	Concentration (mg/L)
Ca^{2+}	101
Mg^{2+}	26.4
P	40.3
NH_4^+	32.6
pH	7.6

Investigation of the thermodynamics and kinetics of struvite precipitation was tested both experimentally on the samples collected, and theoretically assessed with application of chemical equilibrium modeling. The advantage of using verified modeling tools over experiments, besides the faster and time efficient process, lies in their capability to predict equilibrium conditions and ion speciation, based on initial conditions. In this study, the PHREEQC model, an established geochemical modeling tool developed by US Geological Survey (USGS) was used [42]. PHREEQC is capable of performing a wide variety of aqueous equilibria calculations, such as ion speciation batch-reactions, and saturation index (SI) values calculations based on solution characteristics (ionic concentrations, pH, etc.) as input. Version

3.0 of the software was used herein to model the chemical equilibria of the struvite precipitation process. Results were then validated by comparing them with actual laboratory precipitation tests.

3.4.1. Model Description

PHREEQC contains multiple databases that include different chemical species, their corresponding reactions, and the solid phase products that could precipitate as final outcome. The default model database was used in this work, however, as this was not initially optimized for the study of struvite precipitation; it needed modification to describe specific reactions. First of all, struvite itself, for instance, was not defined as a default possible final solid phase reaction product, and hence needed to be explicitly included. Table 3.4 summarizes the final list of possible solid phases that may precipitate in such systems, with their corresponding K_{sp} values. Some of these were added to the initial database, others needed to be removed, as they were highly unlikely to precipitate in the foreseen experimental conditions (e.g., pH levels). For example, magnesium phosphate compounds, other than struvite, were removed from the database, as well as transformations that are known to be extremely slow compared to the operating conditions timescale, and thus also unlikely to precipitate, such as tricalcium phosphates and hydroxyapatite (HAP). Octa-calcium phosphate (OCP) was also removed due to the low pH level (5–6) required for its precipitation [43]. ACP and monetite were the only two calcium phosphate compounds kept in the database. Two main carbonate compounds could form in the system; calcite ($CaCO_3$) and magnesite ($MgCO_3$). Calcite was maintained in the database; however, magnesite was removed due to the high pH (>9.5) required for its precipitation in substantial amounts [44].

Table 3.4. List of solid phases and reactions present/added to the PHREEQC database.

Solid phase	**Representative reaction**	**Operating condition**	**pK$_{sp}$ at 25°C**
Struvite (A) (B)	$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4.6H_2O$	7 <pH< 11	13.26
Newberyite (A)	$Mg^{2+} + HPO_4^{2-} + 3H_2O \leftrightarrow MgHPO_4.3H_2O$	High Mg^{2+}/P, pH<6	5.8
Bobierrite (A)	$3Mg^{2+} + 2PO_4^{3-} + 8H_2O \leftrightarrow Mg_3(PO_4)_2.8H_2O$	Days to precipitate	25.2
Hydroxyapatite (HAP)	$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$	Slow formation from ACP, DCPD	44.3
Tricalcium phosphate (TCP)	$3Ca^{2+} + 2PO_4^{3-} \leftrightarrow Ca_3(PO_4)_2$	Slow formation from ACP, DCPD	32.63
Octacalcium phosphate (OCP) (A)	$8Ca^{2+} + 2HPO_4^{2-} + 4PO_4^{3-} \leftrightarrow Ca_8(HPO_4)_2(PO_4)_4$	Hydrolysis of DCPD at pH =5-6	36.48
Monetite (DCP) (A) (B)	$Ca^{2+} + HPO_4^{2-} \leftrightarrow CaHPO_4$	Fast formation from ACP, DCPD	6.81
Brushite (DCPD)	$Ca^{2+} + HPO_4^{2-} + 2H_2O \leftrightarrow CaHPO_4.2H_2O$	pH<7	6.6
Amorphous calcium phosphate (ACP) (A) (B)	$3Ca^{2+} + 2PO_4^{3-} + xH_2O \leftrightarrow Ca_3(PO_4)_2.xH_2O$	pH>6	25.46

Calcite [B]	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$	Stable at 25°C and atmospheric P	8.42-8.22-8.48
Magnesite	$Mg^{2+} + CO_3^{2-} \leftrightarrow MgCO_3$	Stable at pH<10.7	7.46-8.2
Brucite	$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2$	pH>9.5	11.16
$Ca(OH)_2$	$Ca^{2+} + 2OH^- \leftrightarrow Ca(OH)_2$	pH>9.5	5.2

[A] Added to original database.

[B] Kept in the final database for modeling.

Key operating factors in struvite formation are pH level, magnesium concentration and presence of other competing ions, especially calcium. In most cases, the limiting agent in wastewater streams is magnesium, therefore it could be added to the process in the form of $MgCl_2$, $Mg(OH)_2$ or MgO to ensure its stoichiometrically correct concentration. In addition to stoichiometry, the solution must possess an appropriate pH level. For this, addition of sodium hydroxide (NaOH) is the most common approach. Using added MgO or $Mg(OH)_2$ as a source of magnesium could also provide sufficient pH adjustment to the solution (due to oxides' alkalinity) but their low level of solubility should also be considered.

3.4.2. Experimental Setup

Chemical precipitation tests were performed in triplicate in the laboratory using 200 mL mixed beakers in a jar test apparatus. A NaOH solution was used to adjust the beakers' content to the required pH (at 8.5, 9.0, 9.5). The pH range has chosen from 8.5 where the precipitation starts to be filtrable and observable, to 9.5 after which significant carbonate precipitation would affect the results. $MgCl_2$ and NH_4Cl were used as additional sources of magnesium and ammonium, respectively. Phosphorus concentrations were measured according to the colorimetric method (EPA 365.3) using UV-Vis spectroscopy. 15 separate experiments were performed in total, combining pH and different relevant ionic concentrations: Ca, Mg, NH_4 and P. They were designed based on a Design of Experiments (DoE) approach in order to be further analyzed for optimization. Precipitates obtained in each test were collected after 20 hr in order to allow completion of process equilibrium, results from equal-conditions tests were mixed and filtered with 0.45 um paper filters, washed with deionized water, and dried at room temperature. Analysis of precipitates was conducted using Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer 1600 series, Waltham, MA, USA) in order to determine the presence of different solid phases.

Concentrations of all available ions were then fed to the PHREEQC model as inputs. The output of the model consisted of ion speciation conditions, and values of saturation index (SI) for each of the solid phases in the database. Speciation data were used to calculate the theoretical phosphorus removal percentage for each of the experiments.

3.5. Results and Discussion

Results of experimental tests and PHREEQC modeling are summarized in Table 3.5. Ion speciation and removal yields were determined for all numerical tests and runs, struvite saturation index (SI) values, only for numerical simulations. SI values were all positive, indicating that struvite precipitation could actually occur in the system under the simulated conditions. Some of these values were, however, very low (e.g., 2nd and 9th run), indicating that the possibility of precipitation was low. Furthermore, the range of SI values obtained during the whole cycle of simulations was not excessively high (all values were <1), in contrast with most literature results generally reporting higher values (>1) for this parameter. This is likely due to the fact that most studies have dealt with anaerobic sludges with considerably higher initial phosphorus concentrations (usually 300–500 mg/L) compared to the aerobic extended-aeration sludge from the Nosedo plant (where P is around 40 mg/L) of this study. Fang et al. [45] suggested that, as the initial phosphorus concentration increases, SI value will also increase, up to P concentrations of around 1000 mg/L, after which it would decrease.

Table 3.5. Results of experimental tests and PHREEQC modeling.

Run	Ca (mg/L)	Mg (mg/L)	NH_4 (mg/L)	P (mg/L)	pH	P rem. Predicted (%)	P rem. Measured* (%)	P precip. Predicted (mg)	P precip. Measured* (mg)	SI Predicted
1	101	84	35	40	9	82.46	84.27	33.23	31.24	0.48
2	101	26	35	40	9	72.76	82.99	29.32	30.85	0.17
3	101	84	82	40	9	82.15	82.05	33.11	29.77	0.84
4	101	26	82	40	9	72.20	82.21	29.10	30.07	0.54
5	101	84	59	40	8.5	70.28	54.72	28.32	23.60	0.54
6	101	26	59	40	8.5	58.03	61.43	23.39	24.14	0.21
7	101	84	59	40	9.5	92.08	91.93	37.11	34.66	0.60
8	101	26	59	40	9.5	86.33	89.28	34.79	33.65	0.32
9	101	40	35	40	8.5	62.40	68.47	25.15	25.74	0.13
10	101	40	82	40	8.5	61.60	62.36	24.83	24.74	0.49
11	101	40	35	40	9.5	88.59	92.15	35.70	34.09	0.22
12	101	40	82	40	9.5	88.29	87.62	35.58	33.65	0.58
13	101	40	59	40	9	75.86	85.74	30.57	31.37	0.52
14	101	40	59	40	9	75.89	82.31	30.58	30.84	0.52
15	101	40	59	40	9	75.89	84.13	30.58	30.78	0.52

* from triplicate tests.

The phosphorus removal percentage and amount of total phosphorus precipitated, both calculated based on the result of PHREEQC modeling, were compared to the measured values in the laboratory precipitation tests to assess the model potential in predicting accurately equilibrium process conditions. Such comparison is in fact essential for understanding the ability of the model to correctly predict new experimental outcomes without implementing all the individual tests in the lab. Results are also shown in Table 3.5. Notwithstanding some inevitable inaccuracies and small measurement errors in the comparison between calculated and observed values, some of them attributable to laboratory procedures, it could still be concluded that the model had a more than acceptable performance overall in reproducing laboratory experiments.

Analysis of the precipitates using Fourier Transform Infrared (FTIR) spectroscopy confirms the presence of struvite and calcium phosphate compounds in the solid phase final products of precipitation tests. Figure 3.3 compares the FTIR spectra of final precipitates at different pH levels and different components' molar ratios. It can be clearly seen that all the spectra follow the same pattern, with the main difference between them being the intensity of the peaks. Peaks associated with PO_4^{3-} and H_2O groups, at 1000–1100, and 2200–3800 cm^{-1}, respectively, can be identified in all the spectra obtained, and can be attributed to the presence of struvite and calcium phosphate compounds in the final solid phases [46]. However, FTIR spectra within the range of 1200 to 1900 cm^{-1} indicate no direct evidence of the presence of struvite since visible peaks could be typical of carbonate groups (around 1440 and 1650 cm^{-1}) and also of ACP water molecules (at around 1600–1650 cm^{-1}). This suggests that, in all the laboratory experiments, precipitates obtained were in fact a mix of struvite, ACP and calcite. Comparing the intensity of FTIR peaks, it could be concluded that as pH increases there will be more phosphate groups in the final precipitates, and thus higher phosphorus removal from the system. However, as expected, final precipitates could also be highly affected by the presence of calcium as a competitive ion in the solution, thus allowing formation of high amounts of calcium phosphate compounds (mainly ACP) at the highest values of pH.

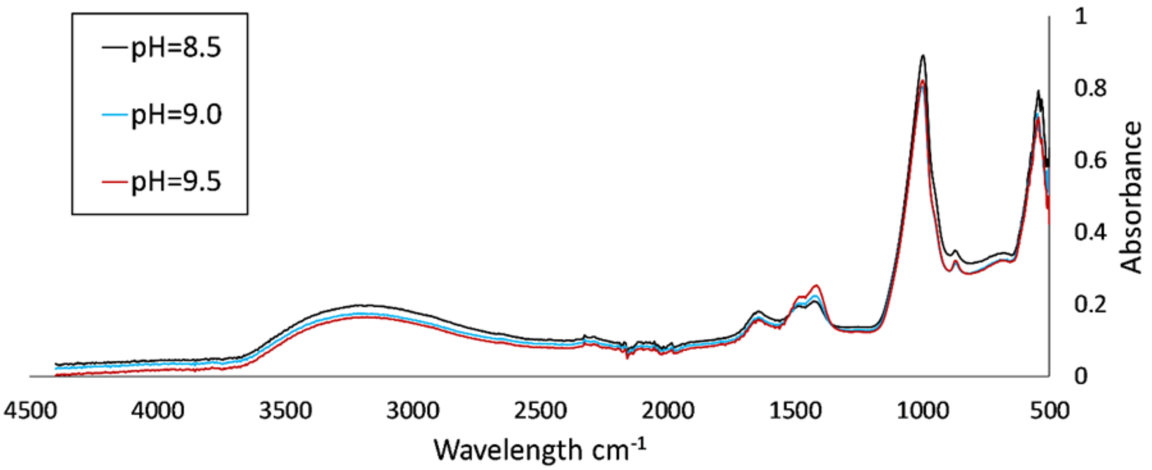

Figure 3.3. Fourier Transform Infrared (FTIR) spectra of the precipitates obtained at different levels of pH.

Although the main objective of this study is to assess the possibility of P recovery in the form of struvite, in a form as pure as possible, the presence of ACP and calcite in the precipitate seems to be inevitable in experimental conditions. One important aspect to mention is that the presence of ACP still represents a more favorable situation than that of calcite. Due to its P content, in fact, ACP can still be considered an acceptable fertilizer, although not as good as struvite. Struvite contains both N and P as essential nutrients for plant growth. In addition, calcium phosphate materials are not consistently available for the plants and it depends highly on the technology used for obtaining them and their quality [47]. It is therefore important, in practice, not to move below a pH value of 9.0 in the tested conditions, as after this point there would be considerably more potential for calcite precipitation in the system.

Laboratory tests on extended aeration sludge show that the level of pH significantly affects P removal yields from the system, and that more than 90% P removal can be achieved at pH > 9. Nonetheless, due to the relatively low initial phosphorus concentration in the Nosedo sludge, the possibility of obtaining a significant amount of struvite in the final precipitates is low, unless adequate quantities of Mg and NH_4 additives could be introduced into the system to improve struvite crystallization and extraction.

Finally, Figure 3.4 shows the theoretical SI values calculated from the simulation results for Struvite, ACP and calcite in solution. These values suggest that in all cases, under present conditions, the final precipitates will be a mixture of struvite, ACP and calcite. As can be seen, in experiments 7, 8, 11, and 12 where pH reached 9.5, values of SI for calcite are higher, which is not an optimal situation for P recovery. The best result was obtained in experiment 3, where pH was 9 and concentrations of Mg and NH_4 at the highest levels. Addition of both these ions is therefore essential for achieving higher struvite precipitation in the solution at hand.

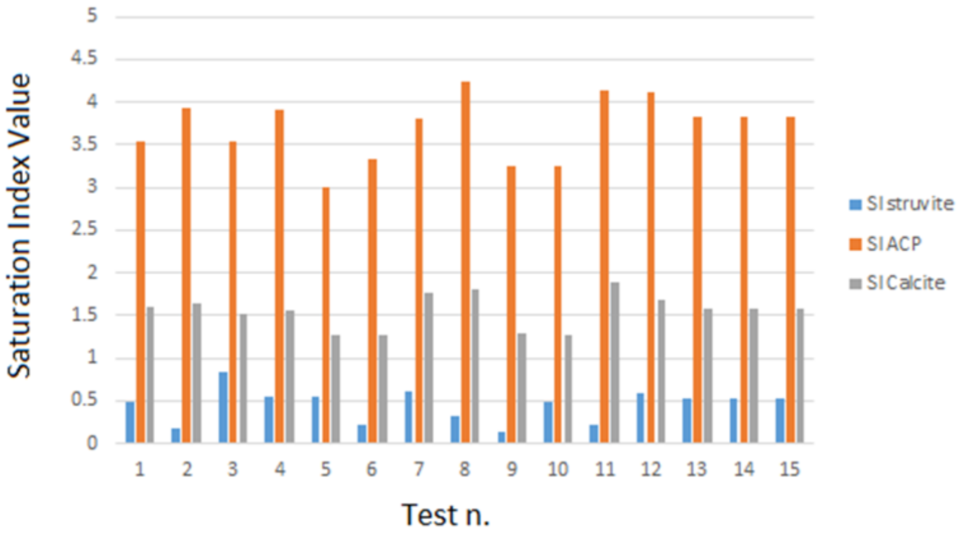

Figure 3.4. Theoretical saturation index (SI) values calculated by PHREEQC for possible solid phases.

The next steps of the study will include additional tests on the extended aeration sludge, to investigate conditions under which more significant amounts of struvite precipitation could be obtained. Addition of higher molar ionic ratios will be tested, and the possibility of using $Ca(OH)_2$ as an economic pH adjustment additive (instead of NaOH) will also be investigated.

3.6. Conclusions

In this study, a chemical equilibrium modeling tool was used, in combination with real laboratory precipitation tests, in order to investigate conditions under which high phosphorus recovery, in the form of struvite, could be achieved from the urban sewage sludges produced by the WRRF facility in Nosedo (Milan, Italy). Values of the struvite saturation index (SI) calculated by the chemical equilibrium model, showed that limited precipitation of this mineral is possible under present circumstances, due to wastewater characteristics, and estimated phosphorus removal efficiency was compared to laboratory results. As solution pH increases above 9, very high phosphorus removal percentages (>90%) could be achieved, but the possibility of achieving high recovery (pure struvite precipitation) is diminished. The presence of low P concentration in the wastewater sludge, in addition to relatively high Ca^{2+} content will lead to achieve a less desirable mix of struvite, ACP and calcite in the final precipitates. Results suggest that in order to obtain higher SI values for struvite, both magnesium and ammonium need to be added to the system in high amounts (as in experiment 3) in order to compete efficiently in precipitation with the presence of Ca^{2+}. Chemical equilibrium modeling showed great potential for predicting achievable equilibrium conditions by further ion addition to the solution, which could be pursued to achieve increased struvite precipitation. Modeling results in terms of P removal percentage and mass confirm a very good fit to the laboratory tests. Hence, model performance is confirmed by experimental evidence and, as such, the model could be a valuable tool for the optimization of the process and the development of a pilot-scale struvite precipitation system.

On the practical side, it was observed that struvite crystallization was hindered by small particle size and slow crystal growth, and therefore, modification of reactors' structure, compared to the laboratory's beakers used herein, and optimization of process parameters to enhance particle size, or minimize loss of crystals should be considered as possible methods to enhance the settleability of this mineral in real scale applications. Although, at the moment, struvite is the product of choice for P recovery, ACP may also have an appeal as final product for similar purposes. Precipitates purity and their market value will have to be compared to evaluate the economic sustainability of either product.

Considering the certainly limited, but uncertain extent of residual global phosphorus resources, development and enhancement of P recovery processes, which could allow recovery of this element, should be pursued, with the aim of extending the useful life of confirmed global reserves while maintaining sustainable levels of production of phosphorus compounds for use in agriculture. Chemical precipitation, in spite of having its own drawbacks, is still the most efficient and common approach for P recovery. Equilibrium modeling of such a process could considerably help in predicting and achieving the best conditions under which highly efficient struvite precipitation can be obtained.

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Chapter 4

Impact of pH and ionic molar ratios on phosphorus forms precipitation and recovery from different wastewater sludges

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4. Impact of pH and ionic molar ratios on phosphorus forms precipitation and recovery from different wastewater sludges

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Abstract

Phosphorus is an essential nutrient for plants, which use as a basic fertilizer component is expected to increase significantly in the coming years. Unfortunately, its available natural reserves are not renewable, and are predicted to decline rapidly in the future. Urban wastewater, due to its abundance and relatively high phosphorus content, is an excellent candidate for phosphorus recovery, while the element's removal from urban effluents was introduced since the 1970's to limit the undesired effects of eutrophication. In this study, the process of struvite (and related phosphorous compounds) crystallization was investigated for three different sludge types, and results were compared. While most studies focus strictly on anaerobically digested sludge for high struvite precipitation efficiency, this investigates the possibility of inducing precipitation on both aerobic (extended aeration) and anaerobic sludges produced by two wastewater treatment plants in northern Italy. Analysis of precipitates from sludge samples is compared, then focus is shifted mainly on the aerobic sludge, and on its potential for struvite recovery. The effect of different reaction parameters is studied under different operating conditions, and the use and effects of $Ca(OH)_2$ addition as inexpensive pH adjustment reagent is investigated.

Keywords: Phosphorous recovery, wastewater, Calcium Hydroxide, Calcium Phosphate, Struvite Precipitation

4.1. Introduction

Phosphorus (P) is an essential nutrient for plants. While its use as a basic fertilizer for industrialized crop production is expected to increase significantly in the coming years, its available natural reserves are not renewable, and are predicted to decline rapidly in the future [1]. The current consumption pattern is not sustainable in the long run, and recycling or recovery of phosphorus from waste streams has been proposed as a possible solution for extending phosphorus resources duration, while also helping reduce eutrophication of natural waters, a P-related undesired effect [2,3].

Wastewater from municipal treatment plants (WRRFs), due to its abundance, and relatively high phosphorus content, is an excellent candidate for phosphorus recovery [4,5]. Several technologies have been proposed to recover or remove phosphorus from such waste streams: while removal has been introduced since the 1970's to limit the undesired effects of eutrophication, carried out by chemical or biological methods, it does not originate a readily usable product (mostly ferric or aluminum phosphates) that are not suitable as fertilizer components. The most interesting technologies for P recovery make use of magnesium or calcium precipitation processes, where phosphorus can be recovered as struvite, amorphous calcium phosphate, brushite, octacalcium phosphate, hydroxyapatite, apatite [6,7]. The latter two are also normally considered ineffective as fertilizers due to their low solubility. However, inoculations with phosphate solubilizing microorganisms [8] or precipitation techniques of Nano-sized apatite [9] appear to be promising strategies for the reuse of low-solubility phosphates.

Struvite precipitation is one of the main methods of phosphorus recovery from wastewater treatment. Struvite, or magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$) is a white mineral that frequently precipitates within sewage treatment systems, where concentrations of ammonium and phosphate are relatively high. In uncontrolled conditions, it is considered as a potential problem causing clogging in pumps, pipes, etc. Nevertheless, under controlled conditions, it can be recovered from different stages of the treatment process [10] and, due to its low solubility and high nutrients content (both nitrogen and phosphorus), it can be further reused as a suitable, slow-release fertilizer in agriculture [11,12].
Struvite precipitation occurs according to the following reactions:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \tag{1}$$
$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + H^+ \tag{2}$$
$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + 2H^+ \tag{3}$$

The reaction of HPO_4^{2-} is the dominant one in the pH range 7-11, in which struvite precipitation is likely to happen [13]. Different factors affect the process of struvite crystallization, such as pH, constituent ions (Mg^{2+}, PO_4^{3-} and NH_4^+) molar ratios, presence of other competitive ions such as Calcium (Ca^{2+}), agitation rates, reaction retention time, etc.

The crystallization of struvite consists of three stages; nucleation (crystal birth), crystal growth, and aggregation [14]. All these three mechanisms can be formulated as functions of the struvite supersaturation ratio, which is defined as ratio of the ion activity product (IAP) of constituent ions in solution over its equilibrium solubility product or K_{sp}. Struvite saturation index (SI) (the logarithm of supersaturation ratio) [15] is an indicator of whether precipitation is likely to happen or not. If SI > 0, the solution is supersaturated, and precipitation may occur, if SI < 0 the solution is undersaturated, and there will be no precipitation. SI = 0 indicates an equilibrium condition.

$$IAP = \{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\} \tag{4}$$

$$SI = \log(\frac{IAP}{K_{sp}}) \tag{5}$$

The presence of other competitive ions strongly affects the struvite precipitation process. The main solid phases that can precipitate alongside struvite are calcium phosphate compounds, magnesium phosphate compounds and carbonates. Newberyite ($MgHPO_4 \cdot 3H_2O$) and bobierrite ($Mg_3(PO_4) \cdot 8H_2O$) are the two main magnesium phosphate compounds that may precipitate. However, their chance of forming a precipitate is highly dependent on operating conditions. Newberyite needs a high Mg^{2+}/P ratio and a relatively low (compared to struvite) pH (less than 6) in order to precipitate in significant amount [16,17]. Bobierrite precipitation, on the other hand, is very slow, and it may take days to form a precipitate [18].

Calcium phosphate compounds, at least in some forms, and carbonates have a high possibility to co-precipitate with struvite. Among different calcium phosphate compounds, brushite ($CaHPO_4 \cdot 2\ H_2O$), octacalcium phosphate (OCP, $Ca_8(HPO_4)2(PO_4)_4 \cdot 5\ H_2O$)) and amorphous calcium phosphate (ACP, $Ca_3(PO_4)_2 \cdot x\ H_2O$) are likely to precipitate first [17,19]. These can be further transformed to the more stable forms of hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$), monetite (DCP, $CaHPO_4$) and tricalcium phosphate (TCP, $Ca_3(PO_4)_2$). While the transformation to DCP is relatively fast, HAP and TCP demonstrate very slow kinetics, and could be well out of the typical temporal scale of WRRFs operating conditions [17,18]. Calcite ($CaCO_3$) is the thermodynamically stable form of calcium carbonates that has the greatest precipitation potential in alkaline environments, however, its precipitation is highly affected by the presence of Mg^{2+}, phosphate and dissolved organics [17]. Magnesite ($MgCO_3$) is the stable form of magnesium carbonate compounds in a pH range less than 10.7 therefore its reaction also ought to be taken into account [17]. In addition, calcium hydroxide ($Ca(OH)_2$) and brucite (magnesium hydroxide, $Mg(OH)_2$) can precipitate at high (> 9.5) pH [17]. Table 4.1 summarizes the possible reactions of P minerals precipitation in the process of struvite precipitation.

Table 4.1. Possible solid phases precipitating in the P recovery process.

Solid phase	**Reaction**	**condition**	**pK_{sp} (25°C)**	**Reference**
Struvite	$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O$	$7 < pH < 11$	13.26	[20]
Newberyite	$Mg^{2+} + HPO_4^{2-} + 3H_2O \leftrightarrow MgHPO_4 \cdot 3H_2O$	High Mg^{2+}/P, $pH<6$	5.8	[17]
Bobierrite	$3Mg^{2+} + 2PO_4^{3-} + 8H_2O \leftrightarrow Mg_3(PO_4)_2 \cdot 8H_2O$	Days to precipitate	25.2	[17]
Hydroxyapatite (HAP)	$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$	Slow formation from ACP, DCPD	58.62	[21,22]
Tricalcium phosphate (TCP)	$3Ca^{2+} + 2PO_4^{3-} \leftrightarrow Ca_3(PO_4)_2$	Slow formation from ACP, DCPD	32.63	[17]
Octacalcium phosphate (OCP)	$8Ca^{2+} + 2HPO_4^{2-} + 4PO_4^{3-} \leftrightarrow Ca_8(HPO_4)_2(PO_4)_4$	Hydrolysis of DCPD at pH =5-6	36.48	[23]
Monetite (DCP)	$Ca^{2+} + HPO_4^{2-} \leftrightarrow CaHPO_4$	Fast formation from ACP, DCPD	6.81	[24]
Brushite (DCPD)	$Ca^{2+} + HPO_4^{2-} + 2H_2O \leftrightarrow CaHPO_4 \cdot 2H_2O$	$pH<7$	6.6	[25]
Amorphous calcium phosphate (ACP)	$3Ca^{2+} + 2PO_4^{3-} + xH_2O \leftrightarrow Ca_3(PO_4)_2 \cdot xH_2O$	$pH>6$	25.46	[17]
Calcite	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$	Stable at 25°C and atmospheric P	8.42-8.22-8.48	[17]
Magnesite	$Mg^{2+} + CO_3^{2-} \leftrightarrow MgCO_3$	Stable at $pH<10.7$	7.46-8.2	[25]
Brucite	$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2$	$pH>9.5$	11.16	[25]
$Ca(OH)_2$	$Ca^{2+} + 2OH^- \leftrightarrow Ca(OH)_2$	$pH>9.5$	5.2	[17]

In this study, the process of struvite (and related P compounds) crystallization was investigated for three different sludge types, and results were compared. While most studies focus strictly on anaerobically digested sludge for high struvite precipitation efficiency, the present one investigates the possibility of inducing precipitation on both aerobic (extended aeration) and anaerobic sludges produced by the wastewater treatment plants (WRRFs) of Nosedo (Milan, Italy) and Pavia (Italy) (Figure 4.1), respectively. First, analysis of precipitates from different sludge samples and synthetic struvite is compared. Then, as second part of the study, we focus mainly on the aerobic sludge and on its potential for struvite recovery. The effect of different reaction parameters was studied under different operating conditions, and the use of $Ca(OH)_2$ as an inexpensive pH adjustment reagent was also investigated.

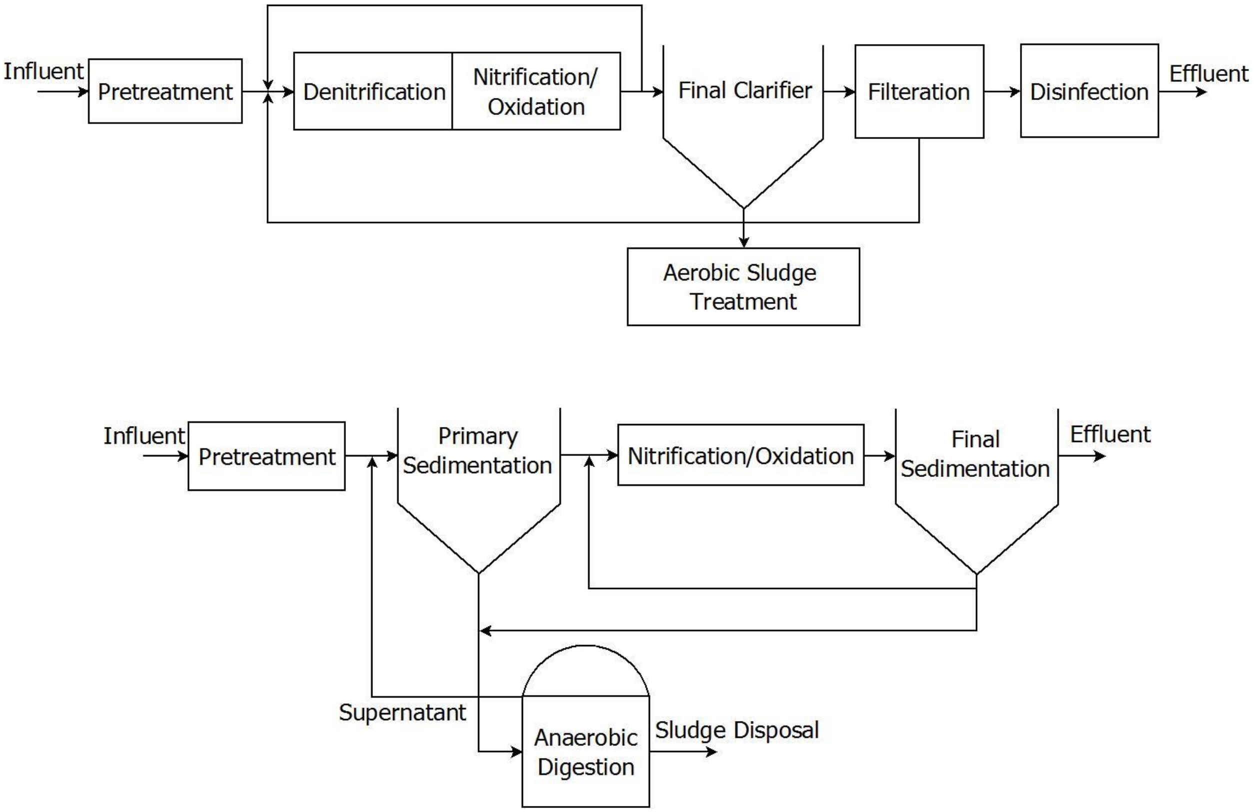


Figure 4.1. Process flow diagram of Nosedo (top) and Pavia (bottom) WRRFs.

4.2. Materials and Methods

4.2.1. Synthetic Struvite

Synthetic Struvite was produced in the laboratory using phosphoric acid (H_3PO_4), ammonia (NH_3) and magnesium chloride ($MgCl_2$) with 1:1:1 molar ratio, in alkaline environment. The precipitated struvite was then dried at room temperature for analysis in subsequent steps (Figure 4.2).

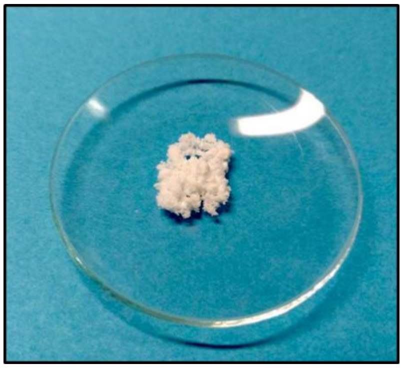


Figure 4.2. Synthetic lab-produced Struvite.

4.2.2. Sludge characteristics

For this study, sludge samples were taken from the Nosedo WRRF near Milan, and from the municipal WRRF in Pavia (both in Italy). Nosedo has an average daily flow rate of around 432,000

m^3 and it serves a part of the city of Milan with the capacity of 1 million P.E. the depuration plant of Pavia on other hand is smaller and has a capacity of 160,000 P.E. with average daily flow rate of 45,000 m^3. The samples were drawn from the (extended) oxidation tanks, and the denitrification units at Nosedo, and from the dewatering phase following anaerobic digestion in Pavia. Table 4.2 summarizes the characteristics of the samples used in this study.

Table 4.2. Sludge filtrate samples characteristics.

Constituent ions	**Extended Oxidation (mg/L)**	**After anaerobic digestion (mg/L)**	**Denitrification pond (mg/L)**
Ca^{2+}	101	30.9	66.4
Mg^{2+}	26.4	17.0	24.2
P	37	8.1 ± 1.5	1.66 ± 0.3
NH_4^+	32.6	1510 ± 340	1.70 ± 0.38
pH	7.6	8.5	7.0

The average concentration of total phosphorus entering the Nosedo WRRF is 3.2 mg/L with minimum and maximum of 1.0 and 6.2 mg/L respectively. Generally, this concentration is not sufficiently high for having significant struvite precipitation. However, during the anaerobic stage of activated sludge process there is a release of phosphorus, which is followed by a “luxury uptake” of phosphorus in the aerobic zone. This increases the phosphorus content of the sludge to as high as 3-7% (dry basis) [26, 27] with a high concentration of 37 mg/L in the extended oxidation tank (after being under anaerobic condition for 1-2 days) and could make it potentially suitable for struvite precipitation process.

4.2.3. Equipment and Analytical tools

Experiments were conducted in 1-liter Imhoff cone-shaped beckers (Figure 4.3) fitted with a tip-valve to extract the precipitate. Initially, pH was adjusted using a fish-tank aeration pump injecting air in the vessels with a tube, while later a NaOH solution was used as pH adjustment reagent. $MgCl_2$ and NH_4Cl were added to the vessels as sources of magnesium and ammonium, respectively. UV-Vis colorimetric (HP 8452A Diode Array Spectrophotometer) method using antimony-phospho-molybdate complex (EPA 365.3) [28] was applied for P concentration measurements. P concentration vs. absorbance levels curve was calibrated using standard phosphate solutions, and absorbance levels of the samples were measured at 712 nm according to standard.

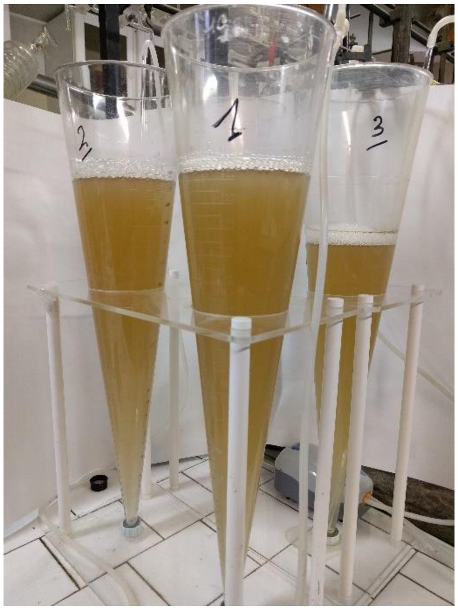


Figure 4.3. Experimental setup of the struvite precipitation process.

Analyses of the final precipitates, and identification of different components, was performed with Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer 1600 series) as the main method. Thermal gravimetric analysis (TGA) (Mettler Toledo TGA 1 STARe System) combined with Quadrupolar Mass Spectroscopy (MS) and X-Ray Diffraction (XRD) (Brucker D5005) were also used to confirm the presence of different minerals in precipitates. Evaporated materials from TGA were fed to the MS to detect different components. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used for quantitative measurements of Ca^{2+}, Mg^{2+} and P in the final precipitates, and Elemental Analysis was applied for determining N, H and C contents.

The final part of the experiments included the study of the effect of using $Ca(OH)_2$ as pH-adjustment reagent, and results were compared with previous runs.

4.2.4. Chemical Equilibrium modeling for SI calculation

A chemical equilibrium model was used to calculate the Saturation Index (SI) values of different solid phases, and therefore to evaluate the possibility of their precipitation in the specific experimental operating conditions. For this aim, the PHREEQC model (USGS) [29] was applied based on samples characteristics and initial conditions as the input values, and optimization of PHREEQC's database for accounting of precipitation processes specified in Table 1 were performed as specified in [10].

4.2.5. Extended-aeration Sludge Experimental Setup

Precipitation experiments were conducted at three pH levels (8.5, 9.0, 9.5), adjusted with NaOH solution, at different Mg^{2+}, NH_4^+, and P molar ratios, according to Table 4.3.

Table 4.3. Different molar ratios for Mg^{2+}: NH_4^+:P used in the study.

Mg^{2+}:NH_4^+:P		
3:3:1	3:1:1	1:3:1
5:5:1	5:1:1	1:5:1

One test was also performed for comparison on the extended-aeration sludge without any Mg and NH_4 additives, using only NaOH for pH adjustment. Two additional sets of experiments were also implemented to evaluate the possibility of using $Ca(OH)_2$ for pH adjustment as a cheaper option. In these additional runs, Mg^{2+}: NH_4^+:P ratios of 5:5:1 and 3:3:1 were used.

4.3. Results

4.3.1. Synthetic Struvite

The synthetic struvite obtained in the laboratory was subjected to FTIR, TGA and MS analyses. In the FTIR spectrum prior to TGA, the associated bands of PO_4^{3-}, H-N-H bonds and water molecules at 1000-1100, 1400-1600 and 2200-3800 cm^{-1}, respectively [30,31] can all be identified (Figure 4.4a). The TGA curve and its derivative, DTGA, (Figure 4.4b) show a weight loss around 150°C, related to the loss of ammonia and water molecules based on reaction (6) [32]:

$$MgNH_4PO_4.6H_2O \xrightarrow{-NH_3,H_2O} MgHPO_4 \xrightarrow{-H_2O} 0.5Mg_2P_2O_7 \qquad (6)$$

This is also confirmed by MS result, showing high intensity values for peaks at 17 and 18 m/z (mass-to-charge ratio), associated to NH_3+ H_2O and H_2O respectively (Figure 4.4c).

FTIR was performed prior and after TGA analysis: the latter results (Figure 4.4a) show the absence of water and H-N-H bonds associated peaks, and presence of $P_2O_7^{4-}$ formed based on the second step of the above reaction in the latter test.

The theoretical weight loss of the struvite decomposition reaction is 54.64%, while an experimental value of 53.94 % was determined, which can be considered quite accurate.

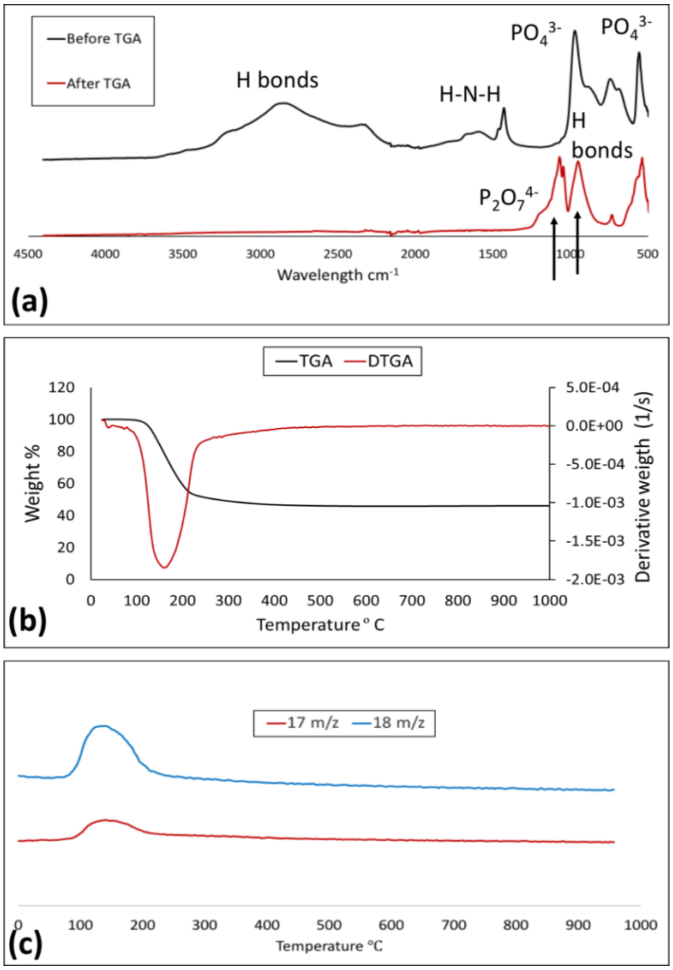


Figure 4.4. FTIR (a), TGA (b) and MS (c) analyses of synthetic struvite.

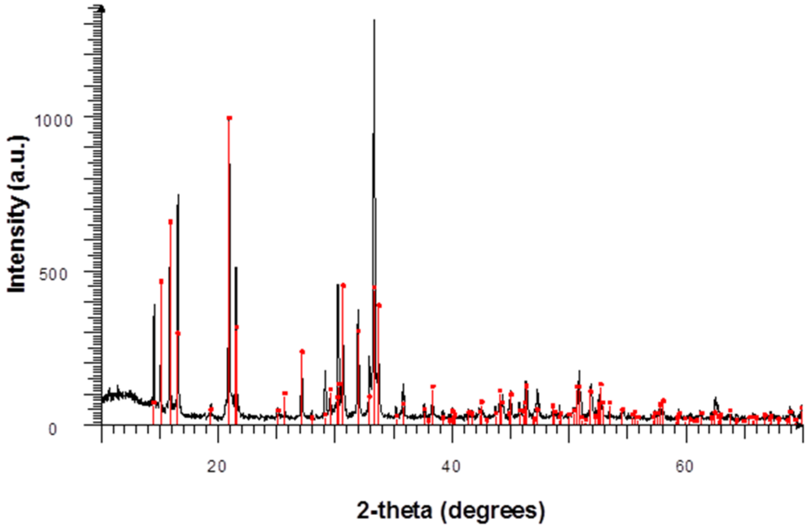


Figure 4.5. XRD analysis pattern of synthetic struvite.

Figure 4.5 shows the XRD outcome of synthetic struvite. The black line represents the synthetic struvite sample, while red dots indicate struvite peaks based on JCPSD 071-2089 [33]. It can be seen that the behavior of the synthetic lab-made struvite is sufficiently comparable to the reference one, since major struvite peaks are visible in XRD.

4.3.2. Analysis of Precipitates

4.3.2.1. Anaerobic Digestion Sludge

Magnesium was added in stoichiometric amount to the sludge samples following AD taken at Pavia. Ammonium addition was not necessary, since AD sludge already contained high ammonium concentrations. Samples were adjusted to pH=9 using aeration as described in section 4.2.3. Final precipitates were analyzed using FTIR, TGA and MS.

Associated peaks of water molecules, PO_4^{3-} and H-N-H bonds are clearly visible in the FTIR of the final precipitates obtained from anaerobic digestion sludge (Figure 4.6a). This suggests presence of struvite in the precipitates. Furthermore, bands related to carbonate groups (CO_3^{2-}) at around 1440 and 1650 cm^{-1} [34] can also be seen in the graph (Figure 4.6a). In this case, TGA results (Figure 4.6b) shows two big weight losses at around 150 and 800 ◦C. While the first one is related to the loss of H_2O and NH_3 (based on equation 6), the second is a typical carbon dioxide weight loss based on the reaction [35]:

$$CaCO_3 \xrightarrow{-CO_2} CaO \qquad (7)$$

This result has also been confirmed by MS (Figure 4.6c) as it can be seen by three intensity peaks: the first two (NH_3+H_20) similar to those for synthetic struvite (Figure 4.4c), related to the presence of H_2O and NH_3 (peaks at 17 and 18 m/z, respectively), the third one referring to CO_2, with mass-to-charge ratio of 44 m/z. The calculated weight loss values show that struvite and calcite comprised 45% and 47% of final precipitates, respectively.

FTIR following TGA shows the absence of struvite and carbonate associated peaks, and the presence of a $P_2O_7^{4-}$ peak at 900-1200 cm^{-1} [36]. A small, sharp peak can also be observed at around 3600-3700 cm^{-1}, associated to OH^- group [31], and which can be related to the presence of hydroxyapatite in the precipitate. This can explain the nature of the remaining 8% (other than struvite and calcite) of the final precipitates, suggesting that is related to the presence of ACP, transformed to hydroxyapatite at high temperature [34].

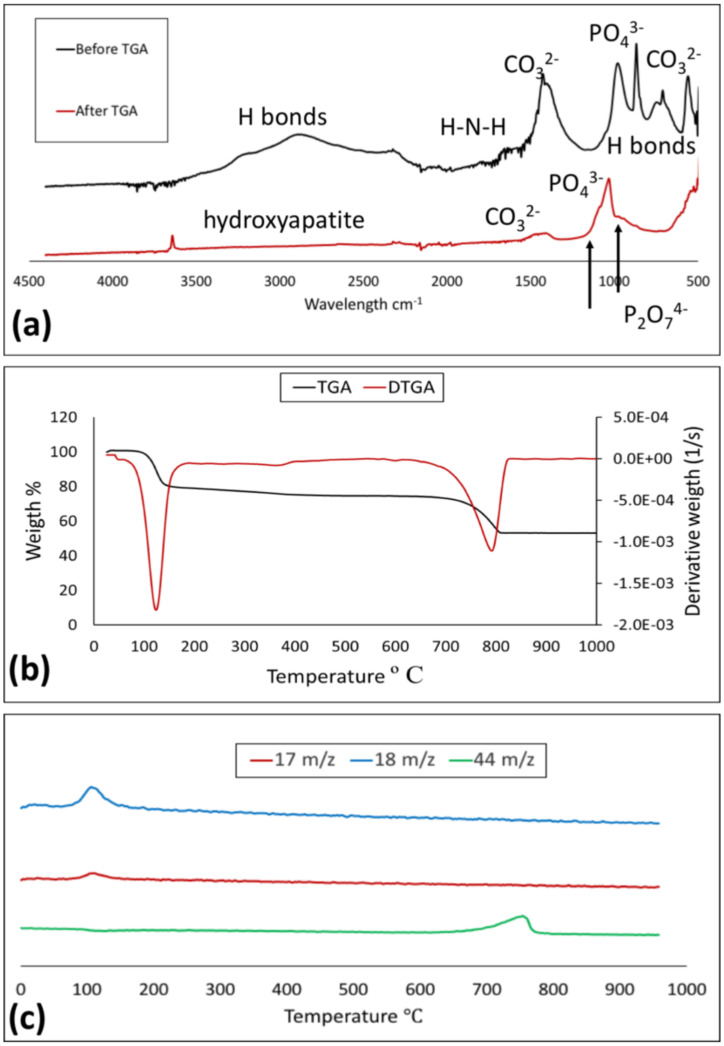


Figure 4.6. FTIR (a), TGA (b) and MS (c) of precipitates from AD sludge sample.

Anaerobic sludge, has been studied for a long time, generally showing great potential for phosphorus recovery (80-85% at pH=9). Significant amount of struvite could precipitate since it has relatively low calcium content (initial Ca^{2+}:Mg^{2+} ratio of 1.07) and very high amount of ammonium. Therefore, it has a great potential for fertilizer production, nevertheless, in the case examined, the precipitation of calcite is significant in higher pH levels.

4.3.2.2. Denitrification Sludge

Magnesium and ammonium were added in stoichiometric amounts to the sludge samples from the Nosedo denitrification section. Samples were adjusted to pH=9 using aeration as described in section 2.3. Final precipitates were analyzed using FTIR, TGA and MS methods. The analyses of precipitates from the Nosedo denitrification sludge sample are summarized in Figure 6. The first notable presence is a HPO_4^{2-} associated peak at around 900 cm^{-1} [37] in the pre-TGA sample (Figure 4.7a), which suggests precipitation of monetite (DCP) or brushite (DCPD). The weight loss at around 150 ◦C visible in both the TGA (Figure 4.7b) and MS (Figure 4.7c) graphs suggests the same phenomenon observed with synthetic struvite, related to loss of water molecules based on reaction (8):

$$2CaHPO_4 \xrightarrow{-H_2O} Ca_2P_2O_7 \tag{8}$$

Post-TGA FTIR analysis confirms this result by showing peaks of $P_2O_7^{4-}$ at around 900-1200 cm^{-1} (Figure 4.7a). The associated carbonate peak (CO_3^{2-}) at around 1400 cm^{-1} in the same graph is related to formation of calcite through the same reaction in equation 7. Three significant weight losses are visible in the TGA graph, in addition to the water loss: one is at around 450-500 ◦C, and the other at 900-1000 ◦C (Figure 4.7b). The MS graph (Figure 4.7c) shows that the second is related to the evolution of CO_2, and thus can be an additional confirmation of the presence of HPO_4^{2-} based on:

$$2HPO_4^{2-} + CO_3^{2-} \rightarrow CO_2 + H_2O + 2PO_4^{3-} \tag{9}$$

The water loss, on the other hand, could be due the reaction of hydroxyapatite with CaO:

$$Ca_{10}(PO_4)_6(OH)_2 + 2CaO \rightarrow 3Ca_4O(PO_4)_2 + H_2O \tag{10}$$

The post-TGA FTIR graph indicates a strong evolution of water reaction according to (10), by showing peaks of OH^- around 3400-3500 cm^{-1} (Figure 4.7a).

Tests on the denitrification sludge suggests that this is not suitable for significant struvite precipitation. Although phosphorus removal is high (nearly 80% at pH=9), it is mostly in the form of calcium phosphate compounds such as monetite, brushite and hydroxyapatite, which are not very efficient and favorable to be used as fertilizers due to their lower solubility and the fact that plant availability of calcium phosphate products is not consistent, and it depends on the technology used to obtained it [38].

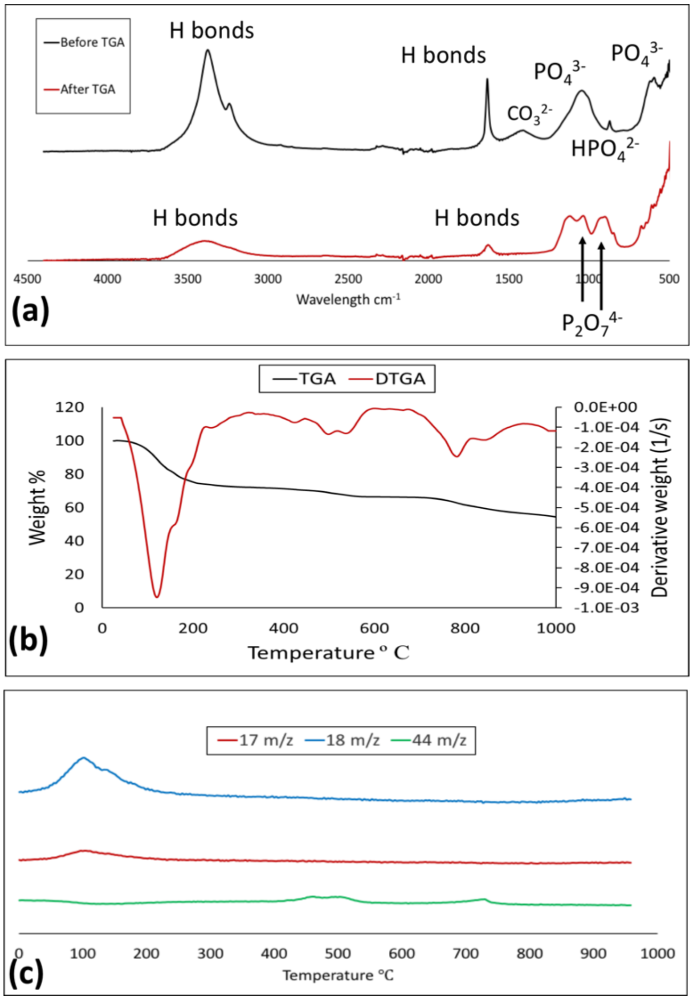


Figure 4.7. FTIR (a), TGA (b) and MS (c) analyses of precipitates from denitrification sludge sample.

4.3.2.3. Extended aeration Sludge

The same procedure of analysis was applied to the aerobic sludge (Figure 4.8). This time the analysis did not provide satisfactory and easily comprehensible results on final precipitates. Based on the FTIR results (Figure 4.8a), the associated peaks of phosphate group and water molecules are present at around 1000-1100 and 3500 cm^{-1}. However, the peaks in the range of 1200-2000 cm^{-1} cannot identify directly the presence of struvite in the final precipitates. The peaks at around 1400-1500 cm^{-1} could be related to H-N-H bonds of struvite but also to the carbonate groups. The peak at 1650 cm^{-1} could be assigned to the H-bonds of amorphous phases. It seems that the peaks at this range are formed based on a convolution of individual peaks of different groups. TGA analysis (Figure 4.8b) result shows a weight loss at around 150◦C that could be related to water and, possibly, ammonia. In addition, there are two other weight losses at around 650 and 800 degrees of ◦C that could be related to carbonate. MS results (Figure 4.78c) confirm this by indicating the presence of carbon dioxide based on the graph with mass-to-charge ratio of 44 m/z.

Consequently, it seems that higher levels of Mg^{2+} and NH_4^+ would be needed in case of aerobic sludge, to achieve significant struvite precipitation directly detectable by analysis of precipitates. Phosphorus removal is around 80-85% at pH=9 in this case and the final precipitates are most probably a mix of struvite, ACP and calcite. Further tests in the following sections investigate the possibility of using aerobic sludge for obtaining a precipitate that is suitable to be used as fertilizer.

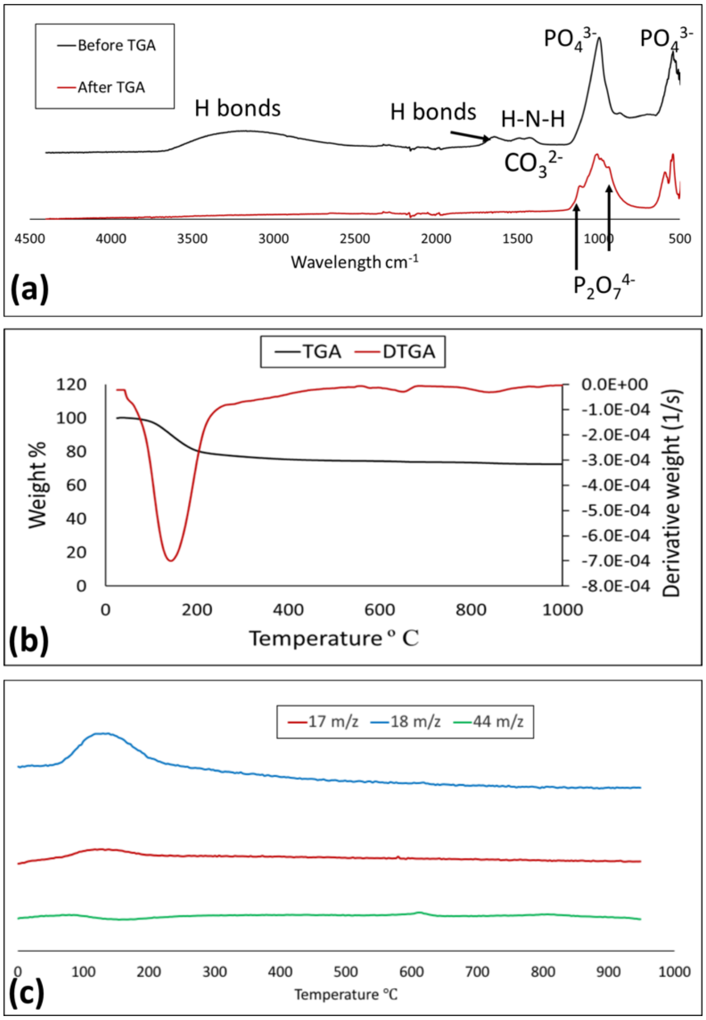


Figure 4.8. FTIR (a), TGA (b) and MS (c) analyses of precipitates from aerobic sludge sample.

4.3.3. Effect of Different Reaction Parameters on Oxidation Sludge

4.3.3.1. Chemical Equilibrium Modeling

Results of PHREEQC modeling for extended aeration sludge samples show positive SI values for four solid phases; Struvite, ACP, calcite and monetite (DCP). This suggests that these solid phases have the possibility of precipitation in the operating conditions of the system, and ought to be taken into consideration for a likely composition of final precipitates. However, in almost all experiments, no sign of HPO_4^{2-} in the precipitates were identified, based on FTIR spectra compared to the typical associated peaks of HPO_4^{2-} (Figure 4.9) [34]. This suggests that struvite, ACP and calcite were the only three major solid phases precipitating in the process and monetite (DCP) was not present in the final product in spite of the positive SI value.

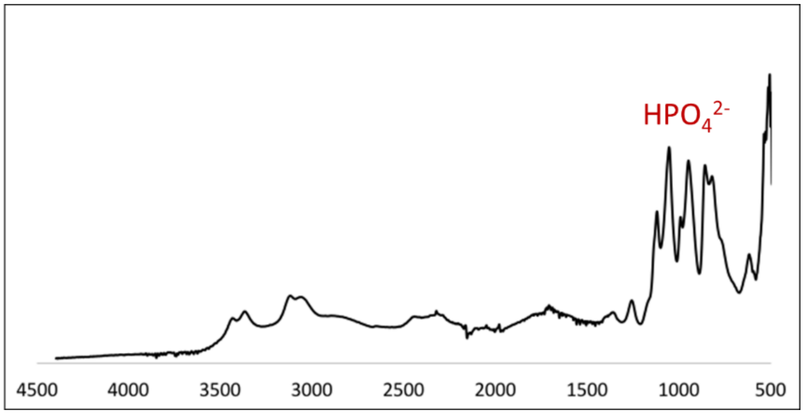


Figure 4.9. FTIR of Na_2HPO_4.

4.3.3.2. FTIR analysis results

Between all the associated peaks of struvite constituents in an FTIR spectrum, those assigned to H-N-H bonds are the most important, as they can directly confirm the presence of struvite in final precipitates. This is because there is no other major solid phase containing the ammonium ion in the system, while phosphate peaks could be related to ACP, as well. Therefore, at this point we focused on a very specific range of the FTIR spectrum between 1200 to 2000 cm^{-1} (Figure 4.10, red rectangle) in order to compare the results of different experiments.

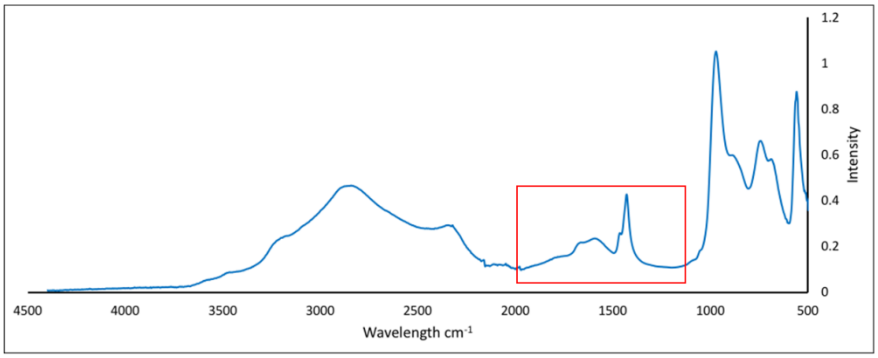
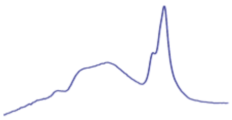
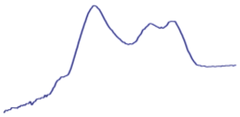
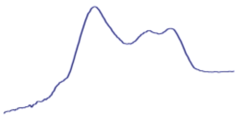
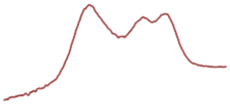
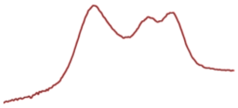
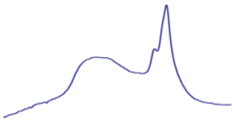
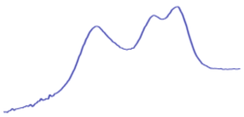
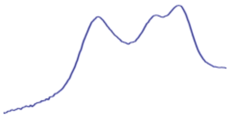
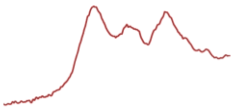
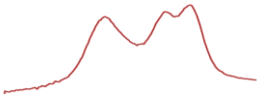
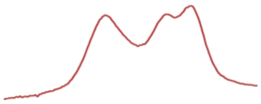
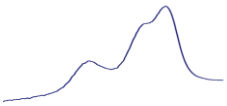
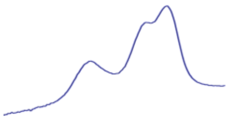
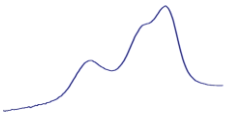
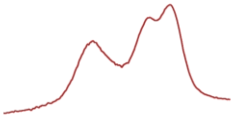
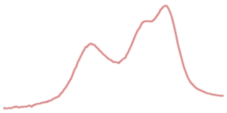


Figure 4.10. FTIR total spectral range, and detail of spectrum used for the analysis (1200-2000 cm^{-1})

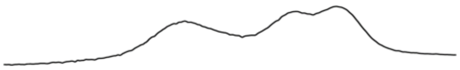
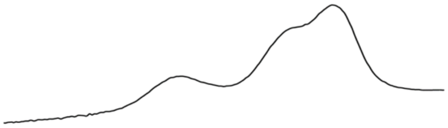
Table 4.4 shows the FTIR spectra of precipitates from different runs of experiments, at different pH levels and molar ratios. The phosphorus removal percentage for each test is also reported in the table. As it can be clearly seen, the only experiments resulting in direct evidence of struvite presence based on FTIR analysis between 1200 and 2000 cm^{-1} are those at pH 8.5 and 9.0, and ionic molar ratios of Mg^{2+}: NH_4^+:P equal to 5:5:1. These experiments produced spectra quite similar to those of synthetic struvite obtained initially. The highest P removal percentages are related to the experiments carried out at pH=9.5, however, at this level of pH there is no evidence of struvite precipitation based on FTIR analysis that could suggest the possibility of obtaining a mix of struvite, ACP and calcite precipitates. It can also be concluded that in order to obtain significant amounts of struvite in the final precipitates, identifiable directly from FTIR analysis spectra, addition of both Mg^{2+} and NH_4^+ sources are necessary. The results of the experiments with addition of only Mg^{2+} or only NH_4^+ are not suggesting the presence of struvite.

Table 4.4. FTIR result curves and P removal percentage results for tests with ionic molar ratios indicated, at different pH

	Mg:NH$_4$:P					
	5:5:1 – 3:3:1		**5:1:1 – 3:1:1**		**1:5:1 – 1:3:1**	
pH	**P rem.%**	**FTIR 1200-2000 cm^{-1}**	**P rem.%**	**FTIR 1200-2000 cm^{-1}**	**P rem.%**	**FTIR 1200-2000 cm^{-1}**
8.5	65.1		53.4		51.2	
	49.7		52.3		41.2	
9.0	85.8		81.0		76.2	
	78.5		79.7		76.9	
9.5	93.2		94.6		90.2	
	91.8		91.1		86.3	

FTIR results and P removal percentages for those sludge samples without additions of Mg^{2+} and NH_4^+ are summarized in Table 4.5. As it can be seen therein, there is no direct evidence of struvite precipitation for any of the experiments, suggesting that the initial ionic molar ratios in the wastewater sludge are not sufficient for significant struvite precipitation. While at pH=8.5 and 9 it can be concluded that final precipitates are a mix of struvite, ACP and calcite, at pH=9.5 FTIR analysis suggests that the major fraction of the precipitates could be calcite, due to the increased peaks of carbonate groups. Nonetheless, P removal percentage is increasing with increase of pH, and P removal could reach up to 94 %, even without the addition of Mg^{2+} and NH_4^+ sources to the sludge, although the final precipitates composition is not favorable in terms of struvite production.

Table 4.5. FTIR and P removal percentage results for experiments without any additives using only NaOH for pH adjustment.

	Mg:NH₄:P	
	Without additives	
pH	**P removal %**	**FTIR 1200-2000 cm^{-1}**
8.5	54.4	
9.0	76.7	
9.5	94.5	

4.3.3.3. XRD Results

Figure 4.11 shows the result of XRD analysis on final precipitates for four samples. The horizontal axis represents (2 x theta), where theta is the angle between incident beam and crystal plane. Red dots represent the peaks of synthetic struvite. The black line represents the results of test with molar ratio 5:5:1 at pH=8.5, where there was evidence of struvite precipitation. The line matches quite well the peaks of struvite shown by XRD, which is a further confirmation of struvite precipitation in this test. The red line is related to the test with molar ratio 3:3:1 at pH 8.5. The only obviously detectable detail in this line is the broad peak at around x=30 (see circle in Figure

11), associated to the amorphous P forms (ACP) [39]. Representing peaks of struvite are not observable.

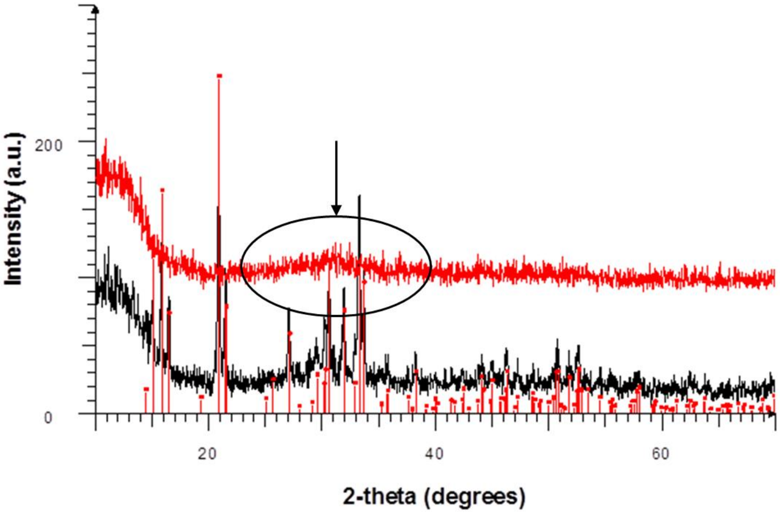


Figure 4.11. XRD pattern for the experiment with 5:5:1 of molar ratio at pH=8.5 (black), with 3:3:1 of molar ratio at pH=8.5 (red), compared to synthetic struvite (red dots), inside circle: broad peak associated to the amorphous phase.

4.3.3.4. ICP-AES and Elemental Analysis Results

The results of the ICP-AES and elemental analysis are reported in terms of Mg^{2+}, Ca^{2+}, P, Nitrogen (N), and Carbon (C) molar contents. Figure 12 shows molar ratios (Figure 4.12a) and contents (Figure 4.12b) of the elements in the final precipitates for 5 selected experiments: the first three are those with the 5:5:1, 5:1:1, and 1:5:1 molar ratios at pH=8.5, the fourth represents that with 3:3:1 molar ratio (same pH), and the fifth one is for the 5:1:1 ratio at pH = 9. Comparing the first three, it can be seen that as we shift ratios from 5:5:1 to 1:5:1, there is a substantial decrease in Mg^{2+} content, which suggests a reduction in struvite precipitation, while there is little difference between tests with ratios 5:5:1 and 5:1:1. Since N content is very small for test 5:1:1, it can be concluded that the Mg^{2+} content in this precipitate is probably related to Mg^{2+} impurities (in the form of bobierryite or newberyite), and not due to significant struvite precipitation. This can be confirmed also by the fact that Mg^{2+}:P ratios are very similar between the two experiments. Furthermore, as we move to the 1:5:1 ratio test, a noticeable increase is visible for the Ca^{2+}:P ratio, related to the calcite precipitation, also confirmed by FTIR results. In conclusion, adding only NH_4^+ to the system is not very effective to induce struvite precipitation, as the major parts of precipitates are ACP (high, similar Ca^{2+} and P molar content) and calcite (slightly higher Ca^{2+} with respect to P, and higher C molar content).

The comparison of experiments with 5:5:1 and 3:3:1 ionic rations at pH=8.5 indicates that relatively high molar ratios are required for Mg^{2+} and NH_4^+, since there is little Mg, and nearly zero N content, substantially lower Mg^{2+}: Ca^{2+}, and higher Ca^{2+}:P ratios in the test characterized by molar ratios 3:3:1. The second and fifth experiments, characterized by equal molar ratios of 5:1:1 and different pH levels of 8.5 and 9 are not very different. Obviously, as pH increases, there is lower Mg^{2+} content, thus lower struvite precipitation. Still, there are high P and Ca^{2+} contents in both situations, and higher C at pH=9, which is due to greater calcite precipitation in this experiment.

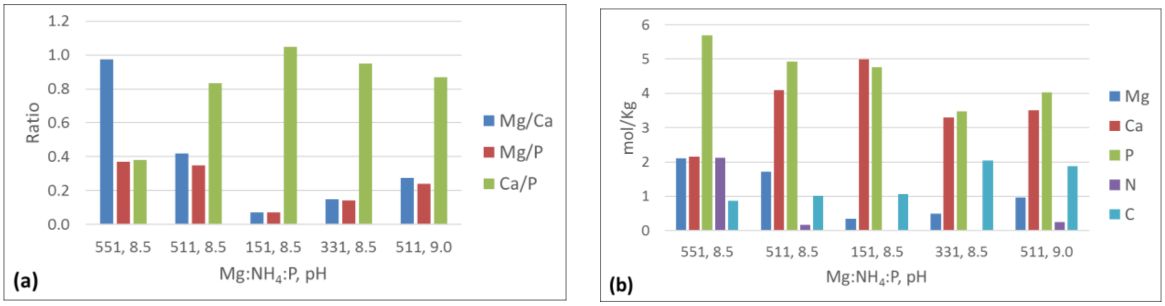


Figure 4.12. Results of ICP-AES and Elemental Analysis, a) Molar ratios, b) Molar contents.

ICP-AES results for experiments without any additives, and only NaOH dosage as pH adjustment (Figure 4.13) indicate that although the Mg^{2+} content increases from pH=8.5 to pH=9.5, it is still dramatically lower than P and Ca^{2+}, and there is also very little N component in all of the precipitates. This suggests that struvite precipitation is almost non-existent in these conditions. Ca^{2+}:P ratio increases with pH increase, and in all cases is higher than 1. This is due to calcite precipitation, also confirmed by FTIR results.

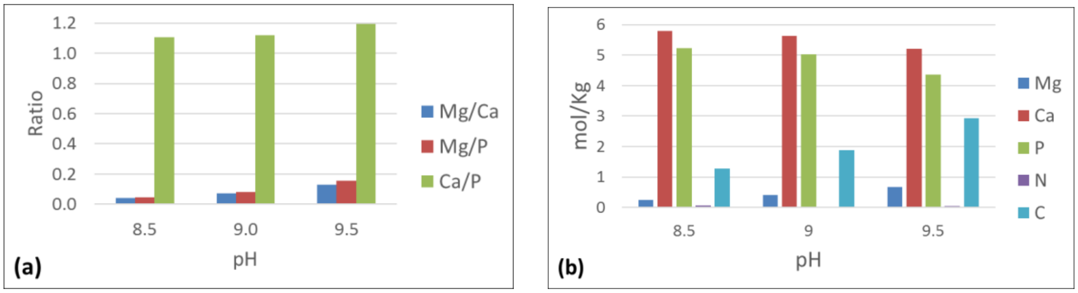


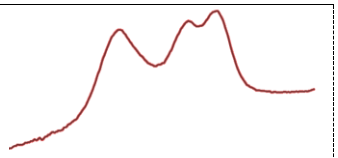
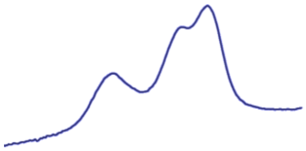
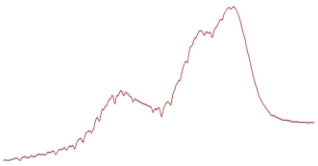
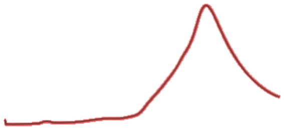
Figure 4.13. Results of ICP-AES and Elemental Analysis for the experiments without any additives with only NaOH for pH adjustment, a) Molar ratios, b) Molar contents

Le Corre et al [40] suggested that in order to obtain effective struvite precipitation the Ca^{2+}: Mg^{2+} ratio must be below 1. In this system, struvite precipitation was observed in experiments with Mg^{2+}: NH_4^+:P molar ratio equal to 5:5:1 at pH=8.5 and 9.0, with Ca^{2+}: Mg^{2+} ratio of 0.39. In the cases where only ammonium was added to the solution, this ratio was 1.95. Although, struvite precipitation was lower in these runs, it was still observed. This can explain the idea that struvite could be still precipitated if sufficient amounts of ammonium is available even with higher Ca^{2+}: Mg^{2+} ratios [41], as was the case in the mentioned experiments.

4.3.4. Using $Ca(OH)_2$ as pH adjustment reagent

Table 6 shows the results of the experiments in which $Ca(OH)_2$ was used as pH adjustment reagent: this is in fact less expensive than NaOH, and the possibility of routinely using it would not only make the process cheaper, but would also be beneficial to phosphate precipitation. As it can be seen from Table 6, P removal percentages are notably higher in these tests, compared to the previous ones. At pH=9.5, up to 99% P removal, could be reached, which is remarkable. This is due to the fact that more Ca^{2+} in the system promotes calcium phosphate compounds precipitation, however, FTIR results indicate that there is no direct evidence of the presence of struvite in the precipitates. In fact, at pH=9.5, there is substantial growth of carbonate groups peak intensity at around 1400-1500 cm^{-1}, suggesting that the addition of $Ca(OH)_2$ will lead to mixture of struvite, ACP and calcite precipitation (small amounts of struvite and calcite, and large amounts of ACP) at lower pH, and mostly calcite-rich precipitates at higher pH.

Table 4.6. FTIR and P removal percentage results for the experiments with $Ca(OH)_2$ for pH adjustment.

Using $Ca(OH)_2$				
Mg:NH_4:P				
	5:5:1		3:3:1	
pH	P removal %	FTIR 1200-2000 cm^{-1}	P removal %	FTIR 1200-2000 cm^{-1}
8.5	68.1		71.7	
9.0	89.5		88.4	
9.5	99.2		99.6	

XRD analysis results confirm this, as it can be seen in Figure 4.14. Herein, the green line is related to the final precipitates of the test with 5:5:1 molar ratios using $Ca(OH)_2$ for pH adjustment to 8.5. Here also, the only clearly visible pattern is the broad peak at around x=30 degrees (circle in the Figure 4.14), related to the amorphous P form (ACP). The peaks associated to struvite are not present in the XRD, as it can be determined by comparing the former to the black line (5:5:1 at pH=8.5 with NaOH), and the red struvite-related points in which they are clearly visible.

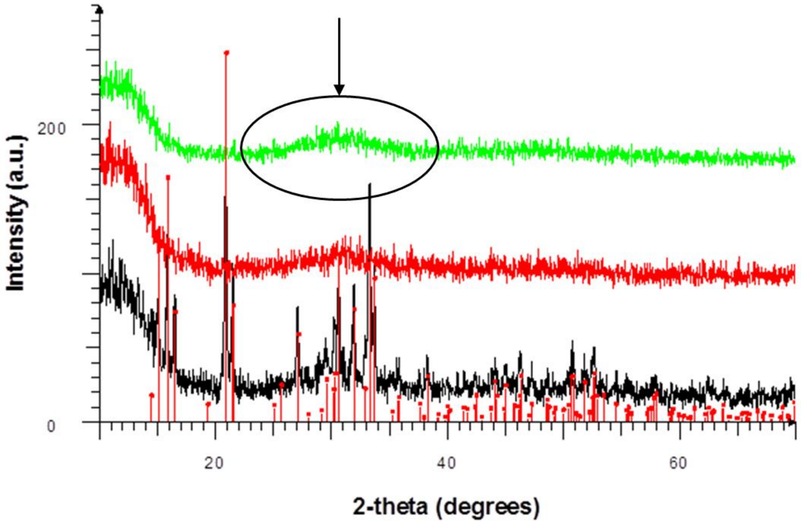


Figure 4.14. XRD pattern for experiments with 5:5:1 molar ratio at pH=8.5 using $Ca(OH)_2$ (green), comparing to the one using NaOH (black) and synthetic struvite (red dots), inside circles shows the broad peak associated to P amorphous phase.

An analysis of the composition of these precipitates using ICP-AES and elemental analysis proves the results obtained above. Figure 4.15 shows Mg^{2+}, Ca^{2+}, P, N, and C content for three of the experiments: the ones at $Mg:NH_4:P$ molar ratio 5:5:1 at pH=8.5, the one at 5:5:1 molar ratio at pH=9, and that at 3:3:1 molar ratio and pH=8.5. It can be concluded that the major fractions of the precipitates, in all these cases, are ACP and calcite, due to high P and Ca^{2+} content and small amount of Mg^{2+}. The amount of N is also very low or nearly zero in these tests. The second test highlights higher Ca^{2+} content than P, this suggests that at higher pH levels there is a higher possibility of calcite precipitation. $Mg^{2+}:P$ and $Mg^{2+}: Ca^{2+}$ ratios are considerably low for all experiments comparing with the $Ca^{2+}:P$ ratio, due to lower precipitation of struvite in these runs. It can be concluded that using $Ca(OH)_2$ as a pH-control reagent is not favorable for struvite precipitation, since in none of the experiments significant struvite was obtained in the final precipitates. However, maintaining the pH level at 8.5 will result in a precipitate consisting in a small amount of struvite and high ACP content. This could be considered as a positive, alternative solution, as ACP could still be used in the fertilizer industry due to their acceptable phosphate content, in spite of having lower solubility compared to pure struvite [42]. As the pH increases to 9 and beyond, calcite precipitation is highly affecting the impurity of the precipitates and their recycle potential.

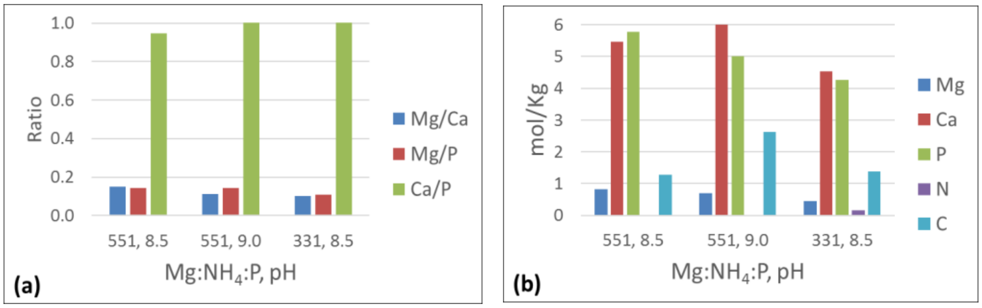


Figure 4.15. Results of ICP-AES and Elemental Analysis for the experiments with $Ca(OH)_2$ for pH adjustment, a) Molar ratios, b) Molar contents.

4.4. Discussion

Based on the results of this work, it can be concluded that using aerobic sludge for phosphorus recovery in the form of struvite is not as effective as using anaerobic sludge, which was the target of most studies. Struvite precipitation is highly affected by the presence of Ca^{2+} as competitive ion, and particularly by the competition of calcium phosphate compounds (mainly ACP) and calcite precipitation. For all the experiments, it was observed the pH of the solution tends to diminish after the precipitation of the crystals. This is due to the acidification of the solution because of H^+ release resulted from the precipitation reactions. It was observed that to achieve significant struvite precipitation in tests with aerobic sludge, high amounts of Mg^{2+} and NH_4^+ addition would be needed, which would also unfortunately make the process economically inefficient. In addition, the cost of adding NaOH, needed for pH adjustment is also relatively high [43]. Using $Ca(OH)_2$ as a more economic pH adjustment reagent proved not to be very efficient in terms of struvite precipitation, however, it might lead to achieve an alternative form precipitate rich in ACP for P recovery. In terms of effects on soil, the Ca^{2+}: Mg^{2+} ratio in the final precipitates could also impact its structure. Although lower ratios, meaning larger struvite content in precipitates, would generally be considered more favorable, this is not always the case, and it would depend on the specific soil of precipitates application. For some soils, a higher ratio would be considered better, improving their drainage [44]. In addition, calcium phosphate minerals could be utilized as fertilizers too, although not efficiently as pure struvite, as their P available content in the soil is lower than struvite, but still notable [45]. Therefore, use of $Ca(OH)_2$ rather than NaOH in the process could be favorable in specific cases, depending on specific situation.

4.5. Conclusions

The process of P precipitation was investigated in this study using different sludge samples from extended aeration, denitrification volume, and post-AD taken form the Nosedo and Pavia treatment facilities in Italy. The first part of the study showed great potential of struvite precipitation for anaerobic sludge based on FTIR, TGA and MS analysis; denitrification sludge did not have any struvite precipitation potential due to its low P concentration. The extended aeration sludge, as the main purpose of this study, was investigated in more detail.

Different tests using varied Mg^{2+}: NH_4^+: P molar ratios, at three levels of pH, were carried out. Results showed that P removal efficiency increases with the growth of pH and up to 94% P removal using NaOH for pH adjustment could be achieved at pH=9.5 (99% using $Ca(OH)_2$). Nevertheless, at higher pH values precipitates are highly affected by the presence of ACP and calcite, mixed with struvite. In order to achieve significant struvite precipitation, significant additions of both Mg^{2+} and NH_4^+ to the system would be necessary.

The only tests that demonstrated direct evidence of struvite presence in the final precipitates based on FTIR spectra were those conducted for tests at Mg^{2+}: NH_4^+:P molar ratio of 5:5:1 and pH=8.5 and 9.0. In all the other experiments, final precipitates were a mixture of struvite, ACP, and calcite with increasing calcite content at increasing pH values.

Finally, the use of $Ca(OH)_2$ as an economic pH-adjustment reagent, instead of NaOH, was evaluated. Results were not favorable to struvite precipitation, since in all the experiments major fractions of the final precipitates turned out to be ACP and calcite. However, at pH=8.5 precipitates were a mixture of a small amount of struvite and high amounts of ACP. These precipitates can still be used in the fertilizer industry as an alternative to pure struvite, due to their high phosphate content. As pH increased to 9 and above, precipitates were affected considerably by calcite formation. It could therefore be concluded that using $Ca(OH)_2$ as pH-adjusting reagent, while the system is strictly kept at pH < 9, may be considered an alternative pathway for P recovery, in the form of a mineral that can be used in fertilizer industry, although not as pure struvite.

4.6. References

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Chapter 5

Statistical Optimization of Struvite Precipitation from Wastewater Sludge by Combining Chemical Modeling and Response Surface Methodology (RSM)

A modified version has been submitted to *Science of Total Environment*.

5. Statistical Optimization of Struvite Precipitation from Wastewater Sludge by Combining Chemical Modeling and Response Surface Methodology (RSM)

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Abstract

Phosphorus resources recovery has drawn much attention during recent years. This is particularly due to its limited available quantities, and harmful environmental impact that it may have when released into aquatic environments. Struvite precipitation from wastewater or its sludge is nowadays one of the preferred approaches for phosphorus recovery as it could lead to the production of valuable fertilizer components. This process of struvite precipitation is mostly affected by pH and presence of competitive ions in the original solution. Modeling and optimization of the precipitation process may help understanding the optimal conditions under which the most efficient recovery could be achieved. In this study, a combination of chemical equilibrium modeling and response surface methodology (RSM) was applied to this aim. Results determine optimum chemical parameter values for best phosphorus precipitation recovery and removal, respectively. Identification of these optimal conditions for process control is of great importance for implementing pilot scale struvite precipitation and achieve an efficient phosphorus recovery.

Keywords: Struvite Precipitation, Statistical Optimization, Response Surface Methodology, Chemical Equilibrium modeling.

5.1. Introduction

Phosphorus is the most essential nutrient for all living organisms on Earth, widely found in nature mostly in phosphate form, due to the high reactivity of its elemental form. In spite of its biological importance (i.e. as element allowing plants growth), it can also generate serious environmental concerns when freely released into water bodies [1,2]. Phosphorous also generates serious sustainability concerns as a finite and nonrenewable resource [3,4], making its recovery a desirable goal, whenever possible. Nowadays, combining its removal and recovery from wastewater streams seems an appropriate and often feasible strategy.

Phosphorus recovery technologies have been studied for many years, and different approaches for achieving that have been proposed [5]. The most common method is the precipitation process [4,6], which product could be in the form of calcium phosphate compounds or most notably magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$), also called “Struvite”. This is an invaluable mineral that, due to its low solubility, low metal and high nutrient contents could be considered a suitable fertilizer. Different parameters impact the efficiency of struvite precipitation, such as pH and concentration of constituent ions. Many studies have investigated the process of struvite precipitation and its modeling and optimization in order to achieve high levels of phosphorus recovery. Wang et al. (2005) [7] studied the theoretical optimum values for pH that may lead to higher process efficiency (8.5-9.5). Le Corre et al. (2007) [8] investigated the kinetics of struvite crystallization reactions, showing that they are affected by the initial concentration of magnesium in the solution. Bhuiyan (2007) [9] studied with great detail struvite thermodynamics, and in particular its solubility at different temperatures and pH. There have been studies on the use of fluidized-bed reactors for struvite crystallization, and investigations on reaction parameters [10]. Morse et al. (1998) [11] conducted a comprehensive review on struvite formation and its different recovery methods.

In addition, studies have been conducted on modeling and optimization of the struvite precipitation process using chemical modeling tools, such as PHREEQC and Visual MINTEQ. Such models are capable of calculating ion speciation, saturation index, equilibrium conditions, ionic strength, etc. based on the initial conditions of a solution or mixture of solutions. Possible solid phases and related occurring reactions in the system may also be simulated. Lee et al. (2013) [12] developed an equilibrium model for struvite formation and precipitation with calcium co-precipitation. Türker & Çelen (2007) [13] used chemical equilibrium to predict ammonia removal in the form of struvite from anaerobic digester effluent. Harada et al. (2006) [14] predicted struvite formation from urine using a new equilibrium model and considering co-precipitation of calcium phosphate compounds and carbonates.

Struvite precipitation can be also modeled and optimized using statistical approaches. Statistical modeling is a powerful class of tools to investigate possible relationships between variables affecting a process and those describing its efficiency. Establishing such relationships could help process engineers to implement future designs in more efficient and possibly cost-effective ways. Statistical modeling approaches are basically a way to detect significant effects of process inputs onto process outputs. Further steps in such approaches could lead to finding an optimum range of the operating parameters, fitting a model in the form of *y=f(x)* where y is the process output or response variable and x is a set of process parameters or predictor variables. Response surface methodology (RSM) is a well-known statistical approach to this aim and, although not widely used for struvite precipitation processes, a few interesting works were conducted during the past decade [15-18] RSM was introduced in 1951 by George E.P. Box and K.B. Wilson [19], based on using a set of designed experiments to optimize a response variable. An advantage of using RSM is that it allows to understand the impact of changes in the degrees of freedom on optimum result, and can help investigate the direction of changing predictor variables needed to move towards, in order to maximize or minimize response variables. Shalaby (2015) [17] investigated optimization of phosphorus removal from industrial and synthetic wastewater streams using pH, temperature, reaction time and ion molar ratios as predictor variables. De Luna et al. (2015) [16] used pH, initial phosphorus concentration and magnesium-to-phosphorus molar ratio in order to optimize a multi-response system, considering total and dissolved phosphate, magnesium and ammonium removal percentages as response variables. Capdevielle et al. (2013) [15] considered also the reaction stirring rate, and the presence of calcium among predictor variables, and studied the optimization of phosphorus removal, particle size and struvite to calcium phosphate ratio.

This study investigates simulation and optimization of struvite precipitation from municipal wastewater stream by combining chemical equilibrium modeling with RSM's statistical approach. Chemical equilibrium models were used to complement previous experimental work by calculating ion speciation and saturation index (SI) values for struvite. Results were then further used as input data for an RSM approach, to optimize both phosphorus removal percentage and struvite's SI, helping determine optimum response values for new sets of conditions without previously calculating them through chemical equilibrium calculations. Although many studies are available on struvite chemical equilibrium modeling, few valuable studies on the application of RSM for process optimization exist but are lacking the possibility of combining both for an overall better understanding of struvite precipitation and its optimization in terms of simultaneous maximum phosphorus removal and struvite crystallization.

5.2. Struvite chemistry, kinetics and thermodynamics

Struvite precipitation occurs according to the following reaction:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O \downarrow \quad (1)$$

However, phosphate in solution may also be present in HPO_4^{2-} and $H_2PO_4^-$ forms, contributing to struvite formation according to equations (2) and (3):

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O \downarrow + H^+ \quad (2)$$
$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O \downarrow + 2H^+ \quad (3)$$

In reality, equation (2) is dominant compared to the others for the pH range at which struvite formation is favorable (7-11) [20]. Therefore, it is important to take all reactions, and particularly the reaction of HPO_4^{2-} into account in the study of struvite precipitation.

Most important factors affecting this process are pH, concentrations of constituent ions and presence of competitive ions, most notably Ca^{2+} [21]. Struvite precipitation might take place spontaneously at different locations of a wastewater treatment facility and consequently could lead to specific problems such as pumps, pipes and valves clogging [22], however, controlled occurrence of the reaction could be a very effective method for recovering phosphorus.

The mechanism of struvite crystallization can be categorized in three steps: nucleation, crystal growth and aggregation [8, 23]. Nucleation is the formation of small crystals of struvite followed by the crystal growth, which is the development of the small sized crystal into larger ones. Aggregation occurs when several crystals come together and form some sort of clusters. Such mechanisms are affected by many factors such as pH, thermodynamics of the system, kinetics of the reaction, initial ionic concentration, temperature, etc. [24]. Studies on struvite precipitation kinetics suggested that these three reaction steps could all be empirically formulated as a function of struvite supersaturation ratio [25, 26]. The latter is basically the ion activity product (IAP) of constituent ions in solution over its equilibrium solubility product (K_{sp}). A solution is supersaturated when ionic concentrations are above their equilibrium levels, and consequently precipitation may occur to return the system into equilibrium conditions. Similarly, when ion concentrations are below equilibrium level, the system is called undersaturated, and precipitation will not occur. Equation (4) formulates the "Saturation Index" concept, which is the logarithm of supersaturation ratio [27]:

$$IAP = \{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\} \quad (4)$$
$$SI = \log(\frac{IAP}{K_{sp}}) \quad (5)$$

Basically, when SI > 0 the system is supersaturated and when SI < 0, it will be in undersaturated condition. SI = 0 means that the system is at equilibrium.

Investigating the thermodynamics and kinetics of struvite precipitation could of course be done experimentally [9, 23], however, chemical equilibrium modeling tools (e.g. PHREEQC and Visual MINTEQ) may also be used to that purpose, with the advantage, besides achievement of the faster results, of predicting equilibrium conditions and ion speciation based on initial solution conditions.

5.3. Materials and methods

5.3.1. Sludge characteristics

Sludge samples were collected in Milan, Italy at Nosedo municipal wastewater treatment facility, the largest in northern Italy and the main serving the city of Milan. The plant is serving 1 million P.E., producing 50,000 tonnes/yr of biological sludge, containing 1400 tonnes/yr of phosphorus, with a considerable potential for recovery. Samples were taken from the oxidation tank in the activated sludge system, where the highest concentration of phosphorus occurs due to its release after being under anaerobic condition for 1-2 days, and therefore where the highest potential of Struvite precipitation may present itself. Table 5.1 shows the main (average) characteristics of the samples.

Table 5.1. Wastewater filtrate characteristics

Ions	**Concentrations (mg/L)**
Ca^{2+}	101
Mg^{2+}	26.4
P^{*}	40.3
NH_4^{+}	32.6

* Solution-phase

5.3.2. Analytical methods

Phosphorus concentrations were measured according to the colorimetric method (EPA 365.3) [28] using UV-Vis spectroscopy. (HP 8452A Diode Array Spectrophotometer). The samples were first filtered using 2.5 µm filtration papers and then the P measurement was made on the solution phase. The precipitates obtained in each experiment were washed with deionized water and dried at room temperature. Analysis of the precipitates was conducted using Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer 1600 series), Thermal Gravimetric Analysis (TGA) (Mettler Toledo TGA 1 STARe System), Mass Spectroscopy (MS), Inductively Coupled

Plasma Atomic Emission Spectroscopy (ICP-AES) and Elemental Analysis to identify different solid phases in the final precipitates.

5.3.3. Experimental setup

The experiments were done with the filtered solution in the laboratory using 200 ml beakers. The solution of NaOH was used to adjust the required pH. $MgCl_2$ and NH_4Cl were used as a source of magnesium and ammonium respectively. The final precipitates were collected after 20 hr in order to let the process reach its equilibrium. To do so, the solutions were filtered with 0.45 µm paper filters and were put at room temperature to dry and be ready for the FTIR analysis.

5.3.4. Chemical equilibrium modeling using PHREEQC

The PHREEQC model is a geochemical software tool designed by US Geological Survey (USGS) [29] capable of simulating a wide variety of aqueous calculations such as ion speciation batch-reactions and calculating saturation index (SI) values based on the solution characteristics (ion concentrations, pH, etc.) as input. In this study, PHREEQC version 3.0 was used to model chemical equilibria.

5.3.4.1. PHREEQC Database modification

PHREEQC includes different databases describing different species with their corresponding reactions and solid phases precipitated in the final product. The default PHREEQC.DAT database, was selected in this study. However, as it is not optimized for the specific case of struvite precipitation, it needed to be modified. The K_{sp} of struvite used in PHREEQC modeling is taken from [30] (K_{sp} = 13.26). There are several solid phases that could theoretically precipitate in such a system, however, their precipitation is highly dependent on operating conditions of the process. Based on the operating conditions of this study, some necessary solid phases were added to the data base and some unnecessary phases that were unlikely to precipitate were removed from it [6, *Chapter 4*]. Table 5.2 shows the list of solid phases that included in the database of PHREEQC for this study.

Table 5.2. List of solid phases included in the database of PHREEQC software with their corresponding K_{sp} values

Solid phase	**Reaction**	**pK_{sp} at 25°C**	**Reference**
Struvite	$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4.6H_2O$	13.26	[30]
Monetite (DCP)	$Ca^{2+} + HPO_4^{2-} \leftrightarrow CaHPO_4$	6.81	[31]
Amorphous Calcium Phosphate (ACP)	$3Ca^{2+} + 2PO_4^{3-} + xH_2O \leftrightarrow Ca_3(PO_4)_2.xH_2O$	25.46	[32]
Calcite	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$	8.42-8.22-8.48	[32,33]

5.3.4.2. Model operation

Concentrations of all available ions were fed to the PHREEQC model as the input. pH level and the amount of NaOH added to the system to adjust its value were also included. The output of the model consists of ion speciation and saturation index (SI) values for each of the solid phases defined in the database. Ion speciation data were used to calculate phosphorus removal percentage for each of the experiments.

5.3.5. Statistical modeling

5.3.5.1. Response surface methodology (RSM)

Statistical testing was conducted according to the Box-Behnken Design (BBD). BBD is a specific type of experimental design introduced in 1960 [19], used for response surface methodology (RSM) applications. It uses factors with at least three levels (maximum, minimum and center point) and fits a second order model to the data. Figure 5.1 shows the schematics of the Box-Behnken Design for 3 factors, and the points at which the experiments need be performed. BBD needs 15 experiments for obtaining three predictor variables, as was the case of our study. Level of pH, calcium to magnesium molar ratio (Ca^{2+}:Mg^{2+}) and ammonium to phosphorus molar ratio (NH_4^+:P) have been chosen as the three predictor variables to optimize struvite saturation index (SI) and phosphorus removal percentage as response variables. Table 5.3 shows the 15 runs of experiments with their associated levels for each factor. The initial value of the Ca:Mg and NH_4:P molar ratios were 2.33 and 1.5 respectively. Ca:Mg ratio is already high and will make calcium very competitive for phosphate precipitation. therefore, it was chosen as the highest level and two lower levels with 0.8 step (1.53 and 0.73) were chosen to reach a molar ratio below 1. On the contrary, the NH_4:P molar ratio lower than the initial does not make much sense since the amount of ammonium will be too low for struvite precipitation. in this case, initial value was kept as the lowest level and two other higher levels were chosen with the step of 1 (2.5, 3.5). for the pH, lowest level was chosen as 8.5 since it was the point that the precipitation started to be significant enough to be filtered and observed. The highest level was set as 9.5 because after this point it was observed that most of the precipitate consists of carbonates. The second order responses for chosen predictors are formulated according to equation (6):

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i<j} \beta_{ij} X_i X_j + \sum_{i=1}^{3} \beta_{ii} X_i^2 \qquad (6)$$

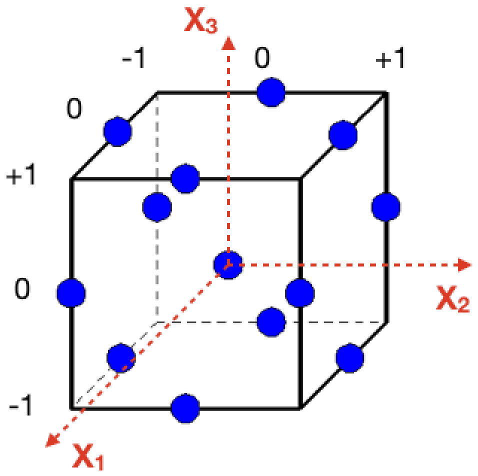

Figure 5.1. Box-Behnken design for 3 factors

Table 5.3. values of predictor variables with their coded values in the Box-Behnken design

Run	**Ca:Mg**	**NH_4:P**	**pH**	**X_1**	**X_2**	**X_3**
1	0.73	1.5	9.0	-1	-1	0
2	2.33	1.5	9.0	1	-1	0
3	0.73	3.5	9.0	-1	1	0
4	2.33	3.5	9.0	1	1	0
5	0.73	2.5	8.5	-1	0	-1
6	2.33	2.5	8.5	1	0	-1
7	0.73	2.5	9.5	-1	0	1
8	2.33	2.5	9.5	1	0	1
9	1.53	1.5	8.5	0	-1	-1
10	1.53	3.5	8.5	0	1	-1
11	1.53	1.5	9.5	0	-1	1
12	1.53	3.5	9.5	0	1	1
13	1.53	2.5	9.0	0	0	0
14	1.53	2.5	9.0	0	0	0
15	1.53	2.5	9.0	0	0	0

The R programming language has been used to perform RSM and statistical analysis of process data (The Comprehensive R Archive Network, CRAN). R is a powerful free software environment developed specifically for statistical modeling, computing and graphics. It supports the use of different packages with built-in functions designed for particular purposes. The "RSM" package [34] was used in this work, as it contains valuable functions for BBD and RSM applications.

5.4. Results and discussion

5.4.1. Chemical equilibrium modeling

The results of PHREEQC modeling are summarized in Table 5.4. The model calculated ion speciation and struvite SI values for all runs. It can be seen that all the calculated SI values are positive, which suggests the fact that struvite precipitation could occur in the system. However, some of these SI values are very low (e.g. 9th run), meaning that in those cases there is just a slight possibility of struvite precipitation, and therefore probably calcium phosphate and other potential compounds will prevail in the final precipitates. The range of SI values obtained during this whole set of experiments is not notably high (less than 1 for all of them), in contrast with most literature results that generally report higher values (specifically, greater than 1) for struvite SI. This may be due to the fact that most literature studies have worked with wastewater having considerably higher phosphorus concentrations than the one used herein (300-500 mg/L compared to around 40 mg/L in our case) due to the fact that anaerobic digester filtrate is being used usually. Fang et al., 2016 [35] suggests that as the initial concentration of phosphorus increases, the value of SI will also increase. This can be true at least up to concentrations of around 1000 mg/L at which the SI will start to decrease [35].

Table 5.4. PHREEQC model results

Run	**X_1**	**X_2**	**X_3**	**SI**	**P rem%**
1	-1	-1	0	0.48	82.46
2	1	-1	0	0.17	72.76
3	-1	1	0	0.84	82.15
4	1	1	0	0.54	72.20
5	-1	0	-1	0.54	70.28
6	1	0	-1	0.21	58.03
7	-1	0	1	0.60	92.08
8	1	0	1	0.32	86.33
9	0	-1	-1	0.13	62.40

10	0	1	-1	0.49	61.60
11	0	-1	1	0.22	88.59
12	0	1	1	0.58	88.29
13	0	0	0	0.52	75.86
14	0	0	0	0.52	75.89
15	0	0	0	0.52	75.89

The phosphorus removal percentage and amount of total phosphorus precipitated, both calculated based on the result of PHREEQC modeling, have been compared to the measured values and the result is shown in the Table 5.5. Although some inaccuracies and errors in the comparison between calculated and measured values is inevitable, it can be concluded that the PHREEQC software had a decent performance on simulating these experiments. Some errors are believed to be related to measurements errors in the lab.

Table 5.5. Comparison of the predicted results by PHREEQC with the measured values

Run	**P rem. Predicted (%)**	**P rem. Measured (%)**	**P prec. Predicted (mg)**	**P prec. Measured (mg)**
1	82.46	84.27	33.23	31.24
2	72.76	82.99	29.32	30.85
3	82.15	82.05	33.11	29.77
4	72.20	82.21	29.10	30.07
5	70.28	54.72	28.32	23.60
6	58.03	61.43	23.39	24.14
7	92.08	91.93	37.11	34.66
8	86.33	89.28	34.79	33.65
9	62.40	68.47	25.15	25.74
10	61.60	62.36	24.83	24.74
11	88.59	92.15	35.70	34.09
12	88.29	87.62	35.58	33.65
13	75.86	85.74	30.57	31.37
14	75.89	82.31	30.58	30.84
15	75.89	84.13	30.58	30.78

RMSE	6.97	1.93

5.4.2. Analysis of the final precipitates

The analysis of final precipitates using Fourier Transform Infrared (FTIR) spectroscopy confirms the presence of phosphate groups (PO_4^{3-}) and water molecules by showing their associated peaks at around 1000-1100 and 3500-3600 cm^{-1} respectively [36] (Figure 5.2a, Before TGA). The spectrum in the range 1200-2000 cm^{-1} has a more complicated explanation. Visible peaks in this range are associated to 1440 and 1550 cm^{-1} and could be assigned to H-N-H bonds. Nonetheless, carbonate groups (CO_3^{2-}) also show similar peaks in this range [37] The small peak at 1650 cm^{-1} could be related to the H-bonds of the amorphous phases, therefore, peaks in this range seem to be the results of individual peaks convolution, related to each group. This could suggest presence of struvite, ACP and calcite at the same time in the final precipitate. TGA/DTGA (Derivative TGA) analysis of the precipitates (Figure 5.2b) demonstrates a weight loss at around 150 °C, which could be related to the loss of both ammonia and water. Two other weight losses are also visible at around 650 and 800 °C that are typical weight loss of carbon dioxide related to the presence of calcite [38]. Figure 5.2c shows the MS analysis of the precipitate. The results of TGA can be confirmed by MS due to the presence of a peak for the graph with mass-to-charge ratio of 17 m/z ($NH_3 + H_2O$) and two very small peaks for mass-to-charge ratio of 44 m/z (CO_2).

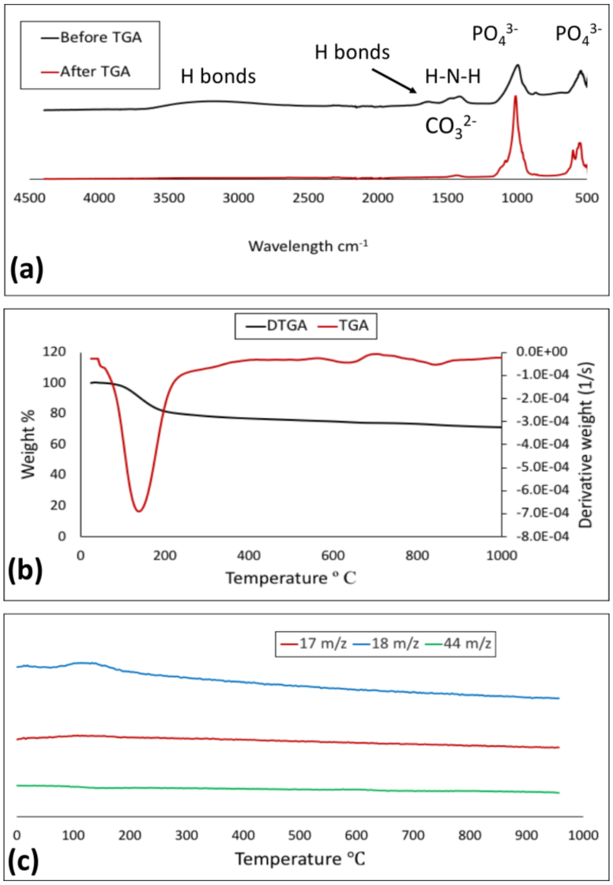

Figure 5.2. FTIR spectra (a), TGA (b) and MS (c) of precipitates from aerobic sludge sample.

The ICP-AES and elemental analysis of the final precipitates (Figure 5.3) show the presence of P, Mg and N that are related to the presence of struvite. Although high amount of Ca is also detected. The higher moles of Ca with respect to the P could be due to the precipitation of calcite in addition to ACP, which is justified by higher P content in comparison to Mg and N.

Very similar results have been obtained for almost all the experiments. The main difference is in the intensity of the peaks in the FTIR results. As the pH increases from 8.5 to 9.5, the peaks assigned to carbonate and phosphate groups are intensified. This suggests the more phosphorus in the final precipitates thus higher P removal percentage. However, the intensified peaks of carbonate indicate high calcite precipitation.

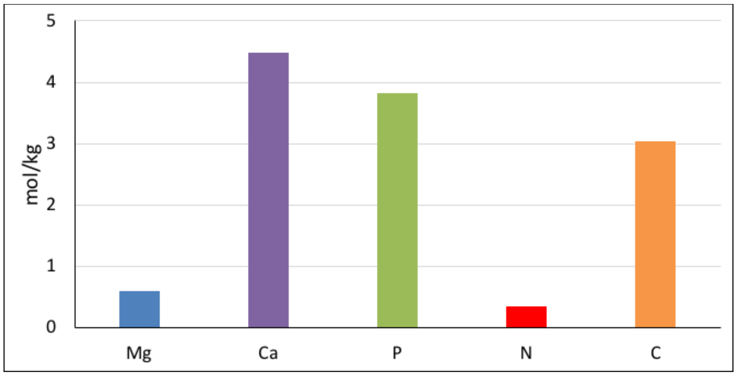

Figure 5.3. ICP-AES analysis of the final precipitates.

5.4.3. Statistical modeling

5.4.3.1. RSM

Results of RSM were obtained for each of the response variables in this study. Analysis of variance (ANOVA) of RSM models shows significant tests for all parameters, the main effects of predictors, two-way interactions and quadratic terms. Results for SI show (Table 5.6) that all terms, except two of the interactions (Ca:Mg.NH_4:P and NH_4:P.pH) are significant, and should be taken into account in the model. The adjusted R-squared value is quite good (0.99), but the ANOVA analysis shows a lack of fit, which may be attributed to the center points. All three center points have the same value for the SI since they are calculated under the same conditions by PHREEQC. The plot of the residuals vs fitted values (Figure 5.4a) confirms the good fit of the model, as there is no specific pattern in the plot. The same analysis for the second response (phosphorus removal percentage) indicates that the only parameters significantly affecting it are pH and its quadratic term (Table 5.7). This was an unexpected result, especially in comparison to other literature studies, however, the authors believe two reasons might be involved. One, as mentioned before, being the concentrations of constituent ions, relatively low compared to similar studies, that could lead to a magnification of pH effect, compared to other factors. On the other hand, the values of the second response are obtained experimentally, unlike those of the first response, which were predicted by PHREEQC. Measurement error and lack of high accuracy for second response values, compared to the first one's, could lead to this observed difference between fitted models. Nevertheless, the insignificant lack of fit suggested by ANOVA, and the residual-vs-fitted plot for the second response confirm the good fit of the model (Figure 5.4b).

Table 5.6. ANOVA for the Saturation Index (SI)

	Estimate	**Std. Err**	**t value**	**Pr(>|t|)**	
Intercept	5.2e-01	1.2910e-03	402.7903	1.790e-12	***
X1	-1.525e-01	7.9057e-04	-192.8989	7.104e-11	***
X2	1.812e-01	7.9057e-04	229.2651	2.996e-11	***
X3	4.375e-02	7.9057e-04	55.3399	3.644e-08	***
X1.X2	2.500e-03	1.1180e-03	2.2361	0.07559	
X1.X3	1.250e-02	1.1180e-03	11.1803	9.989e-05	***
X2.X3	-2.095e-17	1.1180e-03	0.0000	1.00000	
X1^2	2.500e-02	1.1637e-03	21.4834	4.053e-06	***
X2^2	-3.750e-02	1.1637e-03	-32.2252	5.406e-07	***
X3^2	-1.275e-01	1.1637e-03	-109.5656	1.201e-09	***
Adjusted R-squared		0.9999			
F-statistic		1.184e+04			
p-value		2.809e-10			
Lack of fit Pr(>|t|)		2.2e-16			

Table 5.7. ANOVA for P removal percentage

	Estimate	**Std. Err**	**t value**	**Pr(>|t|)**	
Intercept	84.0600	1.8078	46.4986	8.689e-08	***
X1	0.3675	1.1070	0.3320	0.753379	
X2	-1.7050	1.1070	-1.5401	0.184154	
X3	14.2500	1.1070	12.8721	5.039e-05	***
X1.X2	0.3600	1.5656	0.2299	0.827246	
X1.X3	-2.3400	1.5656	-1.4946	0.195243	
X2.X3	0.3950	1.5656	0.2523	0.810852	
X1^2	-2.2450	1.6295	-1.3777	0.226765	
X2^2	1.0650	1.6295	0.6536	0.542251	
X3^2	-7.4750	1.6295	-4.5872	0.005908	**
Adjusted R-squared		0.9296			
F-statistic		21.53			
p-value		0.001754			
Lack of fit Pr(>|t|)		0.1746929			

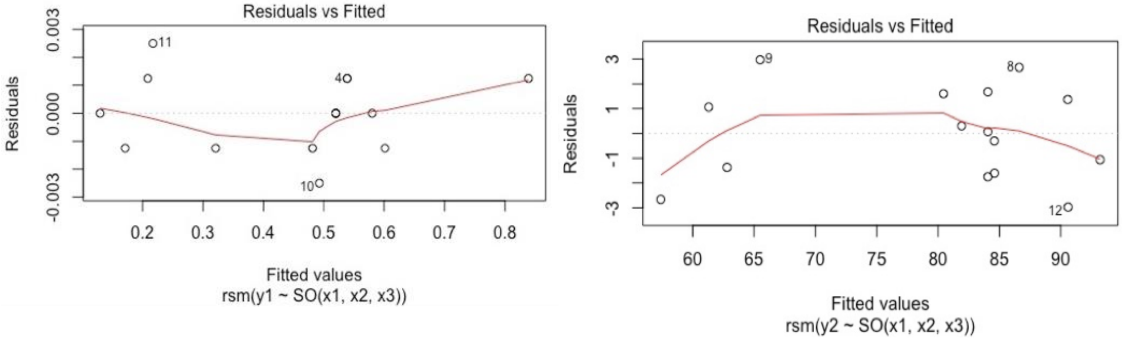

Figure 5.4. Residuals versus fitted values for response variables, a) SI, b) P removal %.

The fitted response for SI and P removal percentage is presented with equations:

$$SI = 0.52 - 0.1525X_1 + 0.1812\,X_2 + 0.04375X_3 + 0.0125X_1X_3 + 0.025\,X_1^2 - 0.0375\,X_2^2 - 0.1275X_3^2$$

$$P_{rem} = 84.06 + 14.25X_3 - 7.475X_3^2$$

RSM shows that for both responses, the stationary point of the fitted response surface is a saddle point. Saddle point is a type of stationary point that is neither a maximum nor a minimum. Therefore, depending on the direction towards which one moves from that point, the response variable can either increase or decrease (Figure 5.5). The stationary points for saturation index and phosphorus removal percentage response variables are Ca:Mg= 3.8, NH_4:P= 5, pH= 9.15 and Ca:Mg=1.2, NH_4:P=3.17, pH= 9.5 respectively. It can be understood that for some of the predictors the stationary point is outside of the region of experimental design. The method of ridge analysis has been used in this work in order to search for the optimum values of the response variables in the experimental design region.

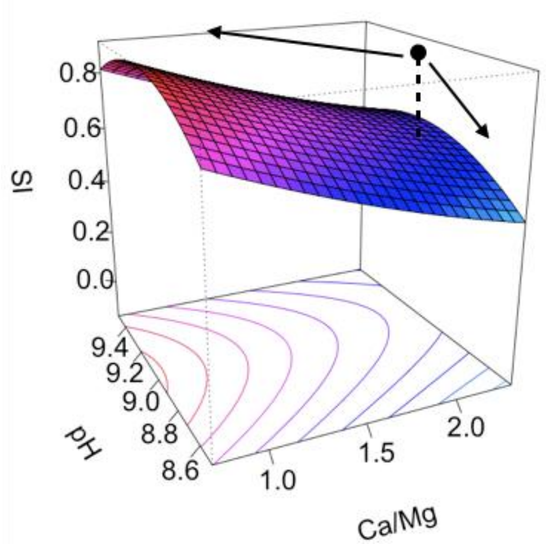

Figure 5.5. A saddle point obtained for the response variables.

5.4.3.2. Ridge analysis

Ridge analysis is a powerful method for exploring the optimum values of a fitted response surface, which has a stationary point outside of the experimental design region. The results of the ridge analysis for both SI and P removal percentage show the directions towards which optimum values of the response variables can be achieved. Figure 5.6 plots the coded values of the predictors vs the distance from the stationary point. It can be seen that the further we move from the stationary point the only predictor variables that are affecting the response variables are Ca:Mg and NH_4:P for SI and P removal percentage respectively. On the other hand, it suggests that in order to optimize the value of SI we need to move away from the stationary point towards the direction that Ca:Mg is decreasing. The similar pattern is true for the P removal percentage, but the direction is towards decreasing the NH_4:P value. Figure 5.7 illustrates the plots of estimated values for the response variables as the distance from the stationary point increases. The red lines show standard error values, which are very limited in case of SI. However, for P removal the error first decreases and then increases as the distance from the stationary point keeps increasing. Therefore, it limits the furthest distance that can be chosen to move forward from stationary point. To avoid high values of errors for the estimated response variables the distance needs to be kept in a specific range (between 1 and 1.5) to keep the error at minimum level.

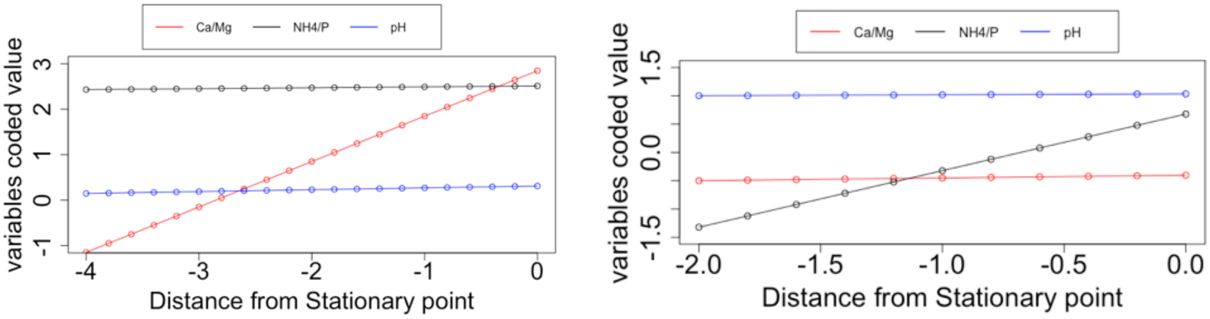

Figure 5.6. Predictor variables coded values versus their distance from the stationary point, a) SI, b) P removal %.

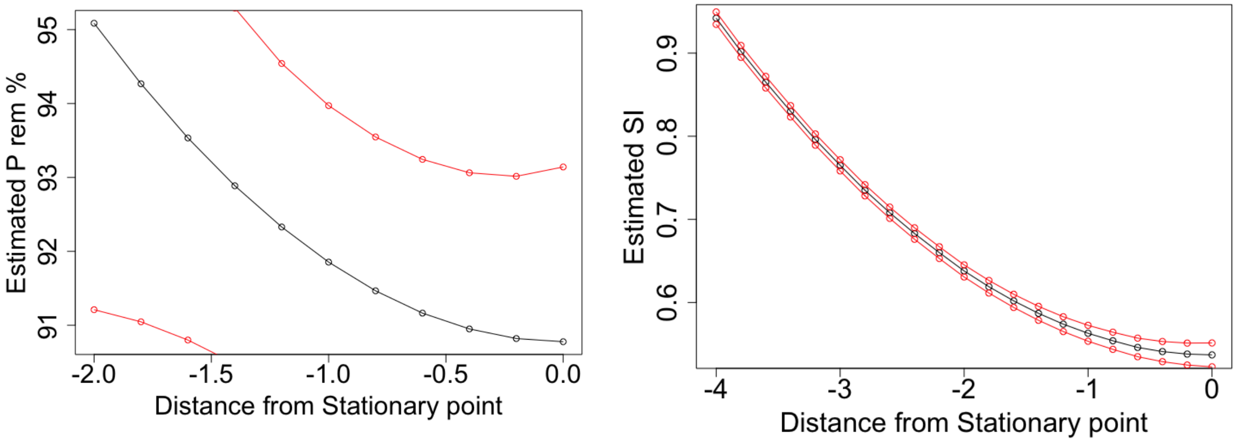

Figure 5.7. Estimated response variables vs distance from stationary point.

Figure 5.8 and 5.9 illustrate the perspective response surfaces for SI and P removal percentage, respectively. The locations of the stationary points and the directions towards which the optimum values will be obtained, are demonstrated in the figures. Each surface plots the values of the response variable based on two of the predictor variables sliced at the stationary point for the third one. It can be seen in Figure 5.8 that the P removal percentage as response variable is highly affected by pH and not much by the other two predictors.

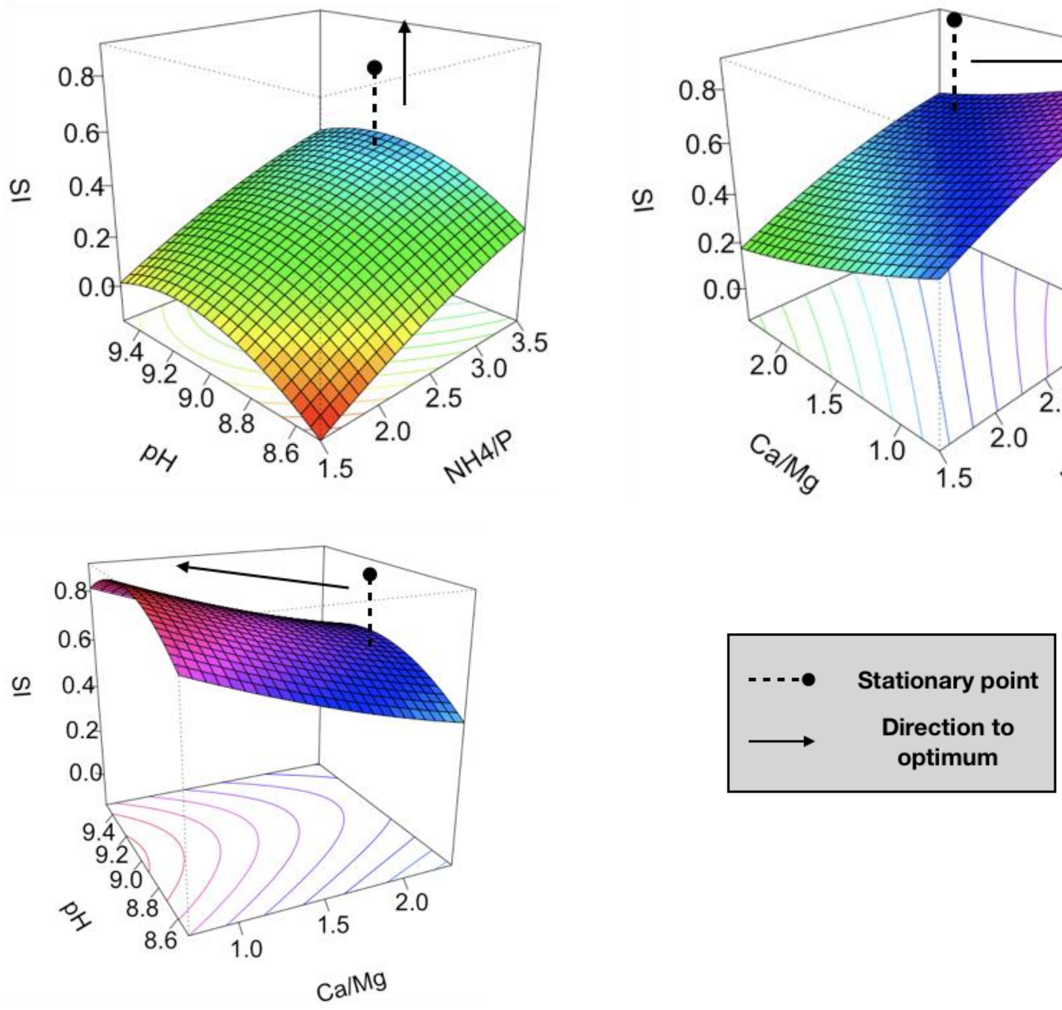

Figure 5.8. Response surface perspectives for SI based on predictor variables.

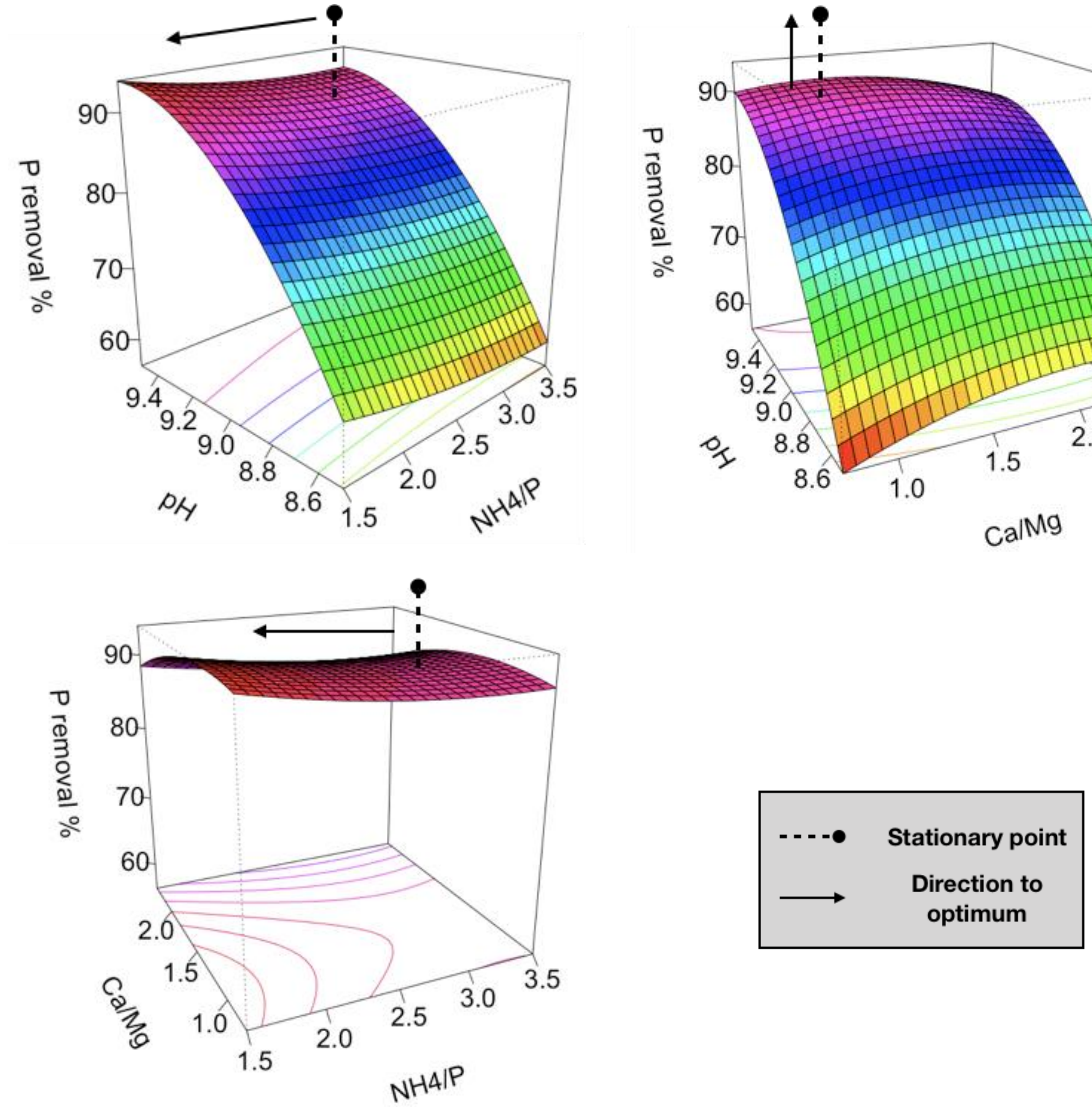

Figure 5.9. Response surface perspectives for P removal percentage based on predictor variables.

Table 5.8 shows the optimum values (or ranges) of the predictor variables obtained by RSM and ridge analysis. It can be concluded that by increasing the value of pH up to 9 both responses are increasing. However, they are not responding in the same way after that: above pH=9, P removal percentage will still increase but the value of struvite SI will decrease. This means that after this point, the possibility of struvite precipitation will decrease, and calcium phosphate compounds will be responsible for increasing P removal percentage. The optimum Ca:Mg ratio for the SI is 0.8, which is aligned with literature, suggesting a value less than 1 [39]. Obviously, higher P removal percentage will need higher Ca:Mg ratios as this promotes calcium phosphate precipitation. Optimum values for the NH_4:P ratio were obtained as 2 and >3.5 for P removal percentage and SI respectively. Although the optimal value of NH_4:P for SI is off the region of design in our experiments, it can suggest that in order to achieve a higher struvite precipitation possibility the ammonium content of the solution needs to be sufficiently more than phosphorus content. This could be explained by the fact that phosphorus definitely gets involved in other competitive reactions, mostly for calcium phosphate compounds formation. However, the model suggests a lower value of NH_4:P ratio for P removal percentage as a lower value favors the precipitation of calcium compounds instead of struvite [15]. The optimum SI calculated for Ca:Mg = 0.8, NH_4:P = 3.5 and pH = 9 is 0.82 and its associated P removal percentage is 84.06. On the other hand, Ca:Mg = 1.2, NH_4:P = 2 and pH=9.5 will increase the P removal percentage to 90.83 but at the same time will lead to have a lower SI of 0.39. It can be concluded that keeping Ca:Mg lower than 1, NH_4:P higher than 3 and pH at 9 will achieve a better struvite precipitation at the expense of lower total phosphorus removal. Therefore, it seems that to achieve high P removal for meeting the limits, struvite precipitation process is not sufficient per se, since obtaining a purer struvite product leads to lower P removal percentage.

Table 5.8. Optimum values (or ranges) for predictor variables

Predictor variable	**Optimum value for Saturation index (SI)**	**Optimum value for P removal %**
Ca:Mg	0.8	1.2
NH_4:P	> 3.5	2
pH	9	9.5

5.5. Conclusions

In this study, chemical modeling was used in combination with response surface methodology analysis in order to investigate the optimum conditions under which high phosphorus recovery in the form of struvite can be achieved. A Box-Behnken design was applied with pH, Ca:Mg and NH_4:P as the 3 predictor variables. The values of struvite saturation index calculated by the chemical equilibrium modeling software (PHREEQC) and phosphorus removal percentage were utilized as the system response variables. The results show the optimum values of pH=9, Ca:Mg=0.8, NH_4:P>3.5 and pH=9.5, Ca:Mg=1.2, NH_4:P=2 for SI and P removal percentage respectively. It can be concluded that in order to have higher phosphorus recovery in the form of struvite the Ca:Mg ratio needs to be kept under 1 and the pH at around 9. As the pH increases above 9, very high phosphorus removal percentage (>90%) can be achieved but the possibility of achieving high struvite precipitation diminishes.

The results of RSM and chemical modeling of struvite precipitation could be very helpful for the design of the precipitation process at pilot scale. Optimized values or ranges of the significant process variables will lead to a more efficient and productive pilot design for recovering phosphorus in the form of struvite as a valuable product.

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Chapter 6

Pilot-Scale Study of Phosphate Precipitation Process from Synthetic Aerobic Sludge

In preparation for further submission.

6. Pilot-Scale Study of Phosphate Precipitation Process from Synthetic Aerobic Sludge

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Abstract

Struvite precipitaion is an excellent method for phosphorus recovery. It leads to the production of a mineral that has high value as a fertilizer. However, this process is not widely used at full scale due to its economic limitation. This study covers a pilot-scale experimentation of the phosphate precipitation paying attention to the effect of pH and reactor retention time. The pH of the solution was controlled using a PID-Time Proportional control system inside the reaction zone to deal with the acidification of the solution due to the crystallization process. Three retention times of 30, 60 and 120 minutes were considered at two levels of pH; 8.5 and 9.0. the results show that phosphorus removal is being affected mainly by the pH of the solution and is not much dependent on the retention time of the reactor. It rapidly decreases at the start of the reaction and then reaches to a stable state. It is also demonstrated that 30 minutes retention time is not enough for the completion of the reaction since there is still a high amount of NaOH required at the end of the retention time for the reaction to be completed, while this amount for RT of 60 and 120 minutes is considerably lower. The weight of the precipitates was increasing in time for all the experiments that means the crystals are growing. The RT of 60 minutes was not enough for the crystals to grow despite being almost sufficient for the reaction to be completed since only after 60-90 minutes the crystals start to grow considerably. The FTIR result did not present direct evidence of struvite in the obtained preciptates, however, there is the possibility of having a calcium phosphate-rich product as an alternative fertilizer to pure struvite.

Keywords: Pilot, Phosphorus Recovery, PID Control, Retention Time, Struvite Precipitation

6.1. Introduction

The environmental concern of the high phosphorus (P) concentration in water bodies has raised the attention towards its removal technologies [1,2]. This is particularly a more critical issue in “sensitive areas” where more stringent regulations are present for nutrients removal [3]. In addition, the increasing trend of P consumption for food production because of population growth and its limited and finite resources around the world, have increased the need for developing new technologies for its recovery [4]. The most common approach for P recovery that has been studied during past years is chemical precipitation mainly in the form of struvite or calcium phosphate [5,6]. Struvite ($MgNH_4PO_4.6H_2O$) is a white crystalline mineral that was initially considered as a potential problem in wastewater treatment facilities because of its spontaneous precipitation in equipment such as pumps and pipes. However, due to its high nutrients content and low solubility it could be used directly as a fertilize [7,8]. The process of struvite precipitation could be affected by many chemical and physical factors such as pH, $Mg:NH_4:P$ molar ratios, initial concentration of P in the solution, agitation rate and retention time (RT) [9-11]. However, probably the most critical factor is the presence of other competitive ions, particularly calcium (Ca). Calcium in the reactor could make reactions with phosphate and carbonate ions and precipitate in the form of different calcium phosphate compounds and calcium carbonate (calcite). This factor makes a considerable impact on the purity of the final product. Amorphous calcium phosphate (ACP) is the most probable form of calcium phosphate that could precipitate in such a system [12,13]. It could then be transformed to more stable forms such as tricalcium phosphate (TCP) and hydroxyapatite (HAP) in long retention time. Although, the main purpose is to recover struvite as pure as possible, ACP could also be used in the fertilizer industries because of its high P content [14,15].

Struvite precipitation process has been studied for many years using anaerobic digestion sludge where the P content is sufficiently high to achieve efficient struvite precipitation. However, some studies suggest the possibility of using aerobic sludge for this aim [16]. Typically, the P concentration entering the activated sludge stage in a wastewater treatment facility is around 1-7 mg/l, which is not sufficiently high for struvite precipitation. Nonetheless, the presence of polyphosphate accumulating organisms (PAOs) in the anaerobic zone leads to a high P release that is followed by a luxury uptake in the aerobic zone [17,18]. This P release makes the condition suitable for achieving struvite precipitation because of the increases P content in sludge that could be up to 3-7 % (dry basis).

While many studies on the struvite precipitation have been published so far, few works have been done on the process in pilot scale [19-23] and to the best knowledge of the authors, there is no study on the pilot scale process of struvite precipitation using the aerobic sludge. This is basically because aerobic sludge was not considered suitable enough for efficient struvite precipitation because of low phosphorus content in the sludge.

This study is based on previous research on aerobic sludge taken from Nosedo wastewater treatment plant, which is the largest facility serving the city of Milan in North Italy. Previous studies were focused on investigating struvite precipitation condition based on lab-scale experiments (Chapter 4). The experiments were designed with different levels of pH and various Mg:NH_4:P molar ratios and an extensive analysis has been conducted on the obtained precipitates to study different solid phases precipitating in operating conditions. A chemical equilibrium modeling of the process in combination with a statistical optimization approach has been studied to achieve optimum conditions under which high P removal and struvite precipitation could be achieved (Chapter 5). This paper presents the study of this process in pilot scale taking advantage of the results of both previous experimental and modeling studies and investigates the effect of different reaction parameters on the process efficiency at larger scale. The preliminary objectives of this study were first to implement a pilot-scale reactor being able to perform a crystallization reaction at constant level of pH (using a pH control system) and second to investigate the possibility of obtaining struvite or alternatively calcium phosphate precipitates as the final product.

6.2. Materials and Methods

6.2.1. Synthetic Aerobic Sludge

For the aim of this study, a synthetic solution has been made based on the characteristics of aerobic samples taken from Nosedo WRRF. Different salts have been added to the tap water for making the synthetic solution including $MgCl_2.6H_2O$, NH_4Cl, KH_2PO_4, $CaCl_2.2H_2O$, $MgSO_4.7H_2O$, Na_3PO_4. The reported value of Ca concentration in tap water was considered for making synthetic solution. The pH of the solution was adjusted to 7.6, which was the average pH of the aerobic sludge samples taken from the plant. Based on the previous studies on the process of struvite precipitation for aerobic sludge (Chapter 4) the Mg and NH_4 were added to the synthetic solution to keep the Mg:NH_4:P molar ratio at 5:5:1, which was the best condition obtained for struvite precipitation in lab scale in which direct evidence of struvite precipitation was visible through FTIR spectra.

6.2.2. Pilot Setup

A reactor with 200 L capacity has been used for the pilot scale experiments. It has a cone-shaped area to facilitate the sedimentation of the crystals. The reactor consists of two parts that are separated from each other using an internal cylinder. The inner part is where the influent enters, and the reaction occurs after dosing with NaOH, while the outer part is where the sedimentation of the crystals takes place.

The influent's flowrate was adjusted to around 4, 2, 1 L/min to set retention times of 30, 60 and 120 minutes respectively. The influent was pumped to the top of the reactor where it was dosed with NaOH 5 M solution to adjust the pH level required for the experiment. The mixed solution then was fed to the bottom of the reaction zone. The aeration system was used for the agitation of the solution in the reaction zone using two aeration pumps. Inside the reaction zone, the pH of the solution is also controlled due to acidification occurring after the process of crystallization. Adding NaOH solution at the top of the reactor basifies the influent solution at the desired pH of 8.5 or 9.0 influencing the equilibriums of the reactions 1-4. However, inside the reaction zone after beginning of the crystallization process the solution will be acidified based on the reaction 5-7. Therefore, it is important to control the pH of the solution also inside the reactor where the process of precipitation occurs. Adding NaOH in the reaction zone is with the purpose of compensating the acidification process due to the reactions 5-7 and allows to measure quantitatively the progress of these reactions. Inside the reaction zone a less concentrated NaOH solution (0.5 M) was used to keep the condition under control. Figure 6.1 shows the scheme of the pilot.

$$OH^- + NH_4^+ \leftrightarrow H_2O + NH_3 \tag{1}$$

$$OH^- + H_2PO_4^- \leftrightarrow H_2O + HPO_4^{2-} \tag{2}$$

$$OH^- + HPO_4^{2-} \leftrightarrow H_2O + PO_4^{3-} \tag{3}$$

$$OH^- + HCO_3^- \leftrightarrow H_2O + CO_3^{2-} \tag{4}$$

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \leftrightarrow MgNH_4PO_4.6H_2O + H^+ \tag{5}$$

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \leftrightarrow MgNH_4PO_4.6H_2O + 2H^+ \tag{6}$$

$$3Ca^{2+} + 2HPO_4^{2-} \leftrightarrow Ca_3(PO_4)_2 + 2H^+ \tag{7}$$

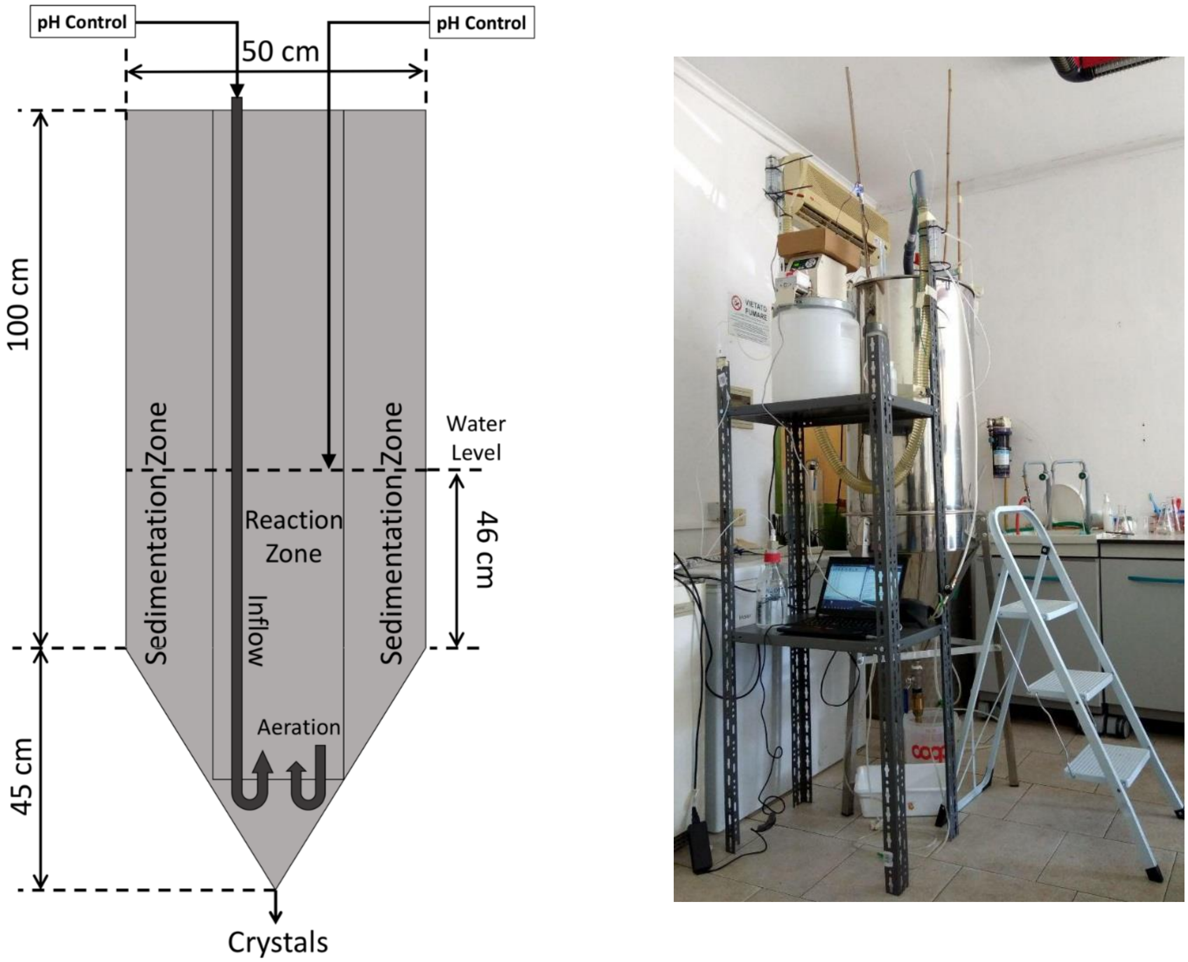

Figure 6.1. Scheme of the pilot plant.

6.2.3. Equipment and Analytical Tools

The influent flow rate was adjusted to 4,2,1 L/min. The solution of NaOH was added to the top of the reactor using STEPDOS FEM 08 chemically-resistant diaphragm metering pump, while for the pH control inside the reaction zone SHENCHEN BT100N peristaltic pump was used for NaOH dosage. The pH at both stations was monitored using DFROBOT Analog pH sensor/meter SEN0161.

The phosphorus measurements were conducted based on EPA 365.3 method [24] using Spectroquant PHARO 100 MERCK UV-VIS spectrophotometer. For the calcium measurements MERCK 111110 Titrimetric method was used [25]. The analysis of the precipitates was done using Fourier Transform Spectroscopy (FTIR) (Perkin Elmer 1600 series).

6.2.4. pH Control System

One of the most critical parameters in the study of struvite precipitation is the pH. It is also one of the hardest parameters to control due its nonlinear variations affected by many factors.

Both pH measurements were monitored continuously using two pH probes. The probes were connected to an Arduino board through the analog input pins. The pH at the top of the reactor was controlled with a continuous flow of NaOH solution to keep the pH at desired value of the experiments.

In order to control the pH inside the reaction zone, a PID-Time Proportional control system was designed using the Arduino board. Proportional-Integral-Derivative (PID) controller is a widely used control loop feedback algorithm. PID system calculates an error value (ε), which is the difference between a set point (SP) and a measured value of a variable (y). Then it applies a correction factor based on proportional (K_p), integral (K_i) and derivative (K_d) terms. In the case of pH control, first the difference between desired pH value of the experiment and the measured value by the probe is calculated. The system then calculates the output of the PID control function. This output is a correction term of the error and thus it is still in the scale of the pH. However, this output needs to be converted to a time-domain format in order to be fed to the peristaltic pump used for the NaOH dosage. On the other hand, the output will tell the pump for how much time it needs to be open to have enough NaOH flowing to the system for pH adjustment. For this aim, a time proportional control algorithm was used. Time proportional control is a mathematical technique that is used to convert a continuous control output variable (pH control) to time-proportioned discrete output control variable (pump on/off time). Following equations demonstrate the basic functions of the PID controller system.

$$\varepsilon(t) = SP - y(t) \tag{8}$$

$$u(t) = K_p\varepsilon(t) + K_i\int_0^t \varepsilon(\tau)d(\tau) + K_d\frac{d\varepsilon(t)}{dt} \tag{9}$$

The equation (9) can also be parametrized in the following form:

$$u(t) = K(\varepsilon(t) + \frac{1}{T_i}\int_0^t \varepsilon(\tau)d(\tau) + T_d\frac{d\varepsilon(t)}{dt}) \tag{10}$$

Where T_i and T_d are integral time and derivative time respectively.

By increasing the proportional gain, the error will decrease but the oscillation of the system will increase. Adding the integral term will improve the output signal by decreasing the steady-state error. However, by using a PI control, the system could still have a large overshoot, which is the distance between the maximum peak of the signal and the set point. By adding a derivative term this problem could be solved. Nonetheless, the value of these parameters needs to be obtained carefully. If the T_d is too large the derivative term does not help the system and it leads to high oscillation. Very large values of T_i will also increase the error [26].

The appropriate values of K_p, T_i and T_d could be obtained through different methods. One the most common approaches for tuning the parameters is the Ziegler-Nichols method developed in

1940s [27] which is used in this study. Based on this method, one first sets both integral and derivative terms to zero and increases the proportional term (K_p) until it reaches its ultimate gain (K_u). At this point, the output of the system has a constant oscillation. Then the ultimate gain as well as the oscillation period (T_u) are used to calculate the parameters according to the Table 6.1.

Table 6.1. Ziegler-Nichols coefficients for Proportional, Integral, and Derivative terms.

Control type	K_p	T_i	T_d
P	$0.5K_u$	-	-
PI	$0.45K_u$	$T_u/1.2$	-
PD	$0.8K_u$	-	$T_u/8$
PID	$0.6K_u$	$T_u/2$	$T_u/8$

The control system is programmed in the Arduino programming language, which is a set of C/C++ functions to be called inside the Arduino Integrated Development Environment (IDE). The Arduino is connected to the pH probes using specific pH sensors designed for converting the values measured by the probe to the analog input. Figure 6.2 shows the scheme of the pH control circuit using the Arduino board.

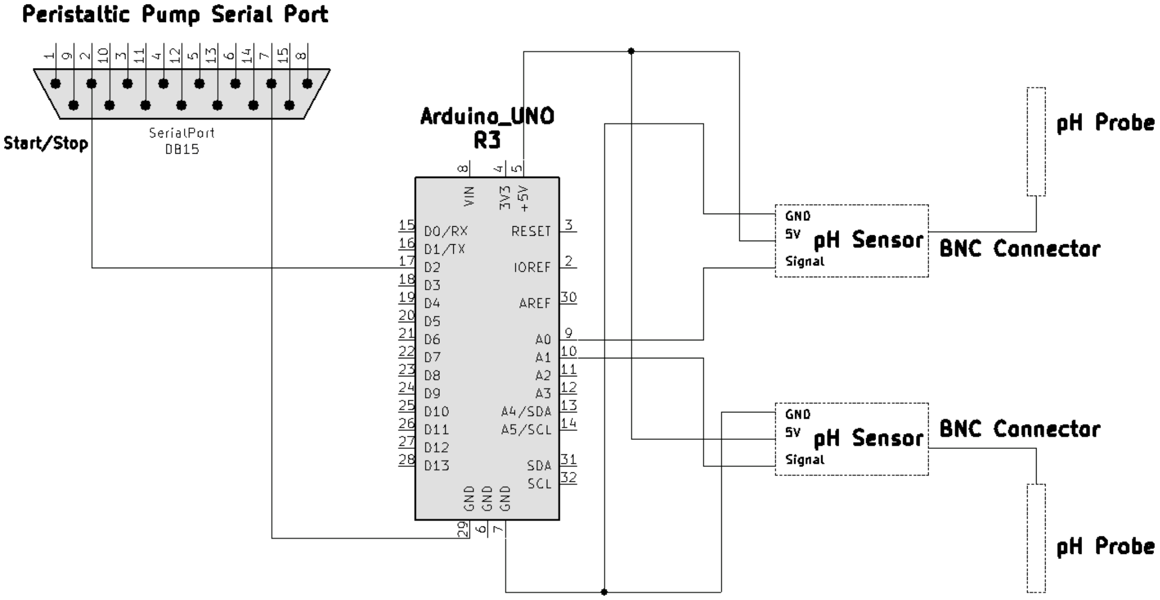

Figure 6.2. The scheme of the Arduino circuit used for pH control system.

6.2.5. Experimental Setup

The experiments have been conducted considering the variations of two parameters; pH level, and retention time of the reactor. All the experiments have been done using the Mg:NH_4:P molar ratio of 5:5:1 according to the best results of the previous studies. Table 6.2 shows different runs of the experiments with their corresponding pH and retention time values. For each experiment, 3 retention time is considered. The first one takes for the reactor to be filled with the solution, followed by two retention times in which the reaction is continuously happening inside the reactor. After this point the inflow is stopped, and the reaction is continued until its completion (Figure 6.3). At this point there must be no further change in the pH of the solution and there will be just the growth and aggregation of the crystals. The phosphorus concentration was measured every 7.5 minutes for the RT of 30 minutes and every 15 minutes for the RT of 60 and 120 minutes. At each point of sampling, a sample of crystal suspension have also been taken for the FTIR analysis and to check qualitatively the enlargement of the crystals through filtration with 2.5 µm filters. The filtered solids are dried at the room temperature.

Table 6.2. Experiments conducted in this study with their corresponding pH and RT.

Run	pH	Retention time (min)
1	8.5	30
2	9.0	30
3	8.5	60
4	9.0	60
5	8.5	120
6	9.0	120

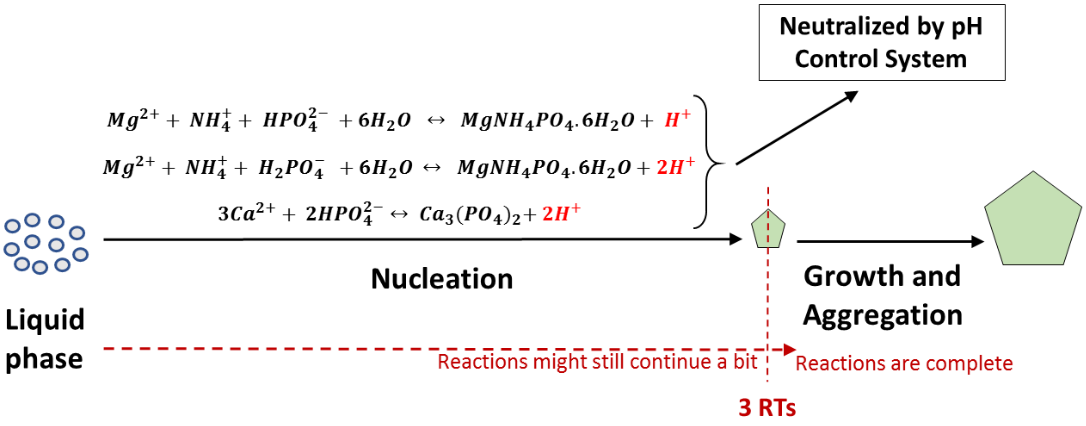

Figure 6.3. Nucleation, growth and aggregation of the crystals inside reaction zone.

6.3. Results

6.3.1. pH control

The PID-Time proportional system showed a very decent control of pH in these experiments. The ultimate gain (K_u) obtained was 20 and oscillation period (T_u) was set to 20 seconds. Figure 6.4 shows the controlled value of the pH compared to the desired pH value as the set point of the control system. However, some small fluctuations are also visible that apart from the small error of the control system, could probably be due to the presence of air particles flowing around the pH probe.

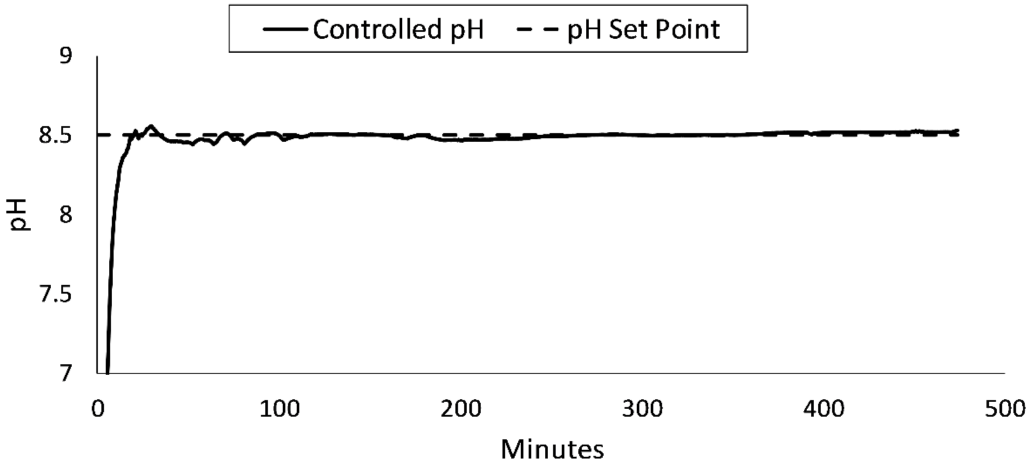

Figure 6.4. Controlled pH using PID-Time Proportional control vs the desired value of pH as the set point.

6.3.2. Effect of pH

The most important effect of pH on the reaction is on the phosphorus removal percentage. Figure 6.5 shows the phosphorus concentration trend in time for all experiments. It is observed that phosphorus concentration decreases rapidly with the start of the reaction and then reaches to a nearly stable state. This means that phosphorus precipitation is mainly related to the pH of the system and not much depends on the retention time of the reaction. This can be noted also with the similar phosphorus concentration of the experiments with the same pH value but different retention times. As it is expected the P removal is higher at pH=9, however it needs more NaOH solution to be added to the system to keep the pH at higher level.

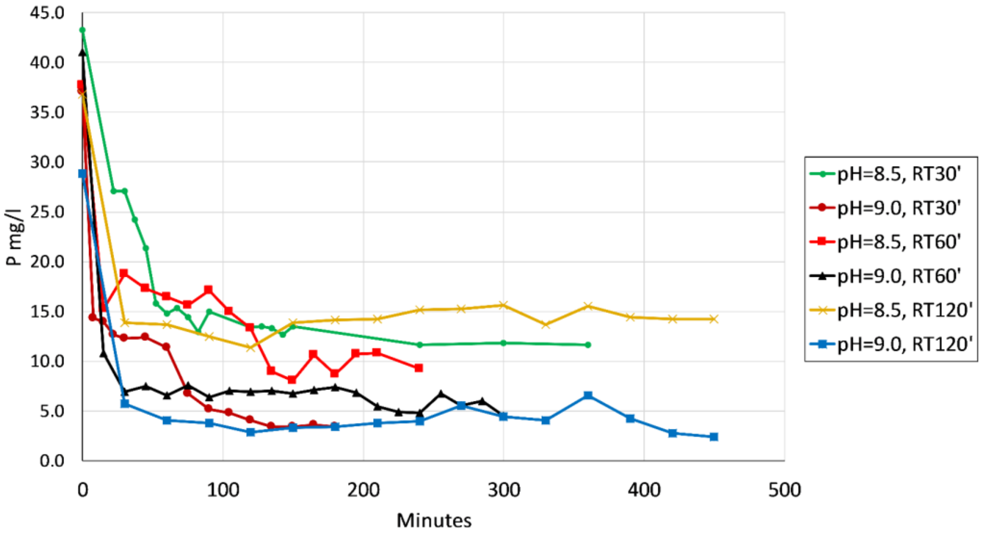

Figure 6.5. Phosphorus concentration trend with respect to the time of the reaction.

6.3.3. Effect of Retention Time

The experiments were conducted with the continuous influent flow rate for three retention times. Then the inflow was interrupted and the NaOH added inside the reaction zone was kept monitored afterwards. Figure 6.6 shows the cumulative mmol of NaOH added inside the reactor to control the pH of the reaction (data not available for the first 40 mins in the experiment with pH=9.0, RT30’). For all the experiments (except for experiments with RT of 30 minutes) the graph reaches a plateau approximately at the point where the inflow was interrupted, after three RTs. This mean that at this point the reaction is complete and the pH of the system is not decreasing anymore due the effect of reactions 5-7, thus no NaOH is added to the solution. However, in the experiments with RT of 30 minutes the NaOH flow inside the reaction zone continues after the interruption of influent (at pH=9.0 it reaches a plateau in 100 mins). It can be concluded that 30 minutes of retention time is not enough for the reaction to be completed, while it is done before 60 minutes. Comparing the experiments 2 and 3 (60 minutes of RT), there is a noticeable difference in the amount of NaOH required for completion of the reaction at pH=8.5 and 9.0. This difference is also visible between experiments 4 and 5 with RT of 120 minutes. more NaOH consumption means more progress of the reactions 5-7 at pH=9.0 with respect to pH=8.5 (more formation of precipitates).

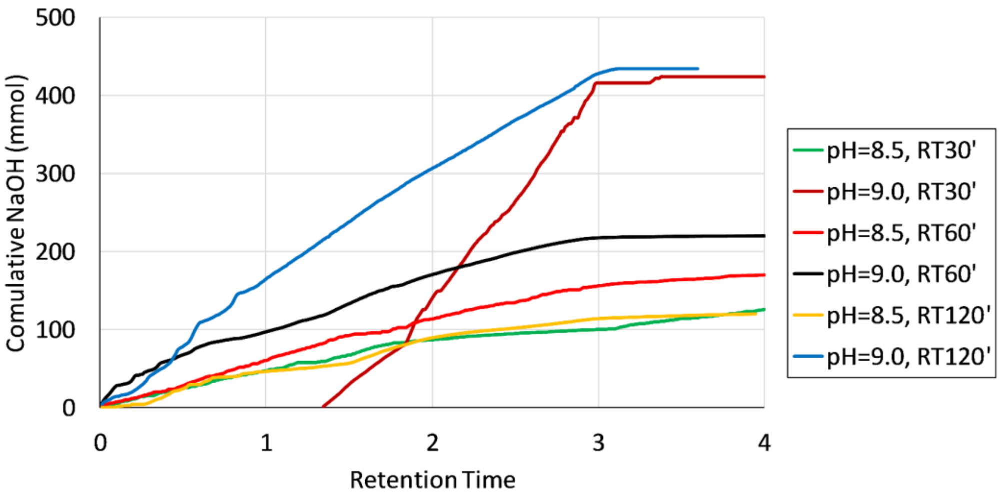

Figure 6.6. Cumulative NaOH added to the system for pH control with respect to the time of the reaction.

Figure 6.7 demonstrates the mmol of NaOH added to the system after stopping the inflow (3 RTs). This could be interpreted as the amount of NaOH required for the reaction to be completed after the completion of the retention time of the reactor. It can be seen a large difference between three RTs used in this study at pH 8.5. This confirms that 30 minutes are not enough for the reaction to be completed since there is a big amount of NaOH added to the system after this point. This amount is considerably lower for experiments with RT=120 minutes and for the same RT is lower at pH=9.0., which could mean that the reaction at higher RT reaches to a greater degree of completion within the retention time and that the process is accelerated by a high pH level. Therefore, based on these results, a retention time of around 60-90 minutes could be enough for the reaction to be completed.

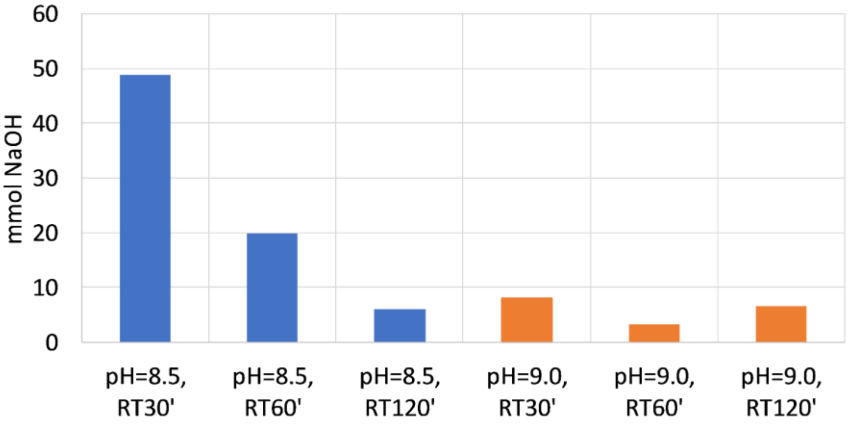

Figure 6.7. Amount of NaOH added to the solution after 3 retention times.

The weight of solids retained on the 2.5 µm filters is presented in the Figure 6.8. For all the experiments the graph has an increasing trend, which could mean that the crystals are growing in time. There is a clear differentiation between the growth of the crystals at pH=8.5, which obtained by filtration after 100 minutes, while at pH=9.0 they are already retained at 50-60 minutes. Moreover, the growth of the crystals, under the same pH condition, is greater at RT of 60 minutes than RT of 120 minutes as an effect of the higher quantity of reagents (higher influent flow rate and consequently more quantity of P in unit of time) that enter the system at lower RT (the one with pH=9.0 and RT of 30' has lower values due to the interruption occurred in the first 40 mins of the experiment).

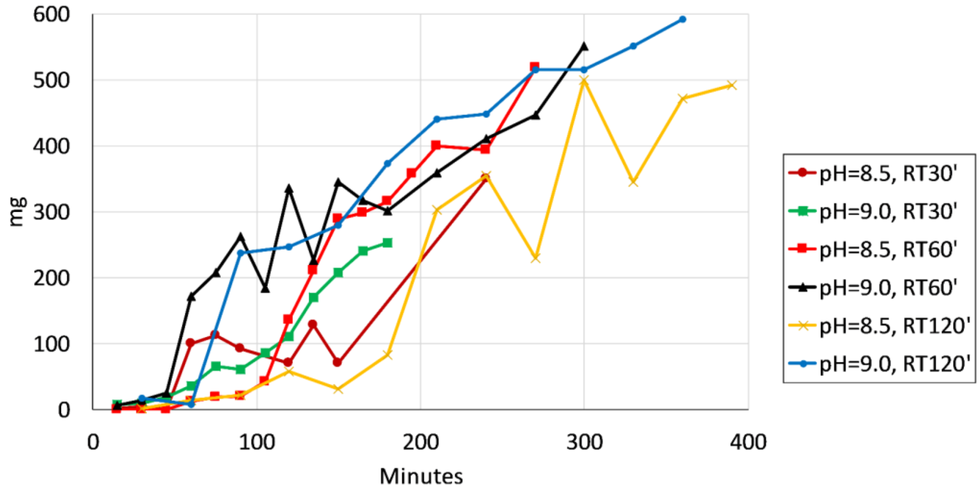

Figure 6.8. Weight of the retained solids collected after the filtration.

6.3.4. Analysis of the Precipitates

The analysis of the precipitates using FTIR showed similar spectrum for all the experiments (Figure 6.9). On the contrary to what was expected there was no direct evidence of the presence of struvite based on the FTIR. The associated peaks of phosphate groups and H-bonds are visible around 1000-1100 cm^{-1} and 3400-3500 cm^{-1} respectively [28]. Although in the range of 1200 to 2000 cm^{-1} the visible peaks could not be assigned certainly to the struvite. Two peaks at around 1400-1500 cm^{-1} could be related to H-N-H bond in the struvite and to the carbonate group resulting from the precipitation of calcite [29]. The other peak at around 1650 cm^{-1} could be associated to the amorphous calcium phosphate. This result is not in accordance with the lab-scale results in which direct evidence of struvite precipitation was observed for the experiments with 5:5:1 molar ratio. This could be because of the synthetic solution that was used in this pilot study instead of real aerobic sludge. There is a possibility of the presence of inhibitors for the precipitation of calcium phosphate in real sludge that is not the case for the synthetic solution. Nonetheless, the precipitation of calcium phosphate could still be suitable for obtaining a product with a value to be used as fertilizer [30].

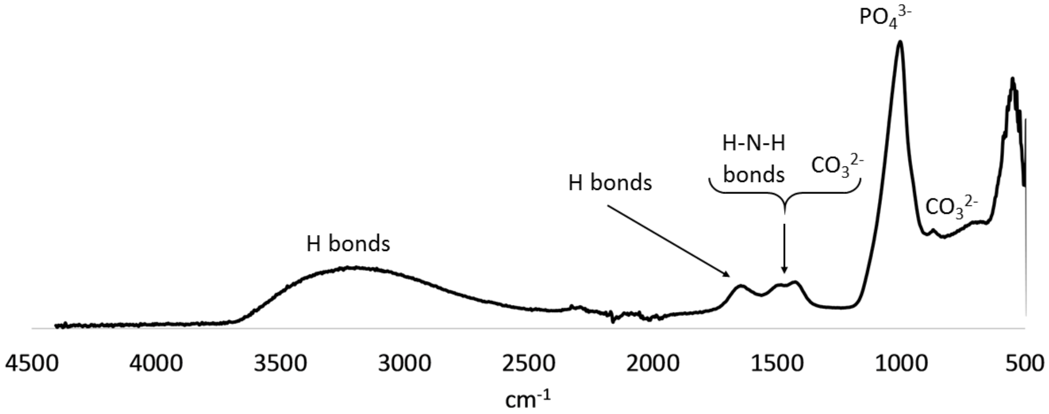

Figure 6.9. FTIR spectrum of one of the samples taken from the pilot reactor.

To have a better understanding, some experiments have been conducted using sodium alginate ($(C_6H_7NaO_6)_n$) to see its effect as an inhibitor for the calcium phosphate precipitation. The calcium concentration prior adding the alginate was measured as 100 mg/L. Then, 50 ml of 0.3% sodium alginate solution was added to 1 L of the synthetic solution. After 18 hours the calcium concentration was measured as 80 mg/L. Therefore, a 20% reduction in calcium concentration was observed. This could be a justification for the struvite precipitation observed from the real aerobic sludge, which might contain organic substances that could act as inhibitors for the calcium phosphate precipitation. These experiments also demonstrate the high potential of using alginate for blocking the calcium ions in wastewater to increase the possibility of struvite precipitation instead.

6.4. Conclusions

A pilot reactor for the process of struvite precipitation has been implemented in this study. The experimental setup of the study considered 5:5:1 molar ratio for $Mg:NH_4:P$, which was the one with the best results in the previous lab-scale studies. Three retention times of 30, 60, and 120 have been studied at two levels of pH; 8.5 and 9.0. the pH of the system was controlled using a PID-Time Proportional control system implemented by means of an Arduino microcontroller and pH sensors. For this study a synthetic solution was made based on the characteristics of the aerobic sludge samples used in the previous studies.

The results of pH control system showed an excellent pH control that was able to keep the desired pH level of the solution as constant as possible. The preliminary results of the pilot experimentation show that phosphorus removal is highly dependent on the pH of the solution and the retention time of the reactor does not have a great impact on that. The phosphorus concentration rapidly decreases after the start of the reaction and then reaches to a stable state. However, the retention time of the reactor was observed as an important factor. It was observed that 30 minutes of RT was not enough for the reaction to be completed. Although the RT of 60 minutes was observed to be sufficient for the reaction to be completed, it is not long enough for the crystal to grow substantially and only after 60-90 minutes they are large enough to be filtered in abundance.

The FTIR of the obtained precipitates did not show direct evidence of struvite precipitation. It is expected that the potential difference between characteristics of the synthetic solution used in this work with the real aerobic sludge resulted in calcium phosphate and carbonates to precipitate in the system. Adding sodium alginate to the synthetic solution resulted in a 20% reduction in calcium concentration that could confirm the potential of struvite precipitation in real aerobic sludge in presence of calcium phosphate inhibitors. Using sodium alginate also showed a potential for increasing struvite precipitation possibility by blocking calcium ions in the solution. Nonetheless, this result showed the possibility of having calcium phosphate in the final precipitate that could be a suitable alternative to pure struvite in fertilizer industry.

6.5. Future Studies

As the future study, two new sets of experiments will be conducted. First, the molar ratio of 3:3:1 for Mg:NH_4:P will be investigated to compare with the previous results obtained by the lab-scale experimental studies. Second, the possibility of using $Ca(OH)_2$ as an economic pH adjustment reagent will be studied in the pilot-scale. Based on the lab-scale studies, it is expected to obtain an ACP-rich precipitates using $Ca(OH)_2$, which could be a suitable alternative fertilizer to the pure struvite due to its high phosphorus content. In addition, an in-depth study on the analysis of the precipitates using FTIR, TGA-MS, ICP-AES and Elemental Analysis will be done to investigate the presence of different solid phases in the final precipitates obtained during the pilot study. All the results will be presented as a published work.

6.6. References

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Chapter 7

Conclusions

7. Conclusions

The process of struvite precipitation for phosphorus recovery from wastewater sludge has been studied for many years so far. The dewatered sludge after the anaerobic digestion was mostly the main stream used for struvite precipitation due to its high phosphorus content. However, this thesis has focused on the possibility of using the aerobic sludge taken from the activated sludge stage of a wastewater treatment facility for this aim. Knowing the insufficient phosphorus content for struvite precipitation in the influent of typical municipal wastewater plants, the focus of the study was on the sludge inside the biological nutrient removal process. the anaerobic zone in the biological process is where the phosphorus release is happening, and it is followed then by a luxury uptake of phosphorus in the aerobic zone. Therefore, this sludge has enough phosphorus content for implementing the struvite precipitation if the required operating conditions are provided. This thesis has investigated this possibility through an in-depth experimentation and optimization study of the struvite precipitation using the aerobic sludge.

First, a literature review on the importance of phosphorus and the need for its recovery was studied. The current situation for consumption and production of phosphate rock as the main source of phosphorus has been presented. It was concluded that the current trend of the population growth and its inevitable need for more food production will lead to the complete depletion of phosphate rock resources in the future (by 2300 for the best scenario). This fact, as well as phosphorus environmental concern due to its highly concentrated discharges in the water bodies, has raised the attention of scientists and engineers to developing new technologies for phosphorus removal and recovery. The state-of-art studies on different phosphorus recovery technologies have been presented and struvite precipitation as one of the most dominant methods for this aim has been reviewed. Some other more recent promising technologies such as assimilation and membrane bioreactors have also been presented.

In the next step, the process of struvite precipitation was studied through many experimentations considering different chemical parameters affecting the efficiency of the process. The effects of pH, Mg:NH_4:P molar ratio and presence of calcium (Ca) as a competitive ion in particular, have been taken into account. It was concluded that the pH was the most important factor that has a significant effect on process. The P removal percentage was increased with the increase of pH and up to 94% P removal at pH=9.5 was achieved using NaOH for the pH adjustment. However, the analysis of the final precipitates demonstrated that the pH level is also affecting the type of precipitates obtained. At pH levels above 9.0 there was no direct evidence of the presence of struvite in the final precipitates and the analysis suggested that the solids are the mixture of struvite, amorphous calcium phosphate (ACP) and calcite. The best results were for the experimentation with 5:5:1 molar ratio of Mg:NH_4:P at pH=8.5 and 9.0. it was concluded that for significant struvite precipitation using the aerobic sludge both Mg and NH_4 needs to be added to the system in high amounts. The possibility of using $Ca(OH)_2$ as an economic pH adjustment reagent was also studied. As a result, $Ca(OH)_2$ did not show favorable results for struvite precipitation in spite of having higher P removal percentage (up to 99%). However, it was suggested that at pH=8.5 using $Ca(OH)_2$ could lead to obtaining precipitates containing a small amount of struvite and high amount of ACP. These precipitates can still be used in the fertilizer industry due their high P content as an alternative to pure struvite. For this aim the pH level needs to be kept less than 9 since after this point the calcite precipitation is significantly increased.

The process of struvite precipitation was also modeled using chemical equilibrium modeling and statistical optimization. PHREEQC chemical equilibrium modeling tools was used for this aim. The results of the PHREEQC were presented as the predicted P removal percentage and saturation index (SI) values for the possible solid phases precipitating in the operating conditions of the experiments. Based on the SI values obtained for struvite, it was concluded that using aerobic sludge, generally the possibility of having significant struvite precipitation is low. This could be due to the relatively lower P content in aerobic sludge compared to anaerobic one. High calcium content of the wastewater sludge is another important obstacle in the way of obtaining a pure struvite precipitate at the end of the process. The model confirmed the previous experimental results predicting the highest value of struvite SI for the experiment where both Mg and NH_4 was added to the system in high amounts.

Statistical optimization of the struvite precipitation process was conducted using Response Surface Methodology (RSM) implemented in R programming language. Three parameters were chosen as the predictor variables; pH, NH_4:P and Ca:Mg molar ratios. A Box-Behnken design was used in order to investigate the significant parameters impact on two response variables; struvite SI value calculated by the PHREEQC and P removal percentage observed for each experiment. The results of the statistical optimization suggested the optimum value of pH=9, Ca:Mg=0.8, NH_4:P>3.5 and pH=9.5, Ca:Mg=1.2, NH_4:P=2 for SI and P removal percentage respectively. It was concluded that in order to have higher struvite precipitation Ca:Mg ratio needs to be kept under 1 that was also aligned with the other literature works. It was also seen that above pH=9 the possibility of struvite precipitation is highly diminished, and the process was affected by ACP and calcite precipitation significantly.

Finally, a pilot study of the process of struvite precipitation was investigated to see the efficiency of the process in larger scale. A pilot reactor with 120 L capacity was used that was fed with a synthetic solution. For the aim of this study the synthetic solution was made based on the real characteristics of the aerobic sludge samples taken for the previous lab-scale studies. The effects of pH and retention time of the reactor were studied. The experiments were conducted using 5:5:1 molar ratio for Mg:NH_4:P at pH=8.5 and 9.0. three retention time of 30, 60 and 120 minutes have studied in order to investigate the process. The pH of the system was controlled at two points of the reactor. One at the top of the reactor where the synthetic solution is mixed with a continuous addition of NaOH and the other inside the reaction zone of the system where the pH is constantly decreasing in the time of the reaction due to the acidification of the solution after crystallization. The control system of the pH was made using a PID-Time proportional control system implemented with an Arduino microcontroller connected to a pH sensor. The results of the PID-Time proportional control showed a very decent control of the pH inside the reaction zone and was able to keep the pH of the system at the desired level until the completion of the reaction. the preliminary results of the pilot study showed that P removal is highly affected by the pH of the solution is not much related to the retention time of the reactor. It showed a rapid decrease just after the reaction begins and then reaches to a stable phase. It was also concluded that RT of 30 minutes is not enough for the reaction to be completed since there is high amount of NaOH needed for the continuation of the reaction after this retention time. It was observed that 60 minutes of retention time could be sufficient for the completion of the reaction. However, it is only after 60-90 minutes that the crystals are growing considerably. In addition, the growth of the crystals, at the same level of pH, is higher for RT of 60 than 120 due to the higher quantity of reagents in unit of time for lower RT (higher influent flow rate). Although there was not a direct evidence of the presence of struvite in the final precipitates based on the FTIR spectra, there is a decent possibility of having a precipitate with high calcium phosphate content that could be an appropriate alternative to pure struvite in fertilizer industry. Furthermore, the use of sodium alginate as an inhibitor for the calcium phosphate precipitation showed the reduction of 20% in calcium concentration in the synthetic solution. This could explain the absence of direct evidence for struvite precipitation in pilot experiments due to the presence of organic substances acting as calcium phosphate inhibitors in the real aerobic sludge.

As a future work, the study of pilot scale experimentation will be continued with additional experimental setup. One set of experiment will be studied on the 3:3:1 molar ratio of Mg:NH_4:P to compare the results with the previous lab-scale studies. Another important set of experiments will include utilization of $Ca(OH)_2$ as the pH reagent instead of NaOH to study the effectiveness of that on the process of struvite precipitation. Based on the previous lab-scale studies, it is expected that an alternative precipitate mainly consisting ACP will be obtained that has a decent value to be used in the fertilizer industry, although not as good as pure struvite. An in-depth analysis of the obtained precipitates using FTIR, TGA-MS, ICP-AES and Elemental analysis will be also implemented to complete the preliminary FTIR results of the pilot study and identify the solid phases precipitating in the pilot reactor. All the results will be presented as a published paper.